

Erosive wear mechanisms of rubber pump lining materials in minerals processing applications

Author:

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Publication Date:

2013

DOI:

<https://doi.org/10.26190/unsworks/2448>

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The University of New South Wales
Faculty of Science
School of Materials Science and Engineering
Department of Materials Engineering

**Erosive Wear Mechanisms of Rubber Pump Lining Materials in
Minerals Processing Applications**

A Thesis in
Materials Science and Engineering
By
Michael Lum

Submitted in Fulfilment
of the Requirements
for the Degree of

Doctor of Philosophy
February 2013

PLEASE TYPE

THE UNIVERSITY OF NEW SOUTH WALES
Thesis/Dissertation Sheet

Surname or Family name: Lum

First name: Michael

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Abbreviation for degree as given in the University calendar:

Ph.D.

School: Materials Science and Engineering

Faculty: Science

Title: Erosive Wear Mechanisms of Rubber Pump Lining
Materials in Minerals Processing Applications

Abstract 350 words maximum: (PLEASE TYPE)

Erosive slurry wear occurs extensively throughout minerals processing equipment for slurry transport applications. Wear resistant materials are designed to prolong the life of equipment used to transport the slurry such as pumps, hoses, grinders, conveyor belts, screens, etc. In this study, the erosive wear mechanisms of rubber pump lining materials used in slurry pumps were explored at a structural level. The erosive wear mechanisms for rubber pump lining materials have not been extensively investigated in the literature. Arnold and Hutchings [1] were the pioneers in this field of tribology, however, a number of key areas for study remain. Although the wear mechanisms of rubber wear in slurry erosion are well documented in the literature, the chemical degradation of the rubber during this erosive wear has not been investigated. Furthermore, the viscoelastic properties of the rubber and their correlation with erosive wear have not been well documented. The approach to this study was to investigate four different rubber compounds used in slurry transport pumps and determine the wear mechanisms and their correlation with physical, viscoelastic and chemical properties of the rubbers. A slurry jet erosion test was used to investigate the wear rate of each compound under different variables. The samples were then chemically analysed using a Fourier Transform Infra Red (FT-IR) Spectrometer to determine the extent of chemical change to the surface of the rubber during erosive wear testing. The physical properties of the rubber were tested using conventional test methods, whereas a Rubber Process Analyser 2000 (RPA2000) was used to determine the key viscoelastic properties. It was important to investigate these properties of the rubber compounds to determine which properties could be correlated with erosive wear. Through FT-IR analysis of heat aged samples of the rubber compounds, it was established that erosive slurry wear does not correlate with aging, however, heat aging influences the hardness, resilience and viscoelastic properties which increases the wear rate of the rubber compounds. The key findings from this study were that heat aging would increase the $\tan \delta$ and hardness, and lower the resilience, hence, causing lower erosive wear resistance in all the rubbers. $\tan \delta$, hardness and resilience could be correlated with erosive wear loss, the heat aging effect and the chemistry of the rubber compounds. The influence of the type of reinforcing filler and cure systems could also be correlated with erosive wear resistance. Rubbers with a high loading of reinforcing carbon black resulted in a low wear resistance in comparison to a high wear resistance for silica and silane filled rubber compounds. $\tan \delta$ was also correlated with the type of reinforcing filler used in the rubber chemistry. The significance of these findings is important for the future design of rubber compounds used in slurry erosion wear resistant pump liners. For a highly slurry erosion wear resistant pump liner, a high resilience, low $\tan \delta$ and hardness (as are found in silica and silane reinforced rubber) would be required.

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ACKNOWLEDGEMENTS

Professor Mark Hoffman – PhD Project Supervisor (UNSW)

Geoff Moore – PhD Industrial Supervisor, Divisional Marketing Director (Weir Minerals Division)

Fred Bradner – Division Director of Technology (Weir Minerals Division)

Edward Humphries – Materials Services Manager (Weir Minerals Division)

Michael Lum – Materials Engineer (Weir Minerals Division)

ABSTRACT

Erosive slurry wear occurs extensively throughout minerals processing equipment for slurry transport applications. Wear resistant materials are designed to prolong the life of equipment used to transport the slurry such as pumps, hoses, grinders, conveyor belts, screens, etc. In this study, the erosive wear mechanisms of rubber pump lining materials used in slurry pumps were explored at a structural level. The erosive wear mechanisms for rubber pump lining materials have not been extensively investigated in the literature. Arnold and Hutchings [1] were the pioneers in this field of tribology, however, a number of key areas for study remain. Although the wear mechanisms of rubber wear in slurry erosion are well documented in the literature, the chemical degradation of the rubber during this erosive wear has not been investigated. Furthermore, the viscoelastic properties of the rubber and their correlation with erosive wear have not been well documented.

The approach to this study was to investigate four different rubber compounds used in slurry transport pumps and determine the wear mechanisms and their correlation with physical, viscoelastic and chemical properties of the rubbers. A slurry jet erosion test was used to investigate the wear rate of each compound under different variables. The samples were then chemically analysed using a Fourier Transfer Infra Red (FT-IR) Spectrometer to determine the extent of chemical change to the surface of the rubber during erosive wear testing. The physical properties of the rubber were tested using conventional test methods, whereas a Rubber Process Analyser 2000 (RPA2000) was used to determine the key viscoelastic properties. It was important to investigate these properties of the rubber compounds to determine which properties could be correlated with erosive wear. Through FT-IR analysis of heat aged samples of the rubber compounds, it was established that erosive slurry wear does not correlate with aging, however, heat aging influences the hardness, resilience and viscoelastic properties which increases the wear rate of the rubber compounds.

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1 Introduction

The erosive wear of rubber materials used in pump lining applications is a complex problem that has been studied for many years. The erosive wear phenomena are not well defined especially at a rubber structural level. The erosive wear mechanisms can be observed through microscopic and macroscopic examination of the worn material. In a previous study [3], it was observed via environmental electron microscopy (ESEM) that sharp particles cause extensive damage to the surface of the rubber through cutting, gouging and ploughing, causing small and large cracks. The presence of these small cracks could also be related to thermal degradation. This damage is caused by the harder sharp particles cutting the softer rubber material surface. As a result, visual examination of the worn surface was somewhat inconclusive.

The possible failure modes involved with erosive wear in general coincide with three distinct variables; (1) the material itself, (2) the environment in which the material is operating in, and (3) the mechanical stress and strain involved in the operation. In our preliminary studies [3], the areas that were investigated included the material and the stress and strain. The environment was not examined. When combining these two variables, it was observed that ‘fatigue’ failure was a suitable assumption for the wear mechanism in the worn samples. Figure 1.1 illustrates the three distinct areas for the failure mechanisms to occur.

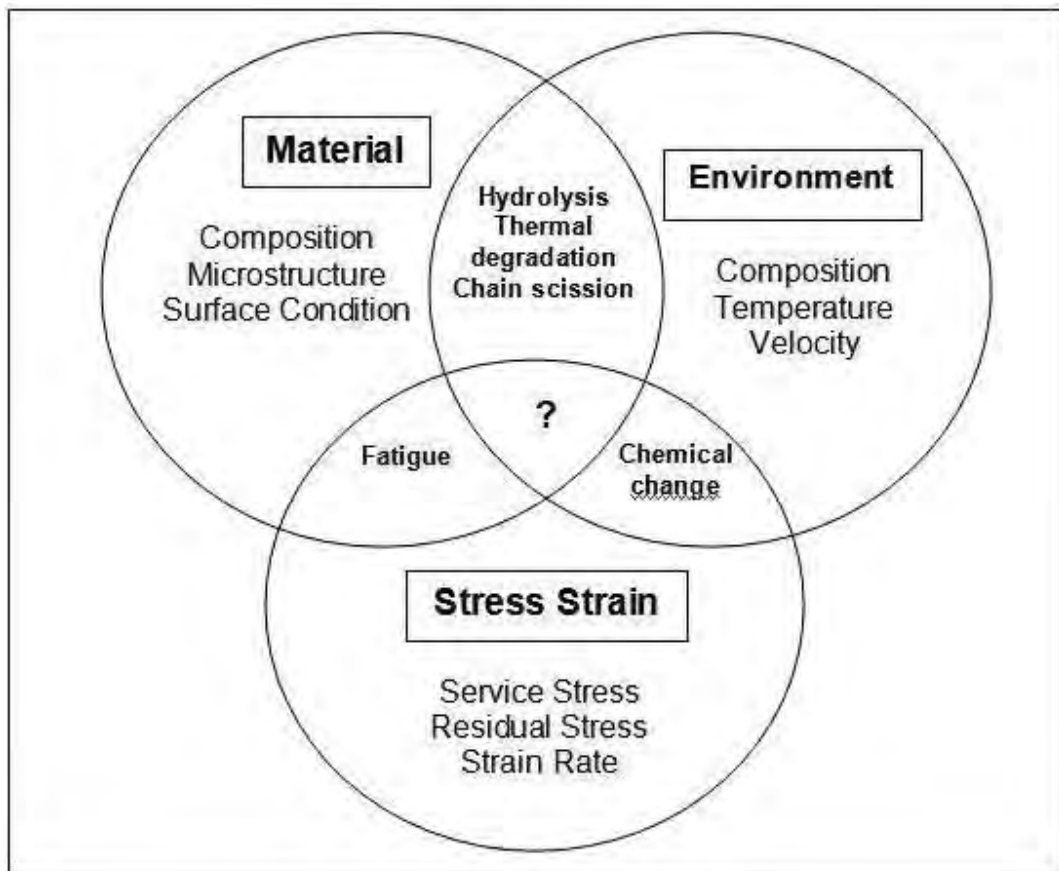


Figure 1.1 Three areas for failure modes to occur as a result of erosive wear in rubber materials.

Laboratory testing and field trials are not well correlated in the literature. Studies have compared the aging affects of rubber tires between laboratory and field trials with some success [2]. However, often the laboratory testing will produce different results to the tests run in the field. There needs to be an understanding between the lab and field results at a microstructural level so that similarities and differences can be analysed and evaluated. More importantly, a fundamental understanding behind the wear mechanisms that cause erosive wear is essential to future rubber development.

The physical properties of the rubber materials will affect erosive wear resistance. In our previous studies [3], it was observed that not one specific physical property directly correlated with the erosive wear resistance of the rubber; but rather combinations of two or more of these properties. The combination of resilience and hardness correlated with the

wear resistance, whereas tensile strength, tear strength and specific gravity did not show any clear relationship. There is a need to have a clear indication of which physical properties correlates with the erosive wear behaviour of the rubber materials used in pump lining applications. Many authors [3-10] have suggested that the physical properties are the major determinates of wear. However, the data obtained in research of erosive wear of rubber pump lining materials suggests no correlation. The viscoelastic properties of the rubber materials are of more interest, as it was concluded that the storage G' and viscous modulus G'' play a major role in the wear resistance.

Polymer chain scission has been mentioned by only a handful of authors in the literature [18, 52, 65, 69]. Chain scission is proposed to occur in the form of micro-cracking as a result of particle impact [11]. Every solid material body contains flaws or points of weakness resulting from heterogeneities in composition or structure [12]. With respect to rubber, the presence of sharp corners, nicks, cuts, scratches, and embedded dirt particles will cause the local applied stress to increase above the mean. It should be noted at this point that reinforcements such as carbon black or silica can be considered as potential flaw and stress raisers although they tend to increase the tensile and tear resistance of the rubber composition [13].

Raman spectroscopy is a powerful tool used in the analysis of polymeric/elastomeric materials. Raman spectroscopy involves the specimen illuminated with a high intensity monochromatic source and the resulting scattered light is investigated and often referred to as the vibration or wavelength shift [14]. However, the use of Raman spectroscopy was not possible for analysis in this study. As inorganic inclusions such as carbon black in the rubber compounds made Raman spectroscopy ineffective as an analysis tool. Alternatively Fourier transfer infra-red spectroscopy (FT-IR) was used to measure the chemistry of the rubber samples. In our study of erosive wear of rubber materials, the area of interest is the carbon double bond in the structure of the polyisoprene. Using the FT-IR, the position of the $\nu_{C=C}$ vibration was discovered to be situated in the 1665 cm^{-1} region, as a result the amount of *cis*- and *trans*- 1,4-isoprene units as well as vinyl units can be determined. This method has also been successfully used in the determination of hydrogenation in rubbers as

the characteristic signal intensity of the carbon-carbon double bond is decreased [15]. Determination of the cross link density of the rubber before testing, after laboratory testing and in field samples can also be beneficial in identification of polymer chain scission. The amount of chain scission can be then correlated with the applied conditions, which would be beneficial for the optimisation of rubber properties.

In a previous study [3], energy dispersive spectroscopy (EDS) was used in the ESEM to determine the elements present in the material before and after testing. However, this form of detector is inaccurate for the study as the polymer itself is organic and a number of the fillers and additives used in the rubber composition are also organic. These results were inconclusive. There is a need for mapping of elements in the rubber compound to ensure what is shown in the ESEM photographs is actually the filler, base polymer, activator, vulcanising agent, etc.

1.1 *Project summary and expected outcomes*

The testing of the rubber pump lining materials was divided into 3 categories: erosive wear testing, heat aging and physical property testing. In erosive wear testing, samples of each rubber compound were tested under different variables including: abrasive particle sizes and impingement angles. Heat aging involved aging the rubber samples in air in a controlled environment (laboratory oven) and also using a rubber process analyser (RPA) with an aging test program. Physical property testing was carried out on the rubber samples before and after aging to develop correlations between these properties, erosive wear and chemical change.

The chemical analysis of the rubber samples using the FT-IR identified many characteristic bonds unique to each rubber. A method was developed to calculate the relative characteristic peaks in the spectra on the control, aged and erosion tested samples. It was found that the rubber chemistry is influenced by heat aging, however, there was no correlation with heat aging and the erosive wear process. Analysing the mode of wear on the rubber samples after the erosion wear test, it was found that the larger the erodent particle size and the lower the angle of impingement, the higher the material wear loss in all cases for each rubber compound tested. Correlations between the wear erosive wear of the rubbers and the physical and viscoelastic properties were established.

This research can lead to future developments in wear models to predict the wear in new rubber compounds. The results should lead to a better understanding of rubber wear resistance and behaviour for slurry transport application in the minerals processing industry.

2 Literature Review

2.1 *Slurry Pumps*

2.1.1 What is a slurry pump?

In mining, large numbers of various pumps are used in the transport of slurries. The most common slurry pump used is the centrifugal pump, however positive displacement pumps are also used such as Venturi eductors [16]. The centrifugal slurry pump utilises the force generated by a rotating impeller to impart energy to the slurry in the same manner as clear liquid type centrifugal pumps. For centrifugal slurry pumps, considerations such as: impeller size and design, its ease of maintenance, the type of shaft seal to be used, and the choice of the optimum materials must be addressed. As the slurry pump needs to withstand wear caused by abrasive, erosive and often corrosive attack, many important material considerations are also required that will be covered later in this research. Extremely large abrasive particles can at times be present in the slurry. These particles must be allowed to flow through the passage of a centrifugal slurry pump [17]. Appropriate designs will ensure the process of the slurry pump will operate smoothly and uninterrupted. Large slurry pumps can transport particles typically up to 500mm in diameter. To accommodate large particles, slurry pumps need wide and heavy impellers. Special materials must be created for these impellers to withstand the wear caused by the solids. Bearings and shafts also need to be robust and rigid. In comparison to clear liquid pumps, slurry pumps are generally larger in size to attain lower operating speeds, and to minimise the wear within the pump.

2.2 Components of a Slurry Pump

A slurry pump comprises of a number of components (see Figure 2.1). These components are exposed to environments where wear is a major factor. Therefore, the components of a slurry pump must usually be made available and easily replaceable [16].

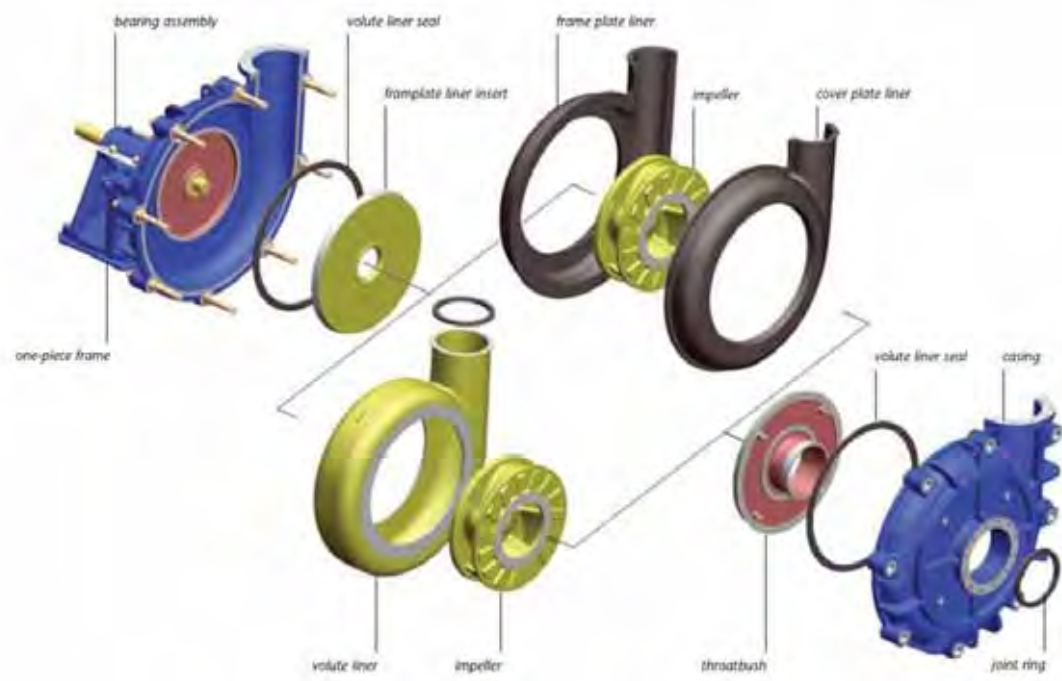


Figure 2.1 Components of a slurry pump. [16]

2.2.1 Impellers

The impeller is the main rotating component of a slurry pump that normally has vanes to impart the centrifugal force to the liquid. While usually made from white cast iron, they are also often manufactured from elastomer materials due to particular corrosive/erosive environments. The general slurry pump impeller will have a plain or Francis type vane, (see Figure 2.2). The plain vane has a leading edge square to the back shroud, whereas the Francis vane has a leading edge projecting into the impeller eye.

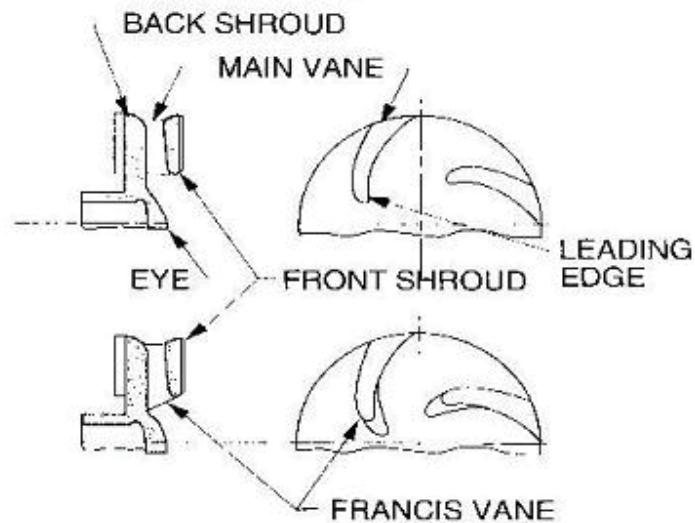


Figure 2.2 Impeller vane profiles. pg 1-2,[16]

The Francis vane profile has the following advantages; higher efficiency, improved suction performance and slightly better wear life in certain types of slurry as the incidence angle to the fluid is altered, while the plain vane type impeller exhibits better wear life characteristics in very coarse slurry applications. Alternatively an elastomer impeller is used. Depending on the size of the particles in the slurry, the number of impeller vanes usually varies between three and six. Slurry impellers are more commonly of the closed type as illustrated (with a front shroud) but open type impellers (without a front shroud) are sometimes used for special applications. Closed impellers are typically used because they are less prone to wear in the front liner region and higher efficiencies. Open impellers are more common in smaller pumps, or where particle blockage may be a problem, or where the shear provided by an open impeller is an aid to pumping froth.

The impeller design is crucial as it influences flow patterns and ultimately, wear rates throughout the pump [17]. The influence of design on flow patterns is illustrated in Figure 2.3.

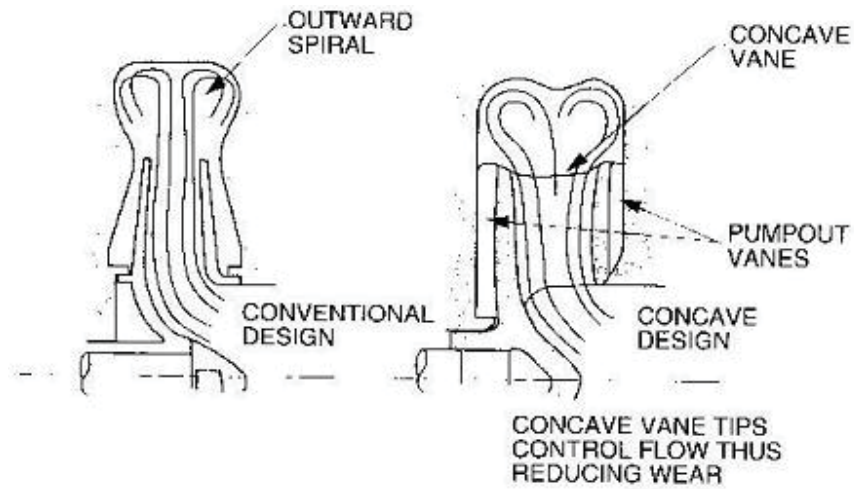


Figure 2.3 Impeller/Casing flow patterns. pg 1-3,[16]

2.2.2 Casings

Casings can be thought of as the container that holds the impeller and the pump together. The casing shape is generally of a semi-volute or annular geometry, with large clearance at the cut water [16]. These differences can be seen in Figure 2.4. Slurry pumps usually operate “slower” than a water pump, primarily to reduce wear through the lower internal velocities.

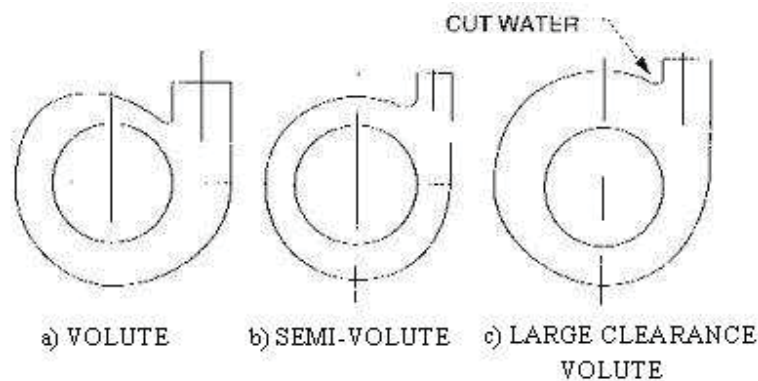


Figure 2.4 Pump casing shapes. pg 1-5,[16]

In terms of wear life, the open casings tend to offer greater wear life in comparison to closed or volute types. However, the efficiencies are less than that of a volute type casing.

2.3 *Slurry Pump Applications*

Slurry pumps are used widely throughout the mining industry where most plants utilise wet separation systems. These wet systems typically require the movement of large volumes of slurry throughout the process. Slurry pumps are also widely used for the disposal of ash from thermal power plants [16]. Other areas where slurry pumps are used include the manufacture of fertilisers, land reclamation, mining by dredges, and the long distance transportation of coal and minerals.

2.4 *A Review of Slurry Pump Wear*

2.4.1 Introduction

The wear of a slurry pump is not well defined in the literature apart from published work by Walker et al. [10, 11]. Walker provides insights into the application of a slurry pump and reports on each part of the pump to help in establishing common wear patterns or trends. It is important to consider all the components in the pump that are in contact with the slurry as different locations may result in different wear mechanisms such as erosion, abrasion and sliding bed wear. Wear mechanisms will be explained in detail in a later chapter, this chapter will give an outline to the specific issues that a slurry pump undergoes during its operation in relation to wear.

Figure 2.5 shows the sectional view of an assembled pump with various components labelled accordingly. These components are exposed to the slurry constantly during the operation of the pump and will be discussed further in this chapter.

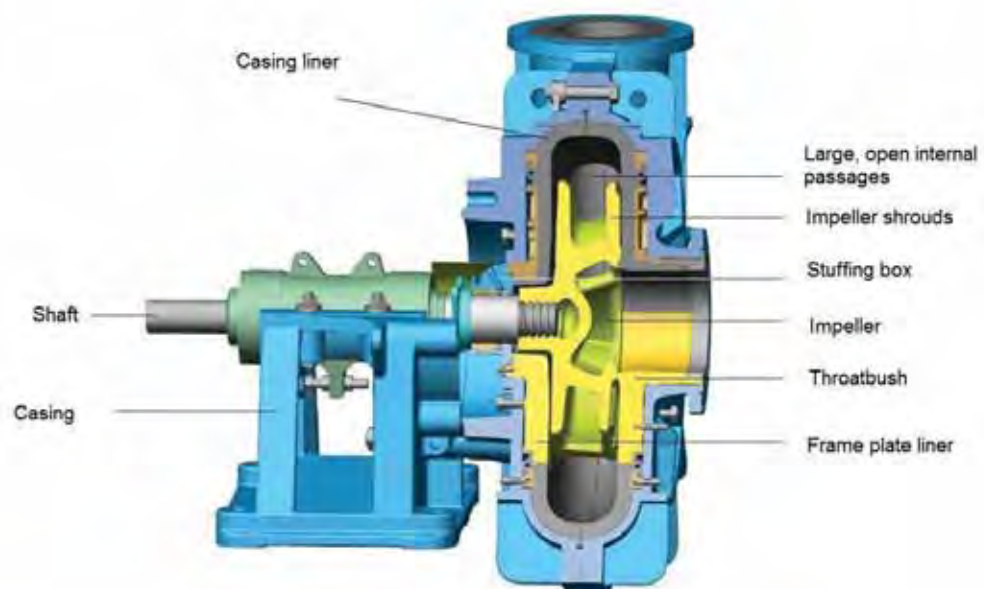


Figure 2.5 Sectional view of an assembled pump. [11]

2.4.2 Specific Areas in a Slurry Pump

During the operation of a slurry pump, there are specific areas that are of interest and relate to the wear life of the pump. Figure 2.6 shows a disassembled AH heavy duty slurry pump. The impeller, liner and throatbush can all be replaced as the wear life is exceeded; however downtime for the change over of spare parts is an issue for the customer which increases the need for longer lasting wear resistant materials.

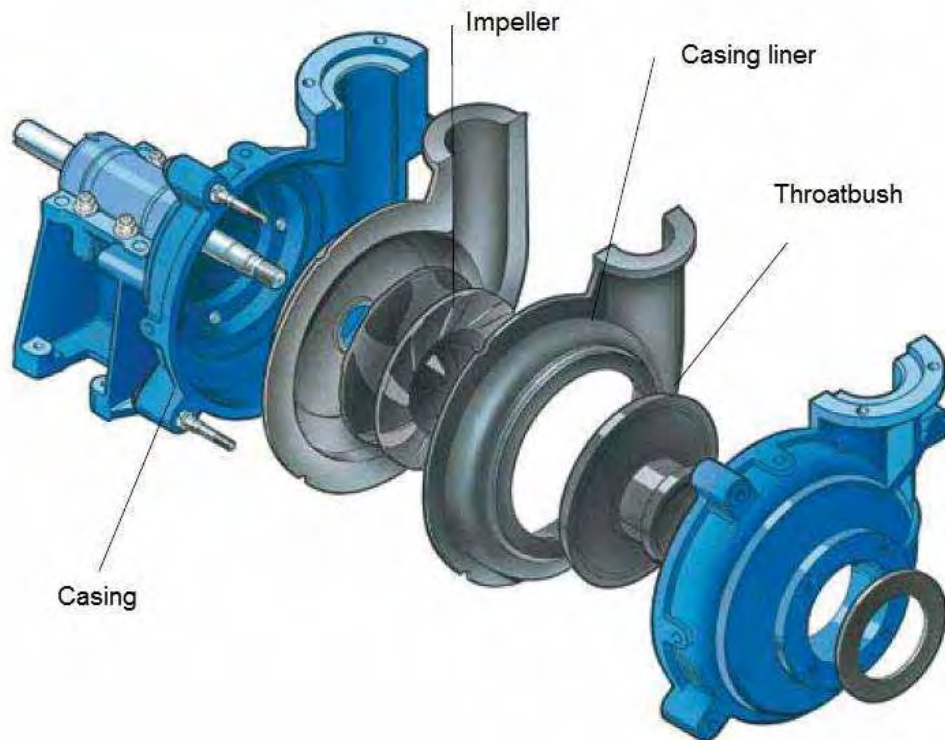


Figure 2.6 Warman AH heavy duty slurry pump. [10, 11]

The impeller bears the main force from the slurry as it enters the pump and has vanes to impart the centrifugal force to the liquid. The directional flow of the slurry is critical to the impeller as this dictates the degree of wear imposed on the vanes. As the impeller rotates to create the centrifugal force, the vanes undergo pressure on one side and suction on the

other. The mechanics of the operation of a pump will not be discussed in this thesis, however, for reference a description of the various locations of the impeller and the various names are illustrated in Figure 2.7.

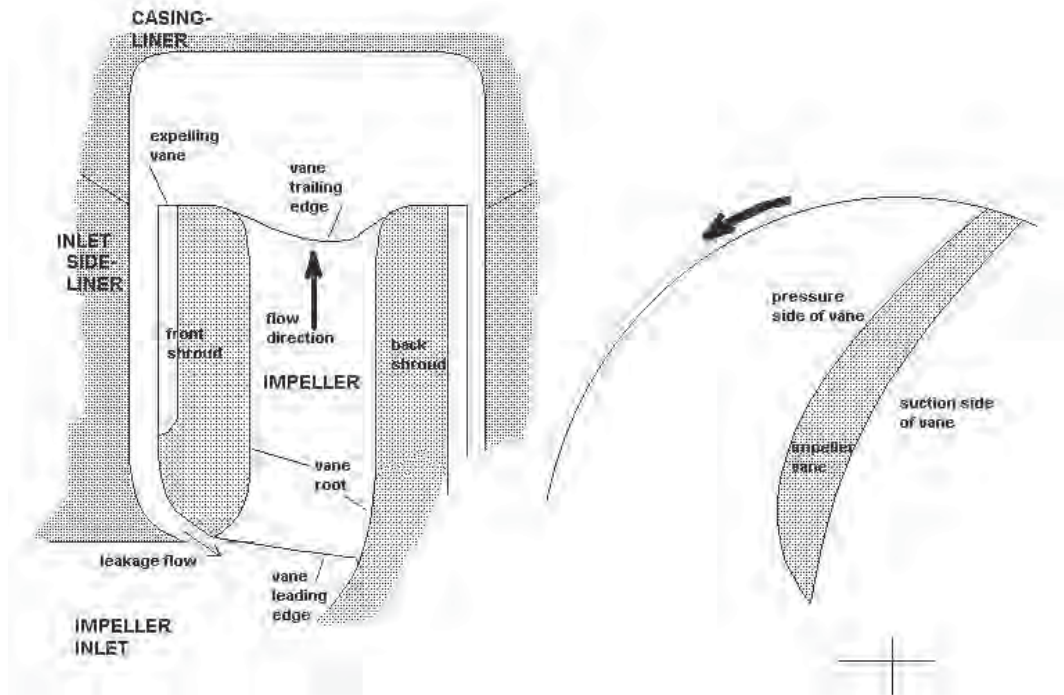


Figure 2.7 Description of slurry pump parts during operation. [10, 11]

2.4.3 Pump Performance Curve

Walker [10, 11] emphasises the importance of a typical pump performance curve as this relates to the wear of the individual parts of the slurry pump. Figure 2.8 shows a typical pump performance curve. The flow (Q) represents the flow rate of the slurry/liquid in the pump during operation while the head (H) is the vertical lift which includes the frictional losses on the pipeline and U-bends the slurry/liquid is required for transporting a specified distance. The size of the pump, impeller and the specific speed is dependant on the amount of head required to transport the slurry/liquid. For example, if the head is large the specific speed needs to be increased to overcome the distance. However, this is not always the case

where slurry is involved and a higher specific speed will result in a higher wear rate of the pump. In this case a larger pump and impeller is required to meet the head need for the application. The “best efficiency point” is represented by the maximum point on the efficiency curve. Q_{bep} is referred to as a certain fraction of the best efficiency point flow [10, 11].

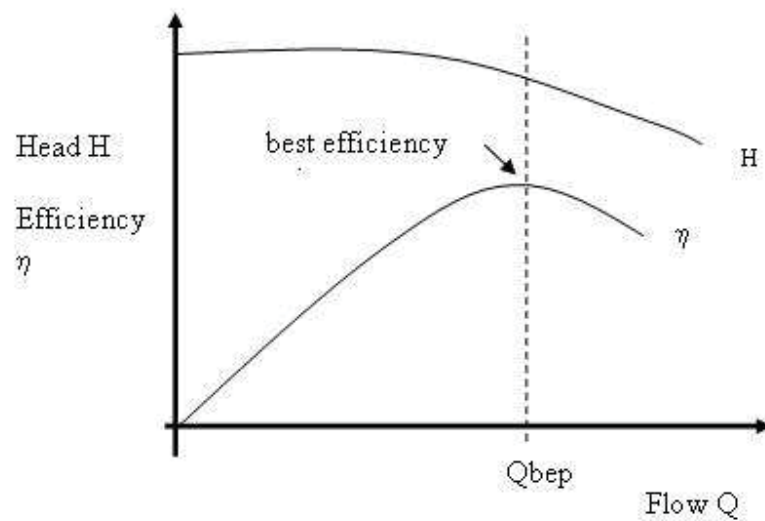


Figure 2.8 Typical pump performance curve. [10, 11]

2.4.4 Impeller Wear

2.4.4.1 Effect of particle size

The impeller bears the direct force of the incoming slurry initially at higher angles. Investigations carried out by Walker [11] highlighted the trajectory deviation of particles through the impeller. Other authors in this area of study believe that under the effects of coriolis and centrifugal forces, larger particles will impact the leading face of the impeller blade and the back shroud while the smaller particles gather close to the leading face of the blade. The smaller particles will then depart the impeller at angles 5 – 15 degrees smaller than the blade outlet angle as represented by β_2 . With the larger particles, these will depart the impeller at angles larger than β_2 as shown in Figure 2.9. Areas labelled I – IV in Figure

2.9 relate to the predicted wear zones in the impeller. It is believed that larger particles cause major wear in zones I and IV.

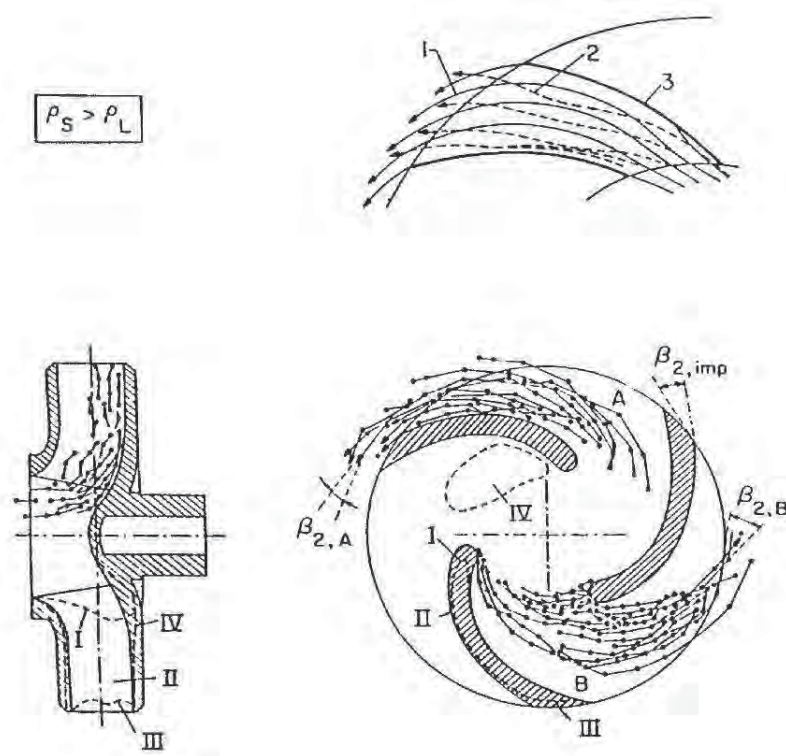


Figure 2.9 Impeller particle trajectories (A – small particles, B – large particles) and areas of maximum wear (I, II, III, IV) in the impeller for different particle sizes.

Other studies mentioned in Walker's paper by Fan et al. (1995) and Hu and Cheng (1993) investigated the effects of particle sizing on the wear of impellers [11]. Fan et al. described the wear in three different regions of a 220HBN nickel alloy impeller in a phosphoric acid and gypsum slurry. No size for the gypsum was given but it can be assumed that the size is less than 100 μ m. Two distinct wear regions were apparent upon analysis: a) the eye region, b) the other periphery of the impeller. In region a), the wear was minimal around the eye extending just beyond the leading edge of the vanes. Region b) resulted in high wear in the form of deep gauges at the pressure side of the vane and at the joint between the vane and back shroud.

Hu and Cheng (1993) studied the wear life of a number of different slurry pumps in a range of different applications. In regards to particle size effects on the impeller, they discovered that an impeller's life would increase 7 times if the particle size is decreased from 160 μm to 100 μm .

2.4.5 Casing-liner Wear

2.4.5.1 Effect of flow rate on wear

The flow rate of the slurry pump is critical to the wear performance of the material as this will often dictate the amount of wear. The most severe wear of the casing-liner is usually just behind the cutwater [11]. Pumps operating at flow rates below the best efficiency point (Q_{bep}) are believed to be the result of this severe wear. The location of the cutwater can be seen in Figure 2.10. Figure 2.11 shows the effect of the flow rate below and above the Q_{bep} point. At low flow rates the fluid separates behind the cutwater creating a vortex and causes deep gouges in the casing-liner [11].

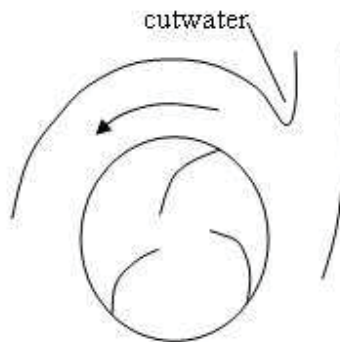


Figure 2.10 Location of the cutwater of the casing-liner. [11]

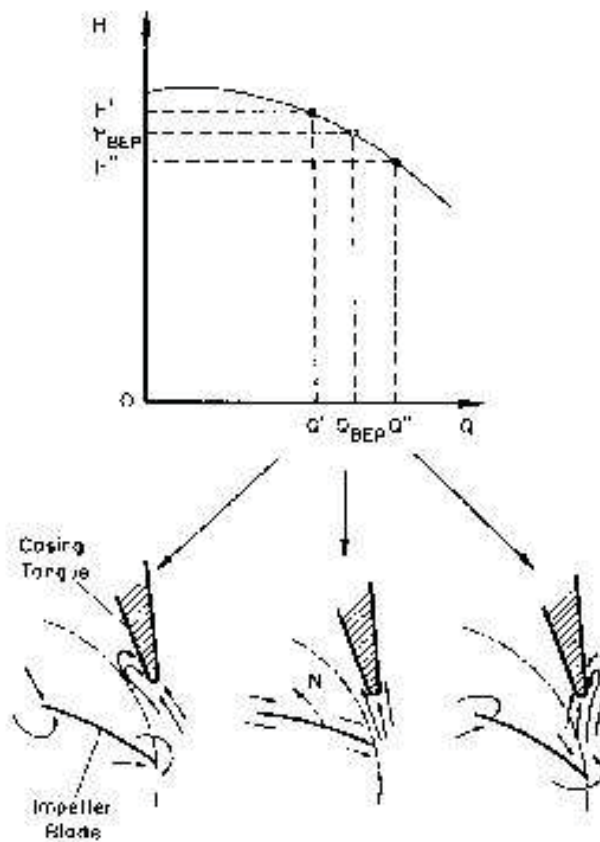


Figure 2.11 Casing-liner wear predictions of flow rates above and below Q_{bep} . [11]

Wear prediction for pump casing-liners was also mentioned by Walker and illustrated in Figure 2.12. As the slurry enters the pump and is dispersed by the impeller into the casing-liner, the side wall that is situated slightly after the cutwater is prone to gouging. As the slurry is then transported along, the wear shifts towards the tongue, then the discharge and finally wear along the tongue tip. Wear occurs predominately at the perimeter of the casing and is dependent on the flow relative to Q_{bep} [11]. Computational fluid modelling (CFX) can be used to simulate wear and flow rate in a slurry pump. Figure 2.13 illustrates the direction of the particles as they are displaced by the impeller and discharged through the casing-liner. It can be seen from this diagram that the flow near the discharge at the cutwater. Here, particles will impinge on that corner as some particles will return into the main flow of the centrifugal force imposed by the impeller [16]. This theory is justified in

Figure 2.14, here a wear simulation is illustrated and the red colour indicates that severe wear is predicted and occurs at this point.

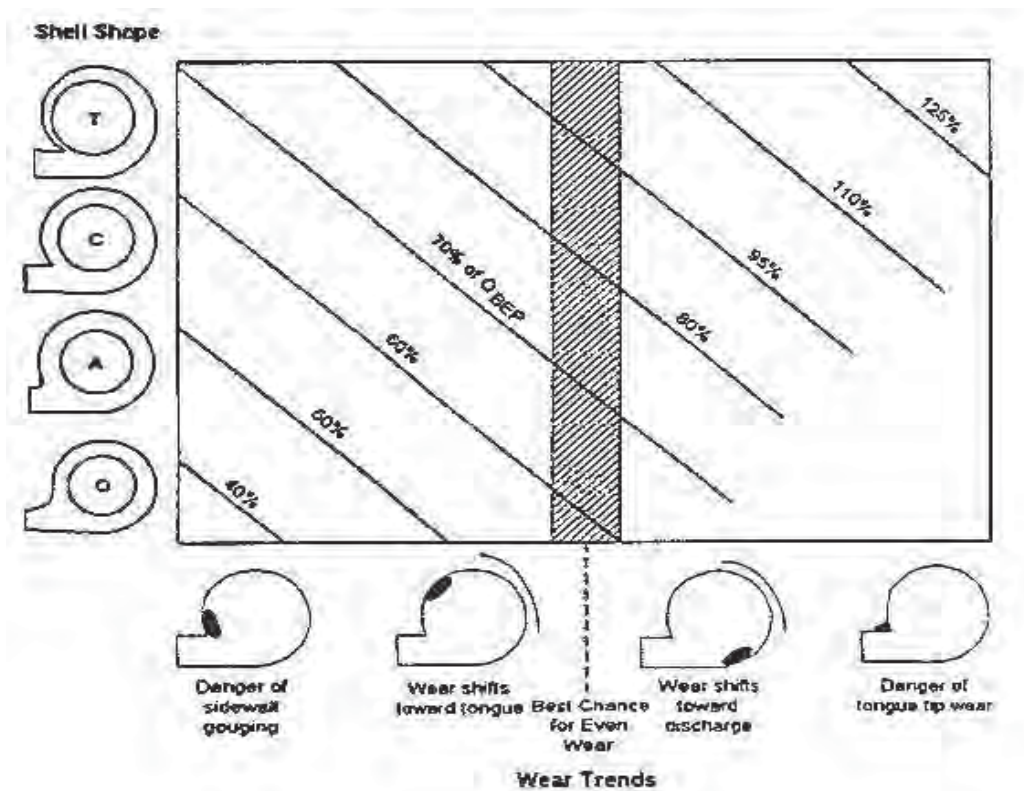


Figure 2.12 Trends in location of casing-liner wear. [11]

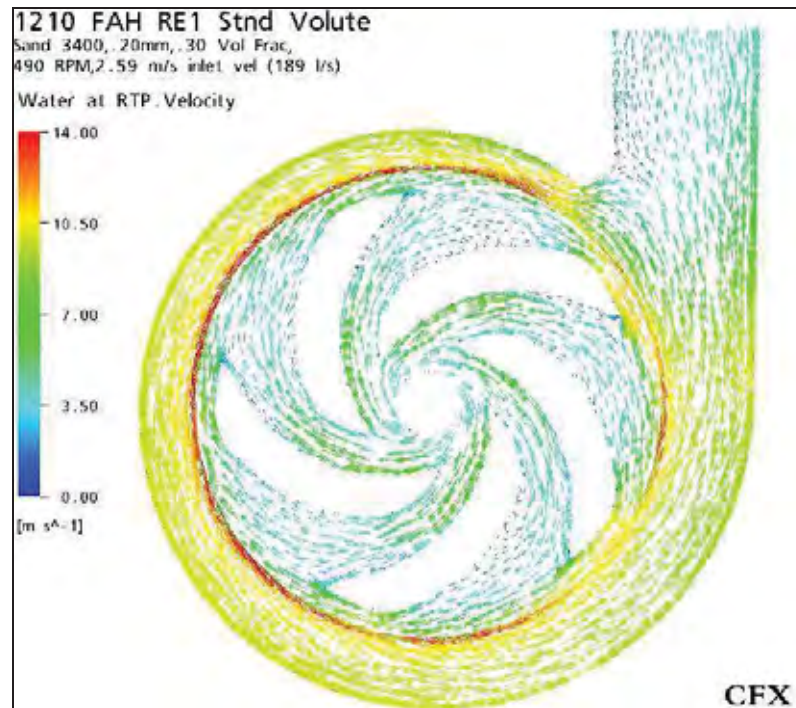


Figure 2.13 CFX model for flow rate simulation of a slurry pump. [16]

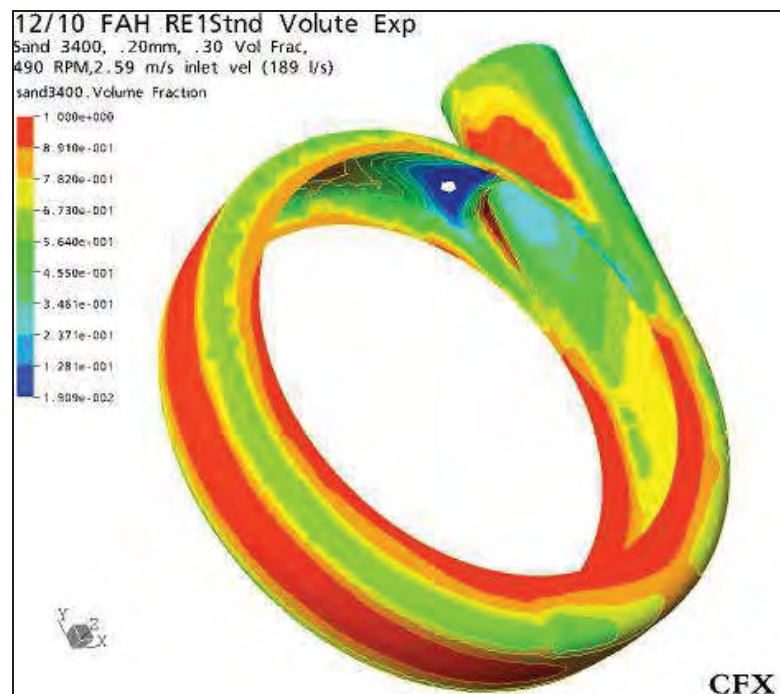


Figure 2.14 CFX model for wear simulation of a slurry pump. [16]

2.4.6 Wear Principles

Wear relates to all processes that have two contacting surfaces made of different materials. In relation to the general wear of slurry pumps, there are a number of issues that are important which include the material itself, particle size, slurry concentration and operating conditions. The materials used in slurry pumps are usually made from the three large material families; metal, polymer and ceramic. Each material will perform according to the exposed conditions, for example a metal will perform better than an elastomer in a high temperature application. Walker describes gouging wear to be the limiting factor to wear in many applications in particular to the slurry pump [10, 11]. Gouging occurs throughout the slurry pump due to geometric discontinuities or flow problems causing wear to concentrate at those areas. However, this is not always the case as other theories such as micro cutting and cracking, particle drop-out, fatigue and erosion are commonly used to describe wear. This thesis will focus upon the wear of elastomers used in slurry pump applications and the chemistry of the material and its properties.

The particle size of the slurry is of major importance in the study of wear in slurry pumps. The particle size generally dictates the wear mechanism involved and can be either abrasive, erosive, cavitation or fatigue. Walker [11] refers to particle size as the influencing factor for; a) type of wear such as local gouging, b) the appearance of the worn surface, and c) the relative wear of different parts. Lum [3] investigated the particle size effect on erosion to rubber slurry pump liners and concluded that the peak wear loss to occur was at particle sizes of 500 μ m at 20m/s flow rate and at an impingement angle of 20°. Figure 2.15 highlights the three materials used in this study which are as follows; A1 is a natural rubber consisting of pure gum rubber, A3 is a polymer blend of natural rubber and polybutadiene reinforced with granulated silica, and B1 is a natural rubber reinforced with precipitated silica. A particle size threshold theory was also introduced as a form of data point clusters at different angles of impingement. Figure 2.16 illustrates this theory. Apart from a few studies in the literature, there is still no definitive relationship between the particle size,

type of wear and surface wear pattern available. This study will endeavor to ascertain answers this field of tribology so that ultimately the slurry pump life can be extended.

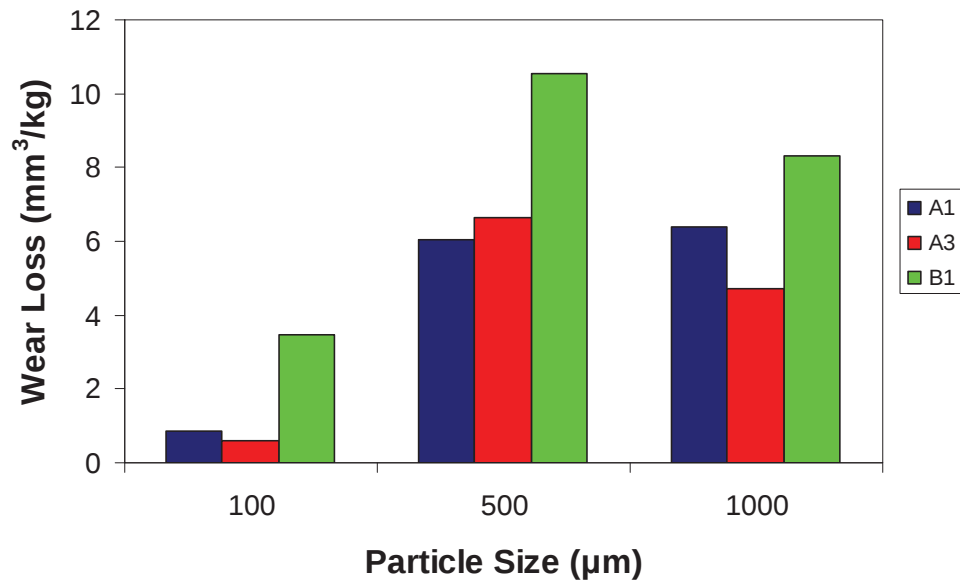


Figure 2.15 The average wear loss vs. particle size for A1, A3 and B1. [3]

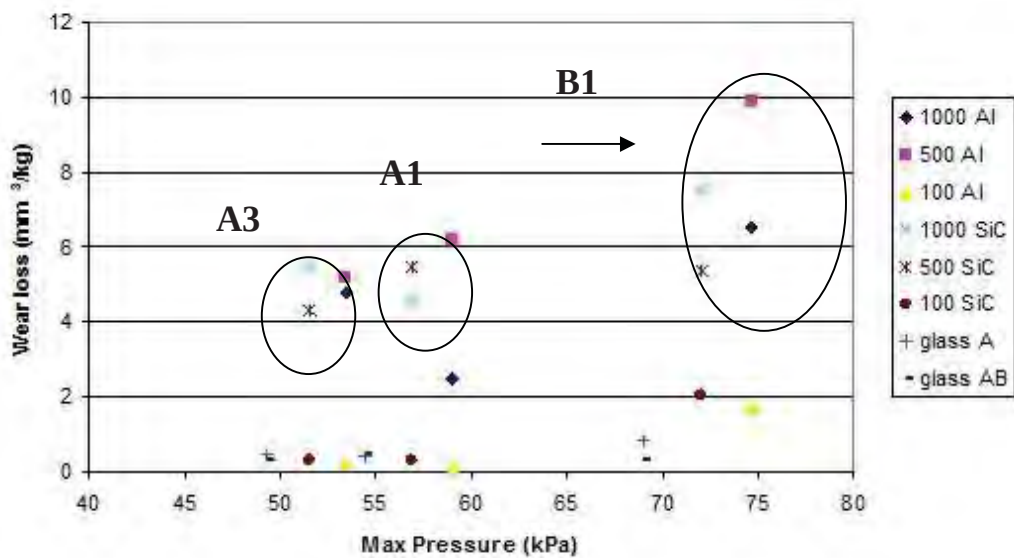


Figure 2.16 Wear loss for A1, A3 and B1 as a function of max pressure at angle of impingement 20°. [3]

2.5 *Wear Mechanisms of Rubber Pump Lining Materials*

2.5.1 Introduction

Wear is an ongoing process in every aspect of material service life. The movement of one material over another will fundamentally cause wear to occur; the wear mechanism depends on the application and conditions that each material are exposed to. This field is often referred to as “Tribology”, defined by Hutchings as the science and technology of interacting surfaces in relative motion [18]. The damage to one or both of the surfaces generally results in progressive loss of material that leads to increased clearances between the moving components, unwanted freedom of movement and loss of precision, vibration, increased mechanical loading, and sometimes fatigue. The result of this damage often leads to complete failure of the machine or process costing time and money to the manufacturer.

In the mining industry, there is an ever increasing need for high wear resistant materials for pump liners. The cost in changeover and downtime of a process is often much higher than the cost of a high wear resistant material. Therefore, in a development point of view, there is a demand to research and develop high wear resistant materials subjected to these harsh conditions. However, the evaluation and investigation into the wear mechanisms involved in field testing is usually inconsistent with the laboratory results. In practice more than one wear mechanism is present during field testing, which makes wear difficult to characterise and quantify the laboratory results in relation to this field result. Single wear tests in laboratory conditions often rank differently on single wear mode tests, these laboratory wear tests can be seen in Table 2.1.

Table 2.1 Laboratory Wear Tests. [19] pg 5

Wear test	Conditions	Variables
Pin-on-disk	High stress abrasion (two-body abrasive wear)	Abrasive material, size, load, velocity
Dry sand rubber wheel	Low stress abrasion (three-body abrasive wear)	Erodent hardness, size distribution, shape, velocity
Erosion jet	Solid particle erosion	Erodent hardness, size distribution, shape, angle of incidence
Slurry jet	Solid particle erosion	Erodent hardness, size distribution, shape, velocity, slurry pH, temperature
Rotary impact crusher	Impact-abrasion wear	Impact velocity, feed type, size
Jaw crusher	Gouging abrasion	Ore mass, type, size
Slurry pot	Sliding abrasion	Particle velocity, concentration, angle of impact (all hard to control)
High speed impact	Impact gouging	Projectile velocity

I.R. Sare et al. state that abrasion, erosion, and corrosion are the most common types of wear in the mining and minerals processing industries [19]. Erosion is the main area of interest in the investigation of slurry pump wear; however abrasion and corrosion may also contribute to the wear [20]. These aspects of wear in tribological systems will be investigated further in this paper as well as building relationships that exist with field and laboratory testing. It should be noted that the erosive and abrasive processes that cause material removal are still poorly understood, and a few models used for the prediction of material behaviour are defined later in this chapter [21].

2.5.2 Erosive Wear

2.5.2.1 Definition

Erosive wear is the result of continuous particles in a fluid system, impacting on the surface of the pump lining material causing material removal and damage [11, 16, 18, 22, 23]. This material removal process is a gradual deterioration rather than an instantaneous process and is very much time and environmental dependant. The ASTM G67 definition of erosive wear states the material removal from a solid surface is due to the mechanical interactions between the surface and the *impinging* particles in a liquid stream. Figure 2.17 illustrates the three main modes of erosive wear.

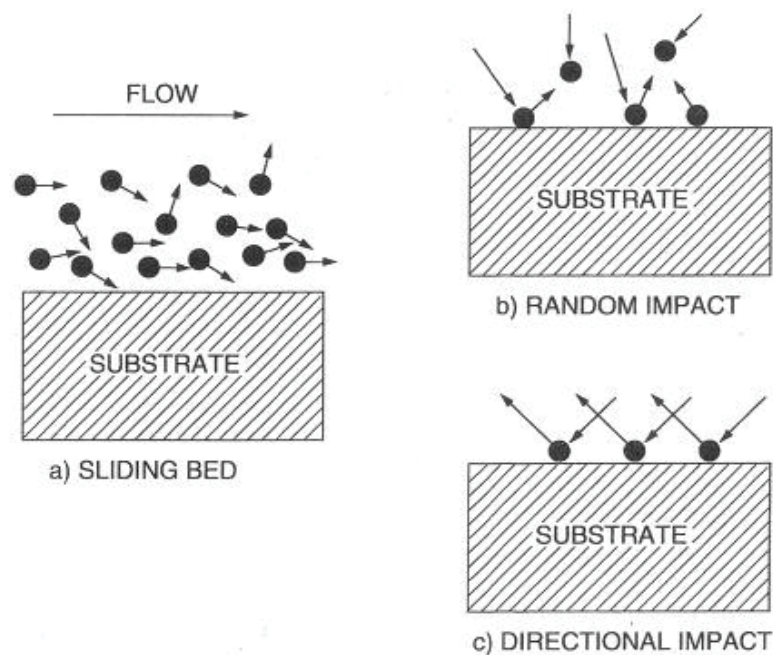


Figure 2.17 Three main modes of erosive wear. pg 2-2, [16]

Hutchings distinguishes between erosion and abrasive wear primarily in the origins of the forces between the particles and the wearing surface [18]. In abrasion the particles are forced to move along the surface of the material as they are pressed together, this is usually due to the design of the slurry pump or because they are trapped between two sliding surfaces. While in erosion, several forces of different origins may act on a particle in contact with a solid surface. Basically, erosion involves the transfer of kinetic energy to the surface, while abrasion does not. Figure 2.18 illustrates the forces that act on a particle at it hits the surface of a material. These forces include neighbouring particles causing contact forces, fluid causing drag forces, and in some conditions gravity may be a factor. However, the dominant force on an erosive particle is usually the contact force exerted by the surface in order to decelerate it from its initial impact velocity. In erosive wear, the degree of wear depends on the number of particles, the impact velocity of the particles, and the mass of the individual particles striking the surface.

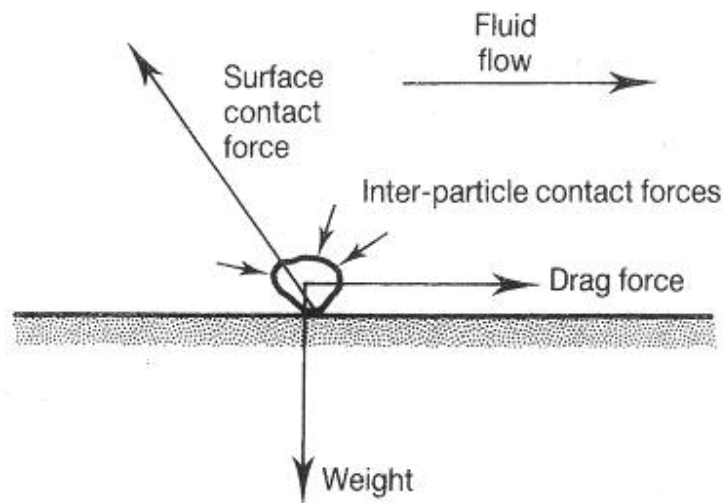


Figure 2.18 Forces which can act on a particle in contact with a solid surface. pg 171 [18]

2.5.2.2 Wear mechanisms

In the erosive wear of pump lining materials, the kinetic energy from the particles is transferred to the surface of the material via particle impact forces and momentum. These usually lead to the deterioration of the surface and hence, wear of the surface material.

Hutchings states that there are several forces that act on a particle in a slurry [18]. See Figure 2.18. These include the following:

- Contact forces from neighbouring particles
- Drag forces from the flowing liquid
- Gravity forces in some applications

In pump impeller vanes, casing-liner periphery or impeller back shroud, a curving and rotating flow field is present. This will involve two additional forces due to:

- Centrifugal acceleration (centrifugal force)

- Coriolis acceleration (coriolis force)

As mentioned earlier, the size and shape of the particles and the applied stress levels are important to the wear mechanisms involved with elastomers. In particular, the wear of an elastomer is most susceptible to wear mechanisms at certain particle impingement angles. A number of studies state that at low impingement angles, tear resistance of the material is critical due to the process of tensile tearing [4, 7, 11, 24-26]. At high angles, closer to the normal incidence, the impact is generally elastic in nature. Therefore, the most important physical property of the rubber in this case is the resilience. Tensile tearing and fatigue are the wear mechanisms under scrutiny, with increasing elastic modulus.

Erosive wear can often be correlated with a number of abrasion wear mechanisms for elastomers [3, 11, 18, 23]. In deformation wear, the initial particle contact with the surface of the elastomer will result in elongation at the rear of the particle which is followed by tearing and recovery of the remaining material into a lip. From multiple impacts of the same nature, a formation of rows of ridges transverse to the direction of slurry motion can be seen. These rows of ridges can be modelled using fracture mechanics and are known as fatigue cracks. Difficulties have been faced when relating the observed wear with the elastomer's physical properties, since degradation occurs at the surface layers of the elastomer. Walker [11] states that the wear processes that occur include chain-scission and free radicals reaction, however this is yet to be investigated at an academic level. In this case it is the wear process that leads to the differences in the surface layer properties to the bulk of the material.

The angles of incidence plays a part in the wear mechanisms showing similarities to that associated with abrasion by a blade [3, 8]. At shallow angles, a series of ridges, running transversely to the impact direction is produced on the surface during the early stages of exposure, and erosion occurs by the progressive growth of fatigue cracks from the bases of the ridges into the bulk. This is the rate determining step in the growth of fatigue cracks that leads to material removal by the tearing of the fragments from the ridges. It is important to note that cracking occurs without the presence of craters due to the viscoelastic behaviour

of rubber. At angles near the normal incidence, experimentally it has been found that in some conditions, large, deep holes can be formed on the surface of the rubber, particularly with large particles at high velocity. A formation of a dense network of fine fatigue cracks in the surface of the elastomer is observed. The intersection of these cracks is the point of material de-cohesion and failure. This leads to the main erosion mechanism for erosive wear of rubber at angles of normal incidence. The fatigue cracks propagate under the action of tensile stresses produced in the surface by each particle impact. It is more the case of the frictional forces during impact, rather than bulk deformation of rubber, that results in tensile stresses in the surface, which in turn leads to fatigue crack growth and erosive wear [27, 28].

2.5.2.3 Erosive wear processes

Some main processes leading to wear by single or multiple impacts of particles are summarised in Figure 2.19.

Where:

- a) microcutting and microploughing
- b) surface cracking (microcracking)
- c) impact craters
- d) subsurface fatigue cracks
- e) formation of thin platelets due to extrusion and forging by repeated impact
- f) formation of platelets by a backward extrusion process

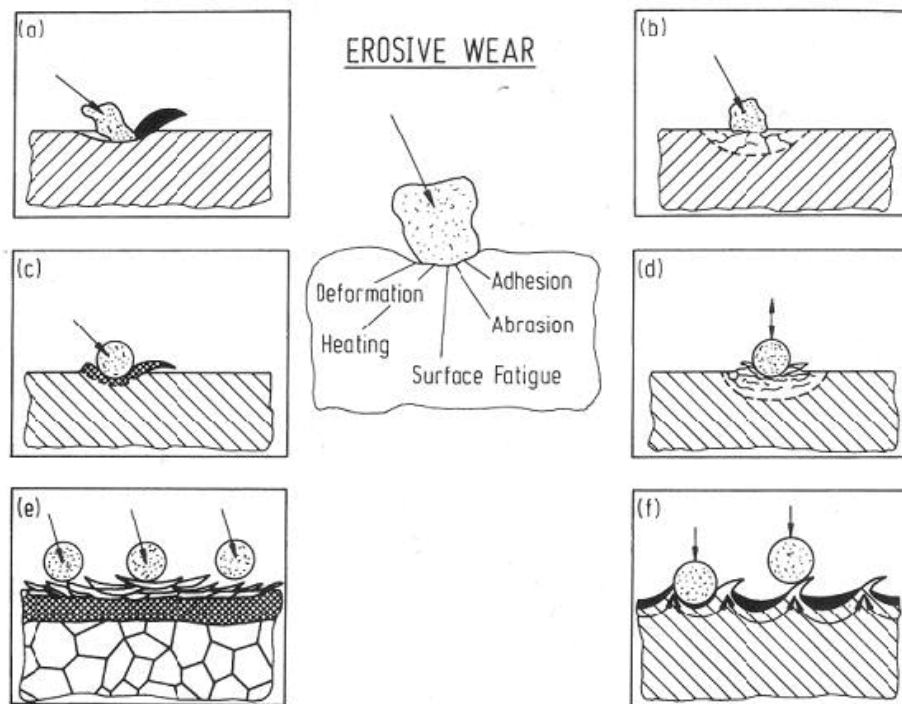


Figure 2.19 Processes resulting in wear loss due to single or multiple impacts of particles. pg 534 [23]

2.5.2.3.1 Micro-cutting & micro-ploughing

Angular particles can remove material from the surface by micro-ploughing and/or micro-cutting when they strike the surface at small angles [18, 23, 29]. The physical interactions between abrasive particles and the surfaces of the materials can be seen in Figure 2.20. The deformation caused will depend on orientation and whether the particle rolls forwards or backwards during contact. Figure 2.21 illustrates the impact sites formed by hard particles on a ductile metal. Ploughing is the process in which rounded particles deform the surface by displacing the material to the sides. Type I cutting refers to the impacting particle rolling forward. As it rolls, the indentation made on the surface will raise the material into a lip. This prominent lip is vulnerable to removal by subsequent nearby impacts. Type II cutting refers to the particle rolling backwards as it strikes the surface. The abrasive particle cuts a chip from the surface; however this only occurs over a narrow range of particle geometries and impact orientations.

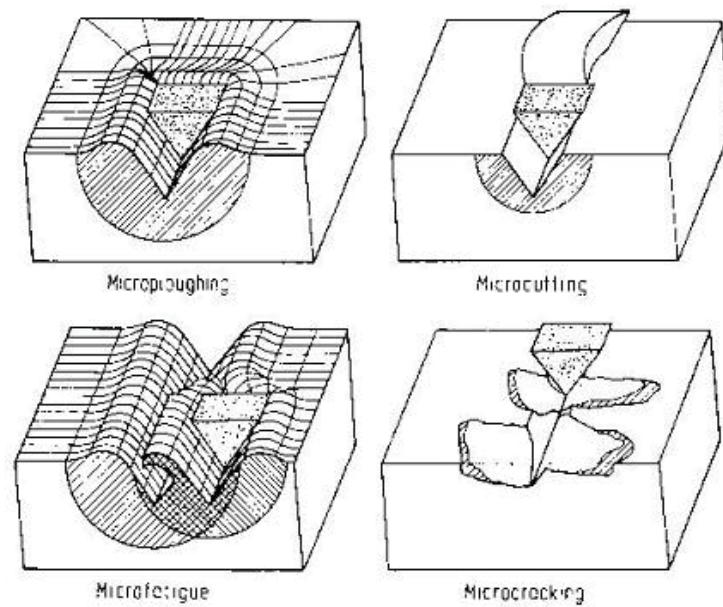


Figure 2.20 Physical interactions between abrasive particles and surfaces of materials. pg 96 [23]

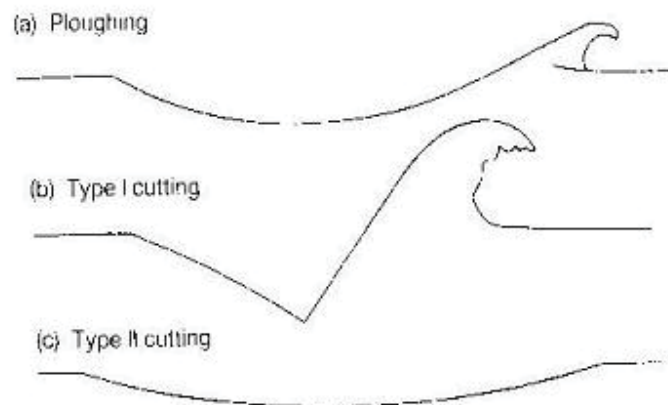


Figure 2.21 Sections through impact sites formed by hard particles on a ductile metal, showing typical shapes. The impact direction was from right to left. pg 176 [18]

- a) Ploughing deformation by a sphere
- b) Type I cutting by an angular particle, rotating forwards during impact.
- c) Type II cutting by an angular particle, rotating backwards during impact.

2.5.2.3.2 *Micro-cracking*

Micro-cracking concerns brittle materials rather than ductile, in that the erosion rates are higher [23]. Surface cracking becomes important to investigate with increasing impingement angles, particle sizes, particle velocities and/or increasing the brittleness of the target material.

2.5.2.3.3 *Impact craters*

Söderberg et al [8] stated that impact craters do not usually occur in the erosion of rubber materials. It was concluded that no craters are formed at single impacts due to the material undergoing high elastic deformation, thus reducing the contact stresses. However, Petit et al. [30] suggests hole and craters are found to occur in the wear pattern for tyres driven on a straight highway and from our prior research [3] the theory of particle “drop out” was established. The formation of craters and holes on the surface of the rubber was also investigated by Arnold and Hutchings [31]. It was stated that single-cycle tensile failure of the rubber leads to the formation of holes which occurs under some impact conditions. Figure 2.22 shows the formation of small to large craters ranging from 50µm - 200µm in diameter for A1 rubber eroded with 500µm SiC particles at 90°. Figure 2.23 shows a similar trend where crater holes are present in A1 after testing using 100µm Al₂O₃ particles at 90°. Arnold and Hutchings assume with larger particles and at higher velocities more hole formation would take place. However, from the experimental results and analysis, it is not always the case, small particles tend to cause hole formation where as larger particles tend to cause cuts and gouges that lead to hole formation.

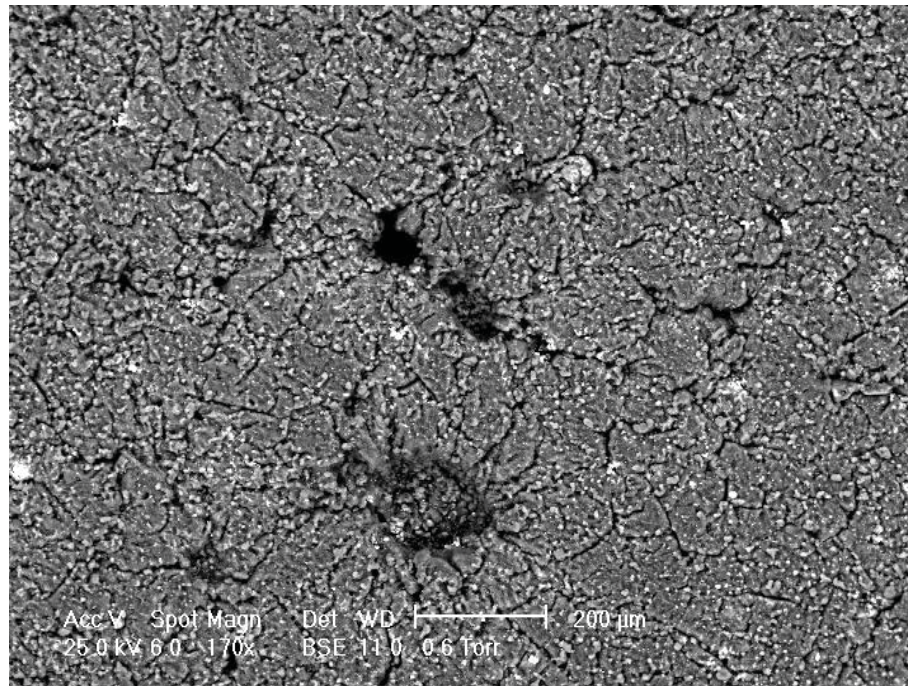


Figure 2.22 ESEM picture of A1 material eroded with 500µm SiC particles at 20m/s with angle of impingement 90° showing micro cracks and crater holes. [3]

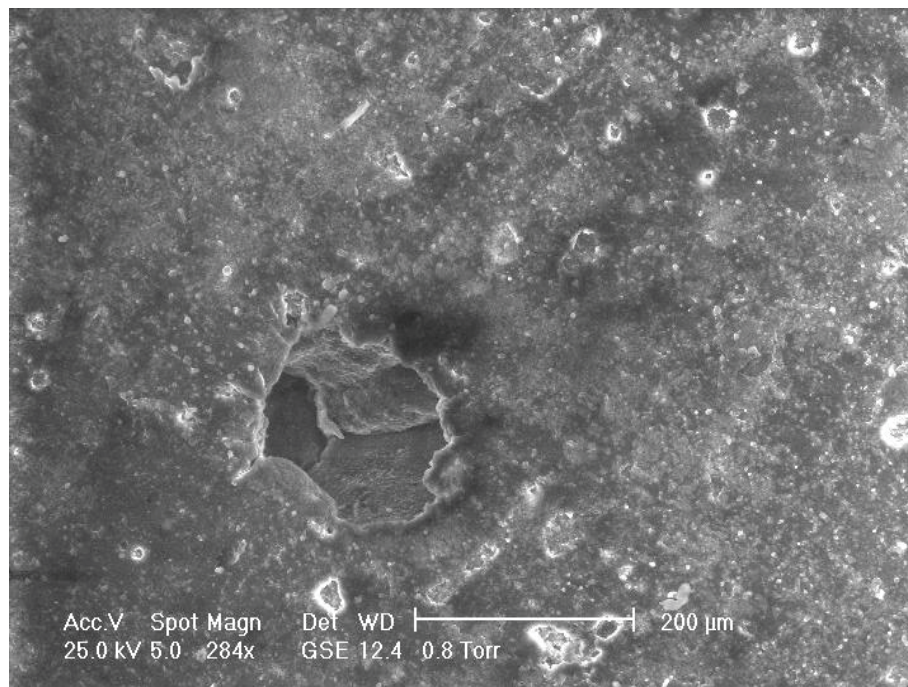


Figure 2.23 ESEM picture of A1 material eroded with 100µm Al₂O₃ particles at 20m/s with angle of impingement 90° showing micro cracks and crater holes. [3]

Petit et al. [30] simulated the crater formation on the rubber samples by using a simple tribometer shown in Figure 2.24. In this process, the rubber sample is rotated by an electric motor and slides against a spherical steel indenter in which a normal force F_n between 5 and 70 N is applied. These craters were then analysed using an optical rugosimeter to obtain the topography of the worn surfaces and the crater shape. Upon analysis of the geometry of the crater, it was found that a hill-like shape at the rear of the hole was present as shown in Figures 2.25 and 2.26. The several geometrical parameters that are characteristics of these patterns are listed by *Petit et al.* [30] as:

- The slope at the rear of the hole, β : from 15 to 40°;
- The width of the hole, v , from 10^3 to $10^5 \mu\text{m}^3$, and of the hill, v_b , from 10^3 to $10^5 \mu\text{m}^3$. From the volume measurement, it was found that the ratio is roughly 1. The crater density is approximately 30 craters per mm^2 .

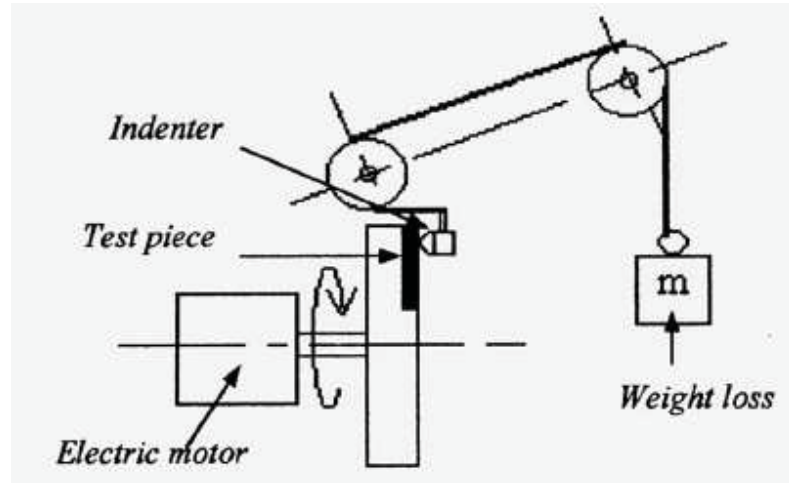


Figure 2.24 Drawing of the experiment's mechanical system. An electric motor rotates a rubber test specimen. An indenter slides against the rubber. [30] pg 314

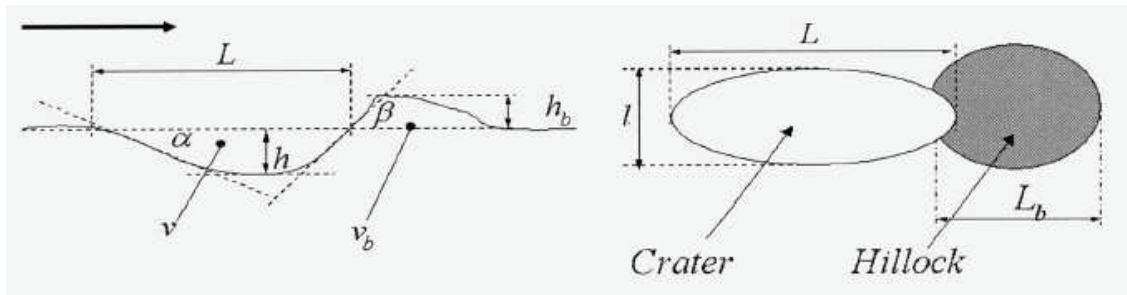


Figure 2.25 Drawings which represent a crater and the geometric parameters of a crater. [30] pg 315

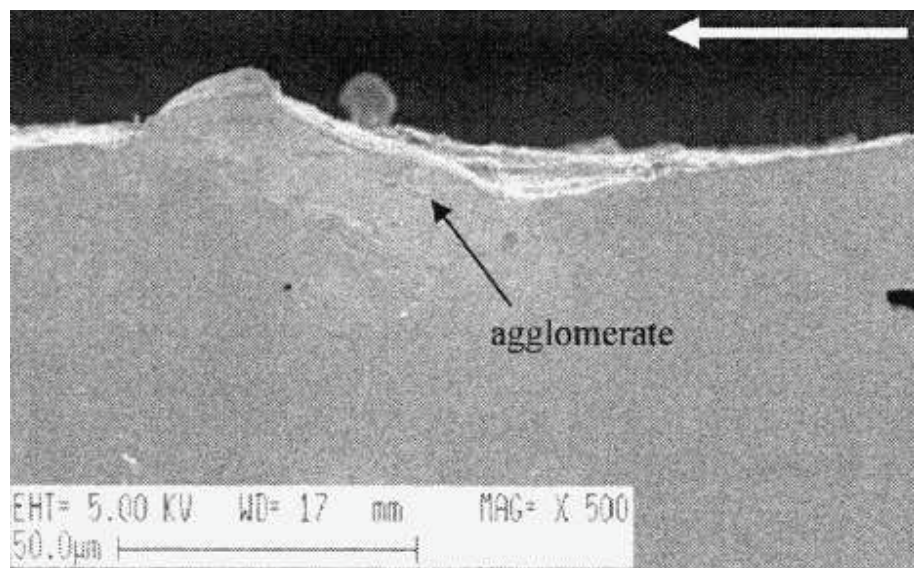


Figure 2.26 Sectional view of crater using an electron microscope. The agglomerate can be seen at the rear of the crater. [30] pg 318

Upon analysis of the craters formed from the mechanical system, Petit et al. [30] states that the craters have the same density and order of magnitude of diameter as the agglomerates. In the geometrical analysis of the craters it was observed that a hill is created at the same time and they also have the same shape. As a result of the strain continuum, the strains are similar in both the agglomerate and the homogeneous compound. The indenter causes the agglomerate to be sheared, plasticised and flattened as shown in Figure 2.27. The change in shape of the agglomerate causes residual stresses i.e. tractional stresses at the front and compressive stresses at the rear. In order to create a stable position, the agglomerate will tilt in resistance to the indenter consequently respecting the equilibrium

moment as seen in Figure 3.11c. The tilting angle β can be related to the apparent friction coefficient shown in Equation (1):

$$\beta = \text{Arc tan} (1/\mu) \quad (2.1)$$

The value of β is usually around 30° mark and it was found that this result was consistent with the slope value at the rear of the hole, which is between 15° and 40° .

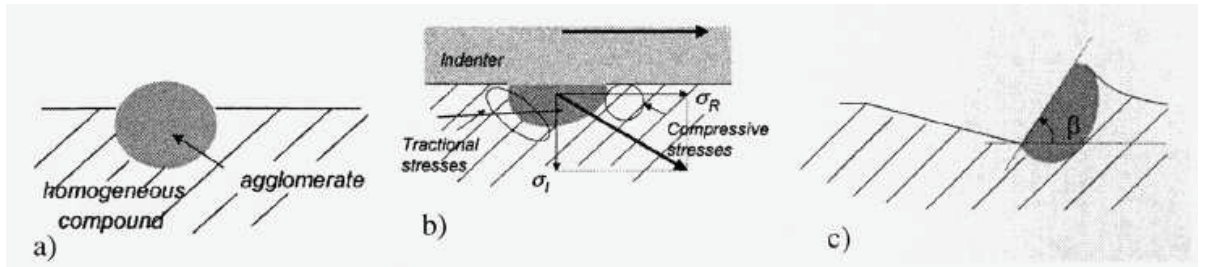


Figure 2.27 Mechanical system of the crater formation. [30] pg 317

Carbon black can also cause agglomerates to form as mentioned by Reincke et al [32]. Similar to the silica particle, the crack propagation will be hindered as it provides the rubber with some reinforcement. However, the theory of “critical filler content” involves a transition in filler morphology occurring after a critical point is reached. This critical point is defined as the point where the formation of filler clusters is present. During loading the crack propagation is hindered through the alignment of clusters forming a barrier to the growing crack [32]. This greatly improves the fracture toughness of the rubber, however if this critical filler content is exceeded the resistance to crack propagation under fatigue-like, impact-like and quasi-static loading conditions are decreased since the clusters tend to overlap each other interfering with the alignment.

2.5.2.3.4 Surface and subsurface fatigue cracks

A number of studies have indicated that erosive wear of rubber materials results in fatigue cracks on the surface [1, 5, 6, 10, 11, 16, 18, 23, 33-37]. The frictional forces on impact

cause propagation of fatigue cracks on the surface of the rubber [27, 28]. With the continual attack from the particles, the cracking is aggravated causing crack propagation beyond the surface. This fatigue mechanism may be the result of oxidation, in that the chemical bonds between the carbon chains are weakened. Figure 2.28 illustrates the surface wear of SBR rubber under the SEM.

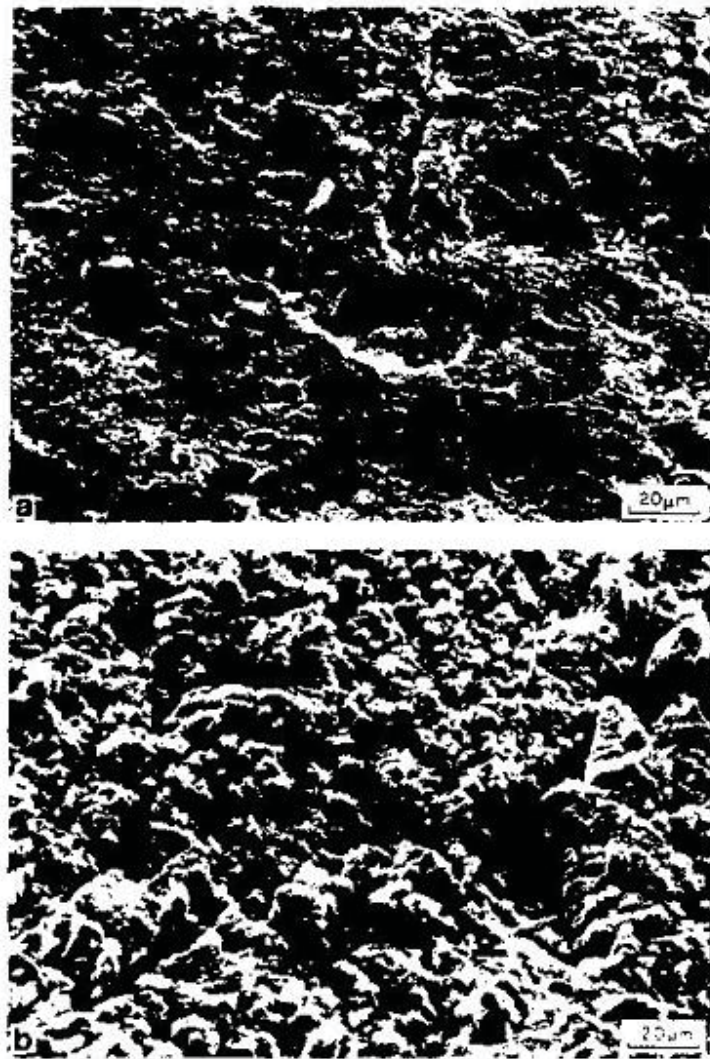


Figure 2.28 (a) Single and (b) multiple impacts in SBR rubber (impingement angle 45° and particle velocity 66 m/s). pg 342 [8]

No specific literature was found in investigating the subsurface cracks on rubber samples. However, it would be expected to find subsurface fatigue cracks as the initial crack propagates into the rubber.

2.5.2.4 Particle “Drop out” Theory

This theory of particle “drop out” was established in our previous studies [3]. At the impingement angle of 90° , with spherical glass particles as the wear media an interesting observation took place. Figure 2.29 and 2.30 show small holes approximately $10\mu\text{m}$ in diameter like craters, almost like bee stings on the surface of the worn rubber. These small holes do not interact with the micro cracks and they look raised above the worn surface. This is where the particle “drop out” theory is investigated with experimental results and ESEM analysis. The rubber blend consists of fillers and other compounding agents as mentioned in earlier sections. As the rubber is mixed, a relatively even dispersion of these particles is spread across the rubber. These particles are often of harder material than the base gum rubber polymer used as the backbone of mixing. The particle “drop out” theory is the result of these harder particles “fillers” dropping out due to particle bombardment at 90° . The stiffer particles in the final rubber compound, constrain the matrix from deformation. This constraint causes a thermal dislocation around the particle causing wear to occur around this particle (Figure 2.33).

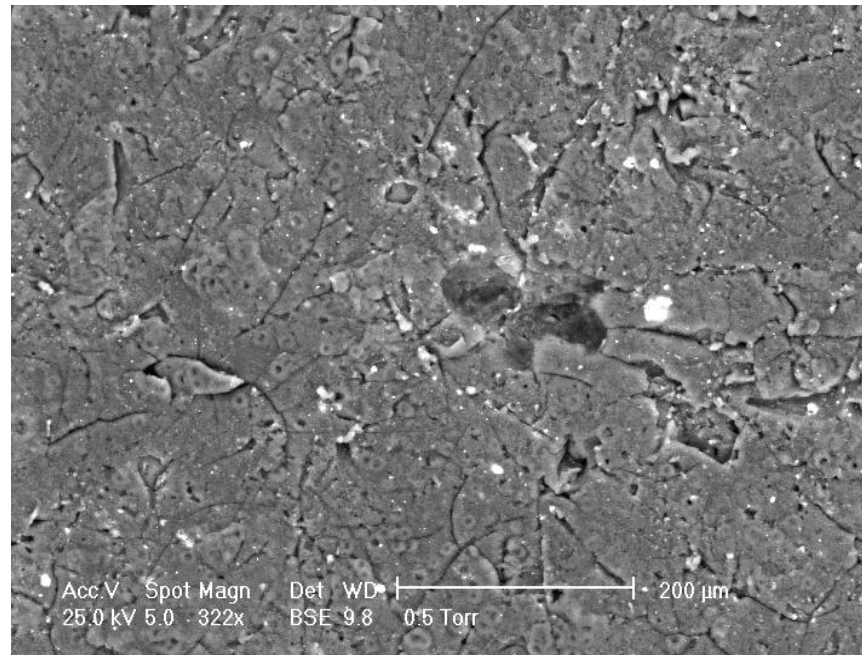


Figure 2.29 ESEM picture of A1 material eroded with 850μm - 600μm Glass spherical particles at 20m/s with angle of impingement 90° showing craters and micro cracks. [3]

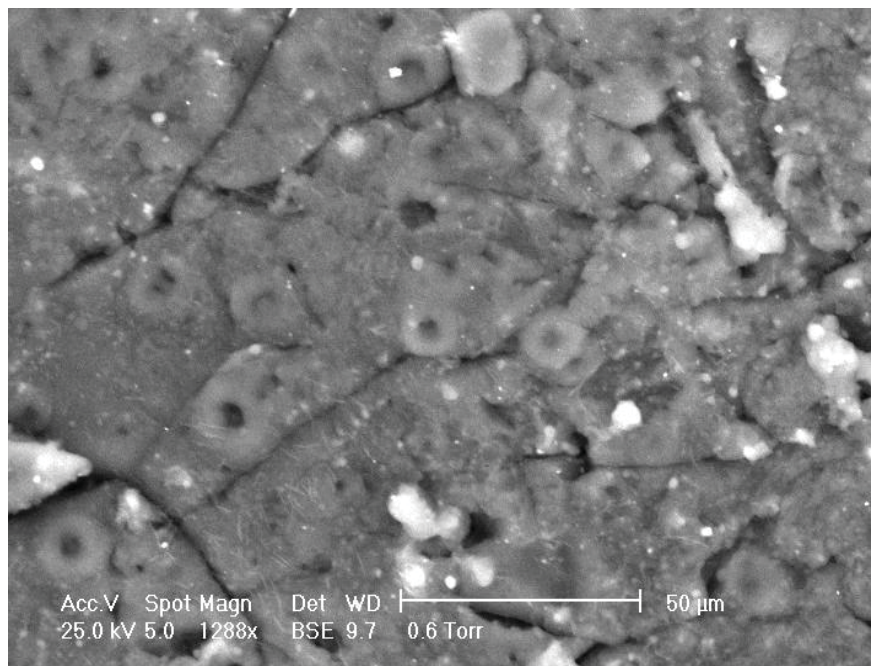


Figure 2.30 ESEM picture of A1 material eroded with 850μm - 600μm Glass spherical particles at 20m/s with angle of impingement 90°. [3]

Figure 2.29 does not indicate any particles still in the rubber matrix, most likely as a result of the large particles used during testing 850 μ m - 600 μ m. Figures 2.31 and 2.32 illustrate the filler particles still situated in the rubber matrix. The bright particles indicate high atomic number element, verifying a filler, possibly Si. The Si particles are approximately 10 μ m in diameter as such, fits the description of the craters in Figure 2.30. From the sizing analysis data sheet of the silica added in the rubber, high percentages (91%) of particles are less than 10 μ m in size. These particles have not dropped out since the amount of force required was not enough to force them out as the wear media particle size was only 300 μ m – 180 μ m.

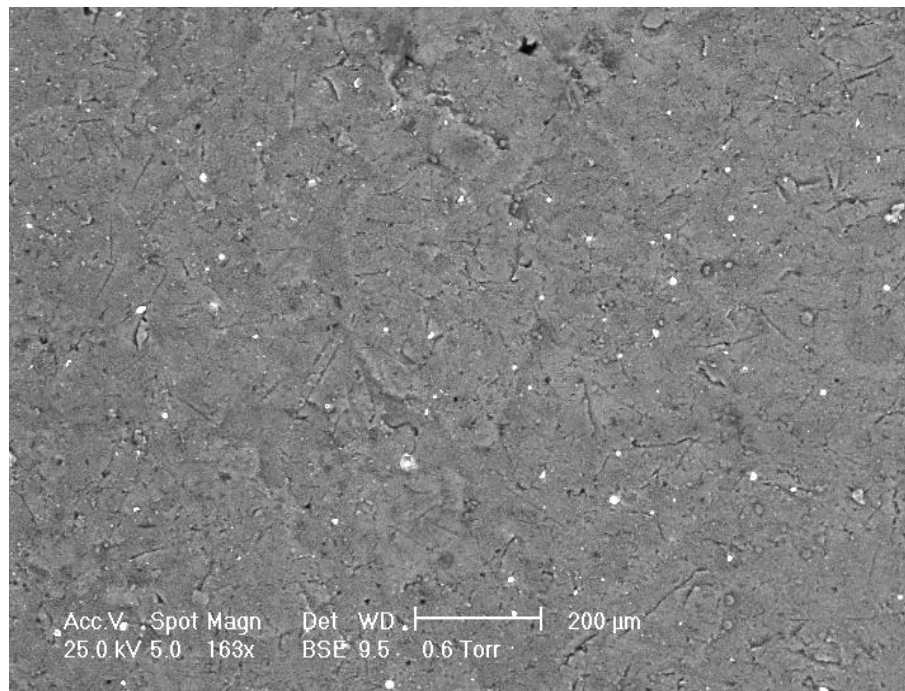


Figure 2.31 ESEM picture of A2 material eroded with 300 μ m - 180 μ m Glass spherical particles at 20m/s with angle of impingement 90° at low magnification (163x). [3]

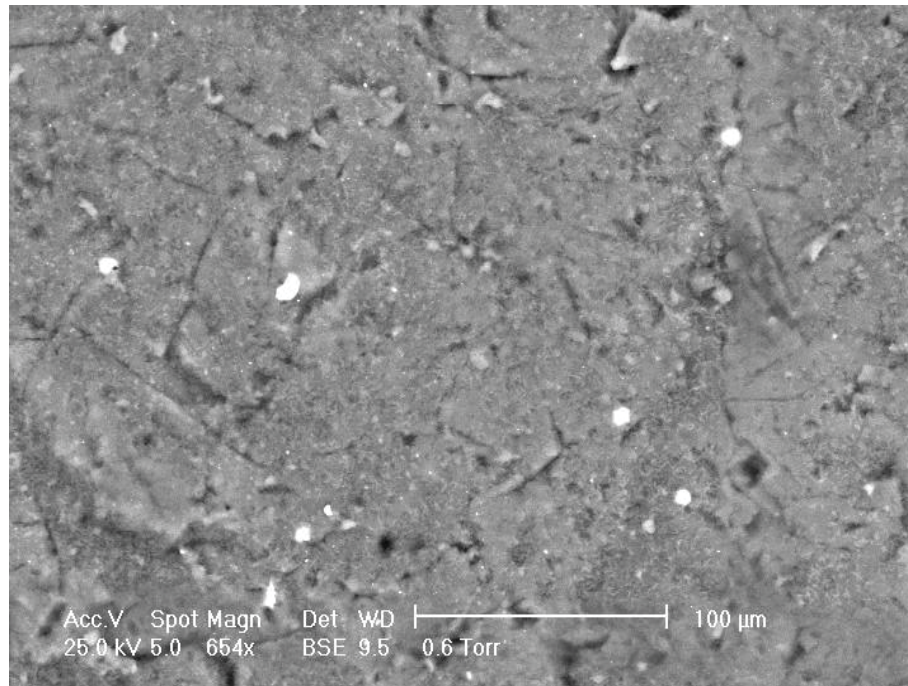


Figure 2.32 ESEM picture of A2 material eroded with 300µm - 180µm Glass spherical particles at 20m/s with angle of impingement 90° at magnification 654x. [3]

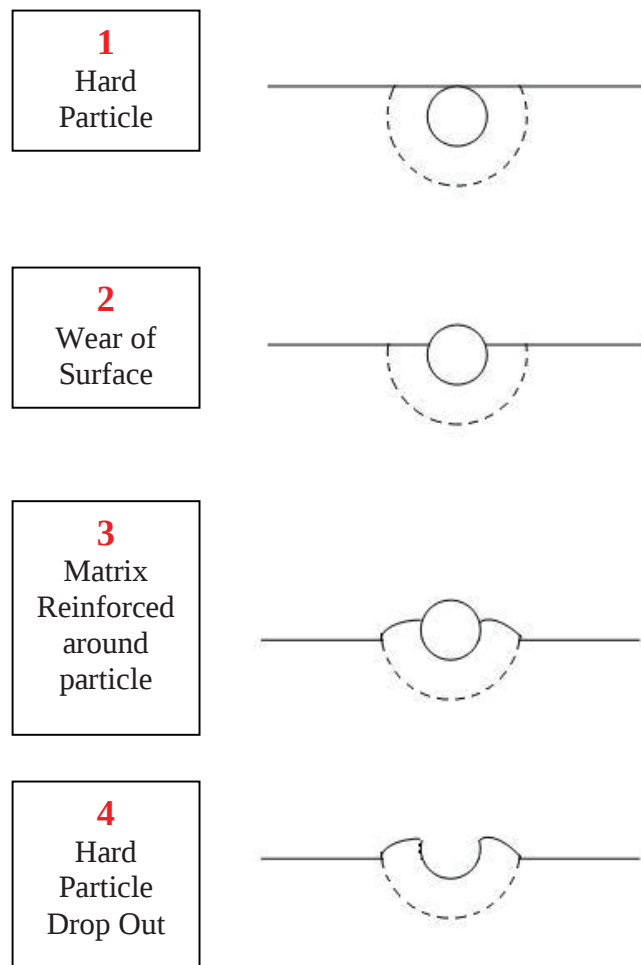


Figure 2.33 A schematic showing the “Particle Drop Out” theory. [3]

2.5.2.5 Erosive wear and depolymerisation

The phenomenon of depolymerisation and erosive wear has not been investigated in the literature. It is often assumed that some sort of chemical or depolymerisation occurs as a result of multiple impacts as the particles hit the surface of the rubber. Walker [11] outlines the research by Stachowiak and Batchelor (2001) as the chemical degradation of the surface of an elastomer occurs when hydrophilic particles (such as sand and silica) impact the surface and the water or oxygen molecules react with the rubber. As a result of this, a chemical reaction is induced and aided by the temperature rise due to the repeated particle

impacts. The surface layer of the elastomeric material becomes mechanically weak and may crack. This process is illustrated in Figure 2.34.

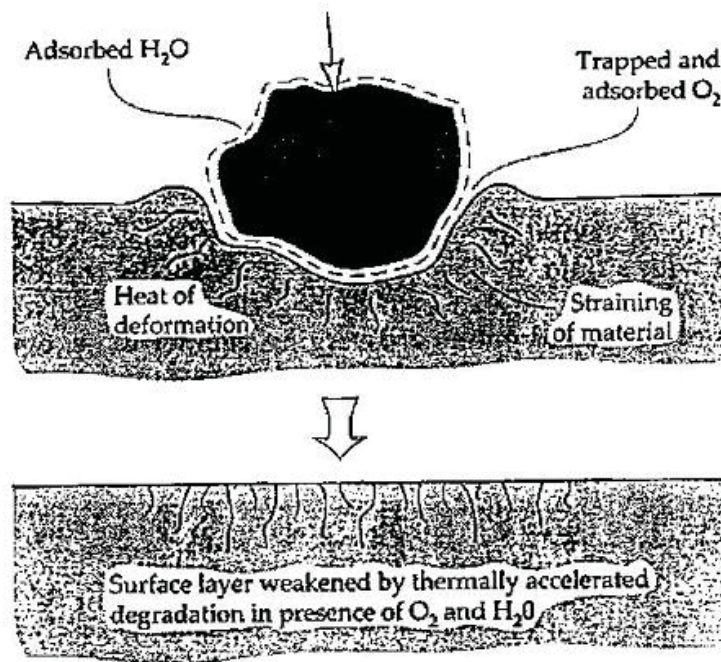


Figure 2.34 Chemical degradation of the surface of natural rubber under particle impact. [11]

2.5.2.6 Erosion wear models

2.5.2.6.1 Fundamental model for erosion wear

A number of researches have covered the fundamental model for erosive wear, in regards to factors that influence erosive wear [3-11, 16, 18, 23, 34, 36, 38-40]. These can be grouped into categories as follows and listed in Table 2.2:

- The properties of the material
- The properties of the abrasive material
- The properties of the fluid carrier or environment
- The contact conditions between the abrasive particle and wear material

Table 2.2 Fundamental wear model table. [1, 11]

Material Properties	Particle Properties	Contact Conditions	Fluid Properties
Tensile strength Hardness Resilience Elastic modulus Tear strength Density Fatigue strength Elongation	Shape Size Density Hardness	Velocity Angle of impingement Particle direction Surface temperature Surface treatment	Temperature Flow rate Flow system Chemistry

2.5.2.6.2 Engineering erosive wear models

Bayer reviewed a number of studies and discovered that these wear situations indicated a number of common elements and trends that could be consolidated to form the basis of an engineering model [38]. For particle erosion, Bayer considered two modes; one is ductile mode and the other is a brittle mode. The actual behaviour of erosion is considered to be the sum of these two components. This is illustrated by Figure 2.37.

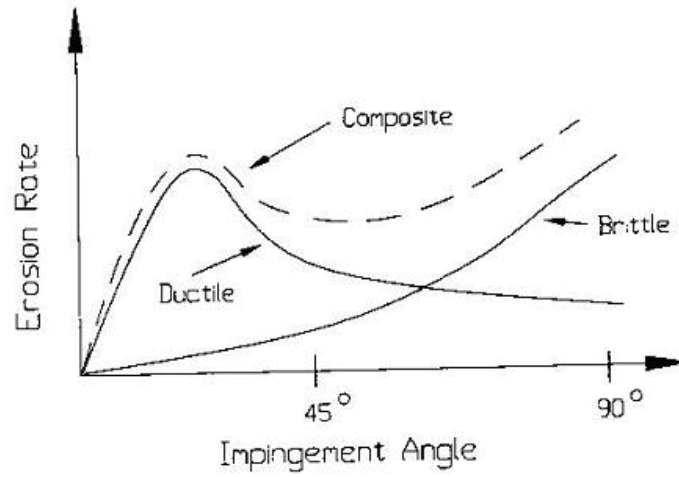


Figure 2.37 Erosion wear modes. pg395 [38]

2.5.2.6.3 Model for erosion under normal impact conditions

2.5.2.6.3.1 Stresses due to indentation

The surface stress induced by the indentation of a spherical particle on the surface was investigated by Arnold and Hutchings [3]. The radial tensile stress $\sigma(r)$ in the surface of an elastic half space subjected to a point load P is

$$\sigma(r) = \frac{P(1-2\nu)}{2\pi r^2} \quad (2.2)$$

where r is the radial distance in the surface from the loading point and ν is the Poisson's ratio. For elastomers, $\nu \approx 0.5$ therefore $\sigma(r)$ will be negligibly small. This model only applies to cases where there is relatively no movement between the indenter and the rubber. For cases where there is slippage between these two bodies, other models are available but will not be discussed further in this research paper. The Boussinesq theory for a rigid flat-ended punch is as follows

$$\sigma(r) = a\mu q \quad (2.3)$$

2.5.2.7 Model for erosion wear at oblique impact angles

The model for erosive wear at oblique impact angles was developed by Arnold and Hutchings [42]. Several assumptions are implicit when defining this model, they are as follows: (1) that the theory of blade abrasion due to *Southern and Thomas* is applicable (this theory assumes all the frictional force is carried at one ridge at a time); (2) that the impacting particles are spherical in shape; (3) that large deformations of the surface occur but that embedment of particles does not; (4) that the motion of the particles is pure sliding throughout the contact period, with no rolling; (5) that the coefficient of friction is constant; (6) that viscoelastic effects can be neglected.

The volume of material removed by fatigue crack growth per unit sliding distance, A , could be expressed as:

$$A = hB \sin \theta \left(\frac{F}{h} (1 + \cos \theta) \right)^\beta \quad (2.4)$$

Where: h – width of contact

F – frictional force

θ – angle to the horizontal at which cracks grow

B & β – constants in the Equation relating to crack growth per stress cycle, dc/dn , to tearing energy.

Southern and Thomas from the literature states that the value of θ lies typically in the range of 5 and 15°. Arnold and Hutchings [42] further investigated these values and assuming that the cracks grow parallel to the faces, the value of θ was about 15° for both natural rubber and styrene-butadiene rubber eroded by silica particles at impact angles between 15 and 45°. The value of θ will vary depending on material, however not to a great extent, therefore the value of θ taken by Arnold and Hutchings was 15°.

2.5.3 Erosion test methods

2.5.3.1 Erosion by solid particle impingement using gas jets

Gas jets have been used to investigate solid particle erosion in order to categorise materials in terms of their wear resistance [39]. This test method has been found to correlate well with erosion situations in particular particle impacts at near normal incidences. A schematic of this test method can be seen in Figure 2.38. [39] Weight loss is the method used for the determination of erosion rate. However, the resistance to erosion is measured in terms of the wear volume per gram of abrasive. This is obtained through the use of a wear curve that is generated by measuring the mass loss at different time intervals. The slope of this curve is then used to determine an average wear rate. The mass loss rate is converted to a volume loss rate by dividing by the density of the specimen. This volume wear rate is then normalised to the abrasive flow rate to provide the erosion value, which is defined as wear volume per gram of abrasive. The general trend is as follows; the smaller the erosion value, the more resistant the material.

Guidelines for the test duration must be set, as the wear depth of the material will result in a variation in impacting angle. Using a test time of 10 mins, the wear depth of the sample should not exceed 1 mm. The reason for this limit is that beyond the point where the shape of the scar becomes significant in determining the angle of impact. Figure 2.39 shows a typical scar and the effect of wear geometry on angle of impact.

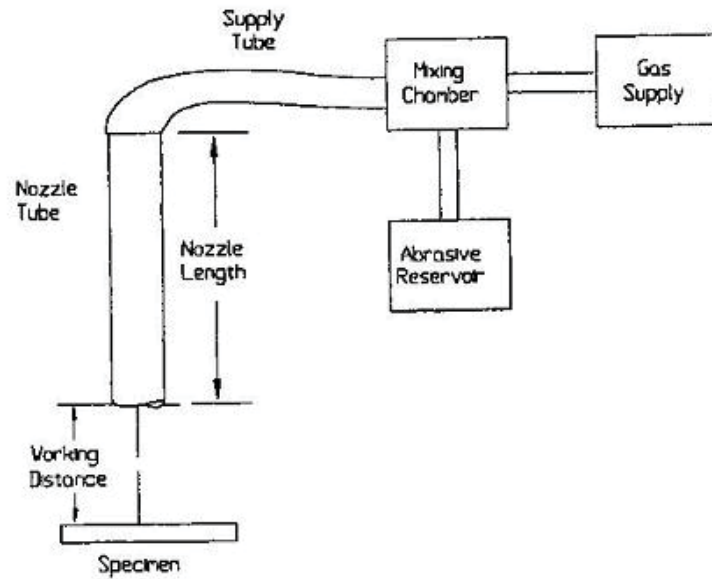


Figure 2.38 Schematic of the solid particle erosion test. pg267 [39]

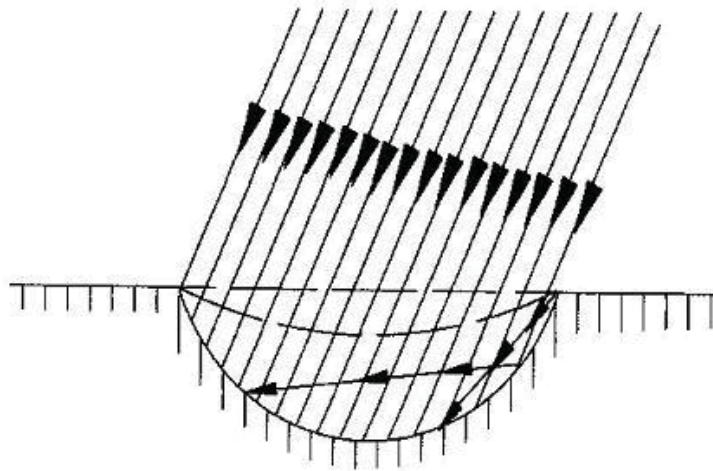


Figure 2.39 An illustration of the effect of erosion wear on scar geometry on particle impact conditions. As a result of wear, the angles of impact are no longer constant across the surface. pg270 [39]

Test conditions and procedures are outlined in ASTM G76, in which reasonable results are obtained. The standard conditions for the test are shown in Table 2.3. The test procedure also requires regular maintenance and monitoring to achieve accurate results.

Table 2.3 Standard Test Conditions of ASTM G76 Test Method for Solid Particle Erosion. pg 268 [39]

Nozzle tube	Dimensions Orientation Position	ID 1.5 mm $\pm$ 0.075 mm; minimum length 50 mm Axis 90 $\pm$ 2° with specimen surface 10 $\pm$ 1 mm from specimen surface
Test gas		Dry air
Particle	Composition Size Shape Feed rate Velocity	Al ₂ O ₃ 50 μ m Angular 2.0 $\pm$ 0.5 g/min 30 $\pm$ 2 m/sec
Flow	Rate Presssure	8 L/min 140 kPa (may be different)
Duration		Minimum, 10 min; maximum, any acceptable provided crater depth does not exceed 1 mm
Temperature		18–28°

2.5.3.2 Liquid impingement erosion tests

Liquid impingement erosion tests refer to the type of wear that is produced when jets or droplets of liquid impact a solid surface [39]. In this type of wear, the liquid provides pressure pulses to the surface, and is similar to that produced by cavitation erosion. There have been a number of wear apparatuses that have been used to evaluate wear of materials to this type of wear. Two examples are shown in Figures 2.40 and 2.41. Generally these tests involve a jet impacting on a specimen or a specimen moving through a droplet field. With jet impacts, the wear is generally focused on a specific region on the test specimen. With a droplet field, the wear is generally distributed randomly over a large area. Repetitive impact tests tend to be more severe than distributed impact tests. Both are satisfactory in practice to develop a wear or erosion curve relating damage to time or amount of liquid impingement.

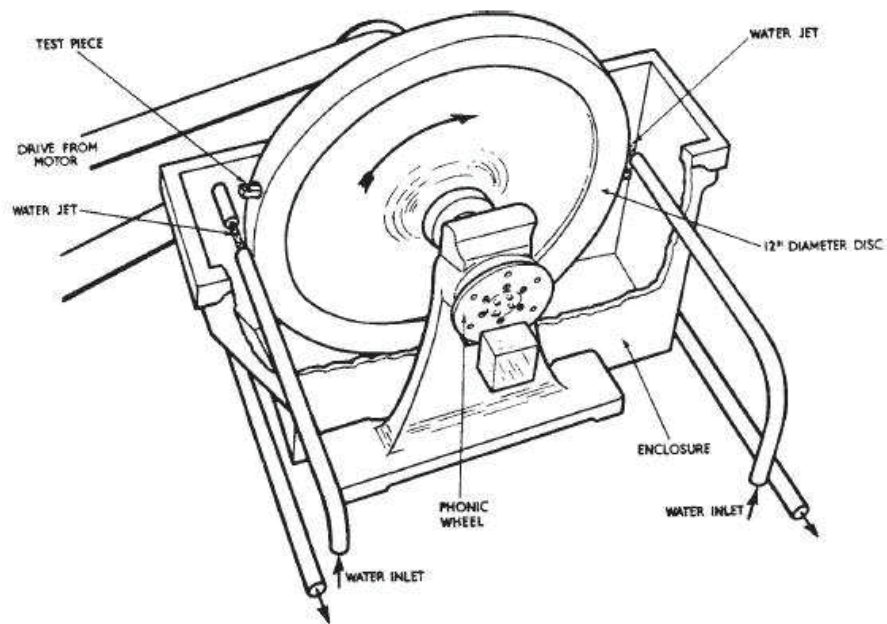


Figure 2.40 A small, low speed apparatus used to investigate liquid impingement erosion. pg 312 [39]

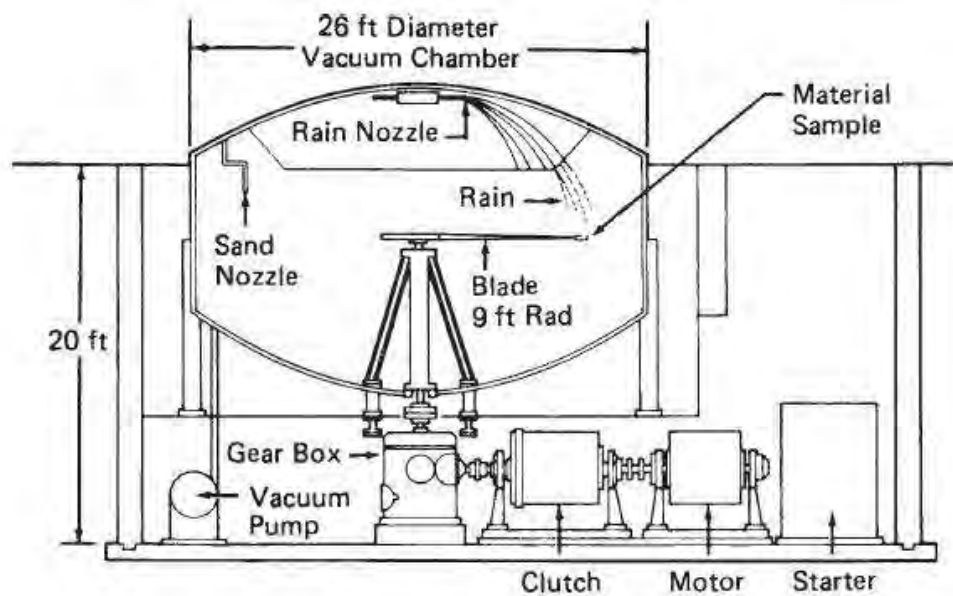


Figure 2.41 A large, high speed apparatus used to investigate liquid erosion. (pg 312 [39])

Liquid impingement erosion tests tend to be more complex than those used for sliding wear. The general method of conducting and analysing these tests is given in the ASTM

G73. Again, similar to the erosion by solid particle impingement using gas jets testing method, these tests should not exceed the point where the wear depth of the scar exceeds the width (see Figure 2.39).

2.5.4 Slurry erosion testing

2.5.4.1 Slurry abrasivity

This test method is used to provide a ranking capability for the wear resistance of a material against particular slurry [39]. It is mainly associated with low stress scratching abrasion, and is used to address slurry abrasion problems in pipelines and slurry pumps. The material is given a SAR number after testing and analysis. SAR stands for slurry abrasion response, and is based on a weight loss technique for measuring wear. This test is also an ASTM test procedure (ASTM G75).

The basic configuration of the test is illustrated by Figure 2.42. A flat rectangular wear specimen slides back and forth across a rubber lap, which is immersed in the slurry. The flat wear specimen is mounted on an arm, which moves back and forth at a controlled speed. The arm lifts the specimen at the end of each stroke to allow the slurry to come between the specimen and the lap. The wear specimen is removed periodically and weight loss determined. By keeping the slurry constant and varying the wear specimen, wear resistance of different materials to that slurry can be ranked.

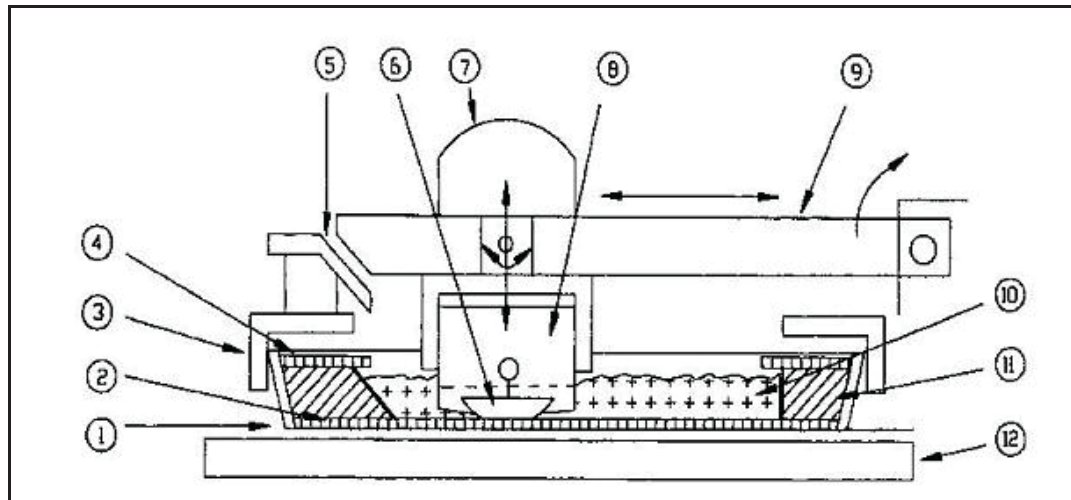


Figure 2.42 Sketch of the slurry abrasivity test apparatus. pg 262 [39]

1. Molded plastic tray
2. Neoprene lap
3. Tray clamp
4. Splash guard
5. Block lifting cam
6. Standard wear block
7. Dead weight
8. Adjustable plastic wear block holder
9. Pivoted reciprocating arm
10. Sand slurry
11. Moulded plastic filler
12. Tray plate

The reproducibility of this test method is consistent and reliable, but as with other test methods, the variation in material properties will result in a lack of precision results. Examples include composition and grain structure. It must be considered that the slurry erosion test does not provide absolute values of wear performances, but rather a material ranking.

2.5.4.2 A net flow-through slurry erosion wear test

The net flow-through slurry erosion wear test involves the testing of metal or rubber materials with the combined test methods of wet erosion and dry erosion [36]. The slurry test apparatus consists of a slurry pot and equipment to feed the slurry pot at a controlled rate. The schematic of the slurry wear test apparatus is shown in Figure 2.43.

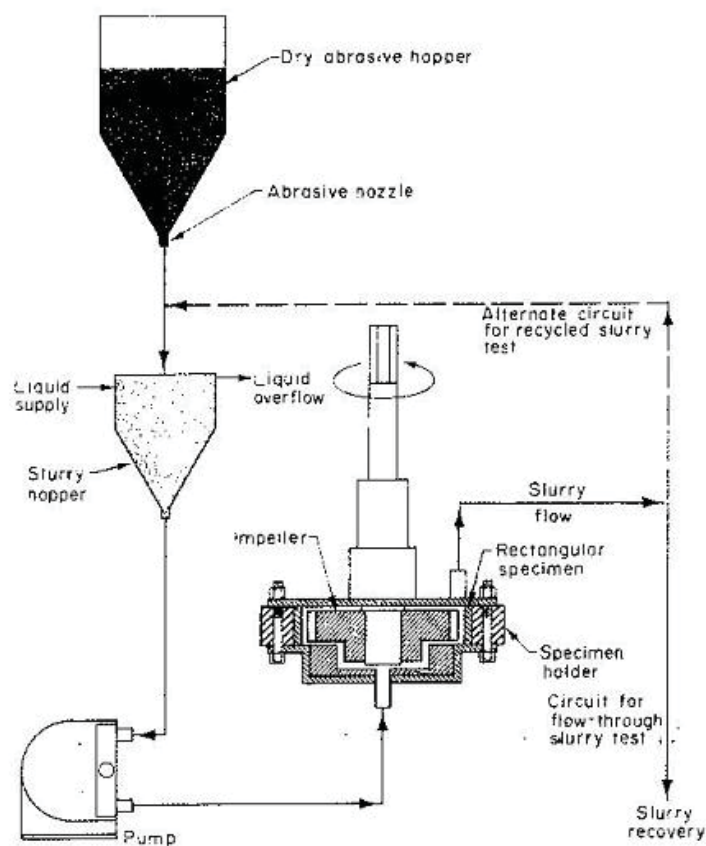


Figure 2.43 Schematic of slurry wear test apparatus. pg 172 [36]

Dry abrasive particles, such as silica sand is feed from a hopper to form the slurry. By varying the size of the nozzle at the bottom of the dry abrasive hopper, the weight percent of the solids can be adjusted while maintaining a constant liquid flow rate. The slurry is then gravity feed from the slurry hopper to the pump where it can be pumped to the bottom of the slurry pot. This slurry pot includes an impeller that rotates the slurry past specimens

located around the inside of the pot (see Figure 2.44 and 2.45). The impingement angle is kept at around about 11.5° between adjacent specimens.

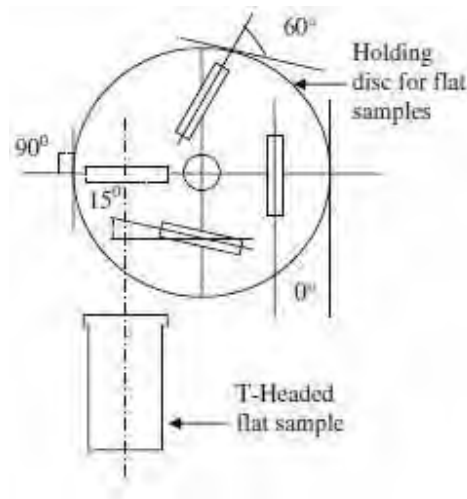


Figure 2.44 Centre section of slurry pot showing plastic ring and alternating metallic and plastic specimens.
Pg 173 [110]

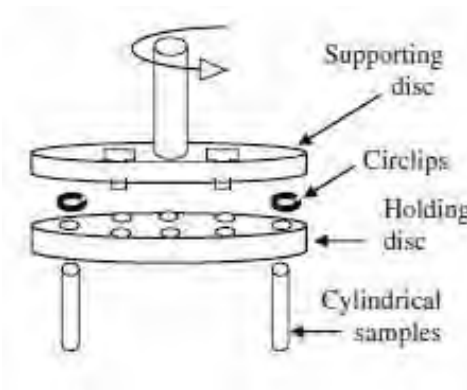


Figure 2.45 Slurry pot and impeller. Pg 173 [110]

Wear is measured as weight loss, which is converted to volume loss by dividing by the specimen's density. Wear rates cannot be reported as thickness per unit time because the wear is not uniform over the wear surface, but can be reported as total volume loss per unit time.

2.5.4.3 Coriolis wear test

The coriolis technique is used to simulate the motion of fine particles in a slurry at low angle interaction with materials used in minerals processing [17, 43-50]. Figure 2.46 shows the schematics of the rotor and the forces acting on the erosive particle, as well as a sample wear scar. The basic operation of the coriolis is as follows; pre-mixed slurry is fed into a diametrically grooved rotating rotor and expelled radially along the grooves by centrifugal forces. Wear is achieved as the slurry particles come in contact with the exposed specimen surfaces by the centrifugal force. It is stated that the coriolis provides a rapid assessment of material performance under low impact angle, erosion conditions. However, due to limitations in the accurate direct measurement of the total volume loss of the wear scar, the erosion resistance of various materials cannot be quantified.

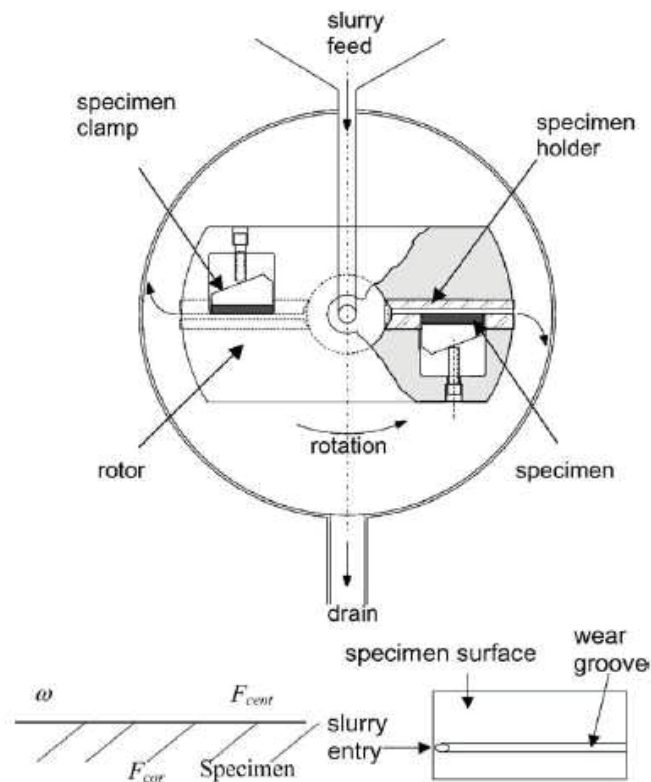


Figure 2.46 Schematics of the rotor, the forces acting on the erosive particle and a wear scar. [47]

Previous studies [48] have investigated the effect of low angle impact wear and sliding wear using the coriolis tester with white cast irons. However, no literature could be found in relation to elastomeric materials. Figure 2.47 shows the wear patterns of typical white cast iron coriolis wear specimens. Although there are many factors that may influence the affect of wear on the test materials, in particular the properties of the erodent materials, test materials, slurry characteristics, environmental conditions, etc. since all the coriolis tests run by Tian et al [48] were conducted using neutral chemical conditions and ambient temperatures. This minimises the material loss due to chemical and corrosion mechanisms as the parameters for testing remain constant.

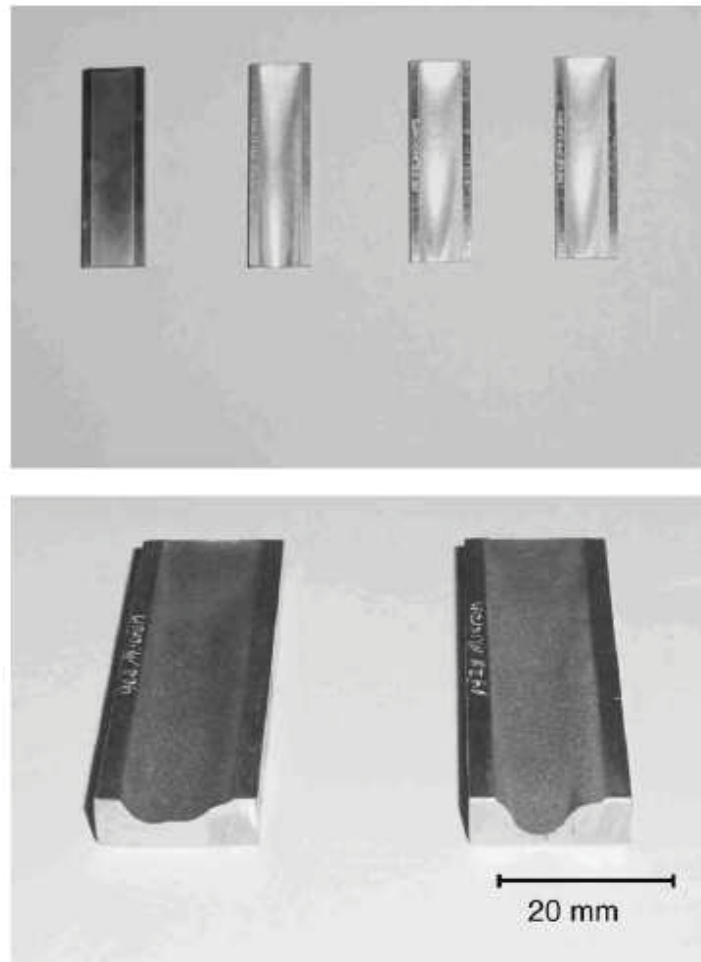


Figure 2.47 Wear patterns of Coriolis wear specimen. Specimen dimensions 63.5 mm (L) $\times$ 19.1 mm (W) $\times$ 6.4 mm (H). [48]

2.5.5 Comparison of laboratory wear tests to field tests

Sare et al. [19] reviewed the different methods of laboratory wear testing and its relationship with field performance. It was stated not only by Sare, but also many other authors in the literature that one cannot accurately predict the erosion resistance of polymeric materials on the basis of material parameters from product specification data sheets, for example the physical properties [19].

As mentioned earlier, abrasion, erosion, and corrosion are the most common types of wear in the mining and minerals processing industries. The standard test methods are generally inadequate for wear simulation as these tests are not based on individual tribological systems. Laboratory tests are run at conditions and variables that are known and can be kept constant whereas field testing results in a number of conditions that may not be known and cannot be kept constant. Simulations are very difficult to achieve, and often give favourable results for laboratory testing for certain materials and not for field testing, and vice versa. Sare et al. mentions research from Blau, suggesting five important aspects of tribosimulation for it to be successful: (1) geometry of the contacting surfaces; (2) transmission of force; (3) interfacial environment; (4) contacting materials; (5) operation and failure observations. The desired outcomes from a tribosimulation are also ranked by Blau and are as follows: (1) numerical wear rates in the laboratory test correspond directly with those observed in service; (2) the ranking and magnitude of the differences between candidate materials is the same in the laboratory and field; (3) the relative ranking is the same in the laboratory and the field; (4) the wear mechanisms are the same in the laboratory and field. Due to high costs, time consumption, difficulty in controlling and quantifying field conditions, field trials and testing are rare. As a result, the analysis and identification of wear is usually carried out during failure analysis. In practice, a range of wear test must be used such that their tribosimulation conditions and variables cover the service environment. However, these tests should only be used to give a ranking for each material, and should not be used as a direct correlation to the field applications and performance.

It is known that subjecting samples to individual tests does not imitate the multiple wear mechanisms found in service [19]. As mentioned earlier, wear of materials involves a combination of two or more wear mechanisms. The materials usually rank differently on single wear mode tests as certain conditions and variables suit each material accordingly. By relying directly from the laboratory testing, this can lead to different rankings of materials on different tests as well as overestimates of predicted life. Hutchings [31, 51-53] and Arnold [31, 52, 53] have extensively researched into the area of erosive wear mechanisms of elastomers. It is stated in the literature that erosive wear tests can be used in accessing the likely service performance of elastomers, as it employs signs of fatigue damage as well as the abrasive wear mechanisms closest to the service reality. Sare et al. has mentioned from experience, that the premature elastomer failure in Australian mining industry is caused by the lack of understanding of the nature of the physical properties of the elastomer. Not only is the understanding of physical properties lacking detail, but also the viscoelastic properties of the elastomer. The process variables must be known before any elastomers are used for that particular application. All elastomers have a narrow operating window in which they perform optimally [19], as a result small changes in wear mechanisms, pH, increases in temperature can lead to failure. Table 2.4 lists some of the elastomer operating environmental parameters.

Table 2.4 Elastomer operating environment parameters. [19] pg 8

Elastomer	Maximum operating temperature (°C)	Problematic chemical/physical environments
Natural rubber	50–105	Oils, greases, solvents
Thermoset polyurethanes	60–75 ^a	Highly acidic or alkaline conditions, polyester containing species may be attacked by fungi, hysteresis can lead to rapid failure
Thermoplastic polyurethanes	50–65	Highly acidic or alkaline conditions, prone to creep under load, hysteresis can lead to rapid failure
Nitrile rubber	105–110	Poor fatigue performance, affected by some aliphatic and chlorinated solvents
Butyl rubber–bromobutyl rubber	~90–115	As for the nitrile rubber but with higher acid/alkaline chemical stability

^a In general with this class of materials, the harder the material the higher the maximum operating temperature.

2.6 *Fracture Failure of Rubber*

2.6.1 Introduction

The fracture failure of rubber is governed by the rubber itself and the conditions which the rubber is exposed to in service. The initiation of fracture is first brought about by flaws or points of weaknesses and at these locations the applied stresses are magnified immensely [12, 25]. The rates at which these cracks develop are a result of local stress levels that can vary with time. Accelerated crack growth under dynamic stressing is termed mechanical fatigue or dynamic crack growth, and will be discussed further in this chapter [54]. Many studies in the literature have attempted to relate failure of rubber with physical properties with limited success. The complete understanding of the physical properties such as tearing, tensile and resilience needs to be defined before any comparisons can be made. In this thesis, these correlations will be attempted but first the properties will be defined in this chapter.

2.6.2 Initiation of Fracture

2.6.2.1 Flaws and stress raisers

In every solid material body contains flaws or points of weakness resulting from heterogeneities of composition or structure [12]. These points can be magnified by the presence of sharp corners, nicks, cuts, scratches, and embedded dirt particles causing the mean applied stress to be greatly exceeded. Fracture will then occur at these sites where the local stress exceeds a critical level and the small flaw starts to grow as a crack. Mark et al. [12] describes the stress concentration factor using Inglis' relation for elastic solids which obey a direct proportionality between stress and strain,

$$\sigma_t / \sigma = 1 + 2(l/r)^{1/2} \quad (2.5)$$

where: l – depth of an edge flaw
 r – radius of the tip in the unstressed state

It is noted that if the flaw is totally enclosed, it is equivalent to an edge flaw of depth $\frac{1}{2}$ shown in Figure 2.48. Therefore, the edge flaws are more serious stress raisers than enclosed flaws of the same size. However, enclosed flaws have been known to cause fatigue cracks internally. In addition to Equation (2.5), when the tip radius is much smaller than the depth of the flaw, Equation (2.6) can then be approximated by,

$$\sigma_b = (\sigma_t r^{1/2}) / 2l^{1/2} \quad (2.6)$$

where the breaking stress is represented by σ_b .

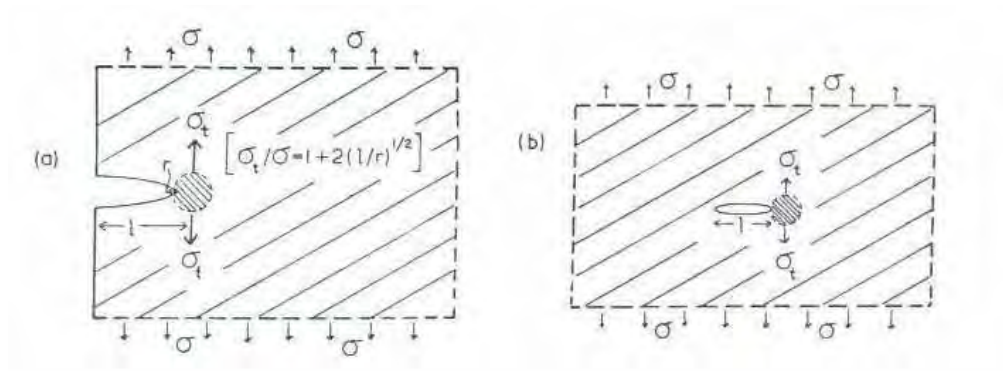


Figure 2.48 Stresses near a crack of depth l and tip radius r . [12]

2.6.2.2 Stress and energy criteria for rupture

A tear will develop a characteristic tip radius r of its own, independent of the sharpness of the initiating stress raiser as it continues to propagate from an initial cut or flaw. As a result it is then more appropriate to treat $\sigma_t r^{1/2}$ as a characteristic fracture property of the material. Irwin proposed that fracture occurs for different shapes of test piece and under varied loading conditions at a characteristic value of a “stress intensity factor” K_c .

$$K_c = (\pi^{1/2}/2)\sigma_t r^{1/2} = \pi^{1/2}\sigma_b l^{1/2} \quad (2.7)$$

Another view on critical stress criterion for fracture was proposed by Griffith for elastic solids in that a flaw would propagate in a stressed material only when it brought about a reduction in elastically stored energy W . This stored energy would have to be more than sufficient to meet the free energy requirements of the newly formed fracture surfaces. Griffith’s fracture criterion is defined by the following equation,

$$-(\partial W/\partial A) \geq G_c/2 \quad (2.8)$$

where: A – surface area of the specimen which increases as the crack grows
 G_c – the amount of energy required to tear through a unit area of the material

2.6.2.3 Tensile test piece

The preparation of a tensile test piece involves taking a strip of rubber and making a small cut in one edge of the sample. Figure 2.49 shows a thin strip of thickness t cut on one edge with length l and is tested under tension until failure. Mark et al. [12] defines the effect of the cut in that it diminishes the total stored elastic energy at a given extension, and may be calculated by considering small triangular regions around the cut as being unstrained and

the remainder of the test piece to be unaffected by the presence of the cut, with stored energy U per unit volume. The reduction in strain energy due to the cut is represented by, kl^2tU where k is a numerical constant whose value depends on the applied strain. k is approximately given as $\pi/(1+e)^{1/2}$ where e is the tensile strain. Referring back to Griffith's fracture criterion Equation (2.8), for the tensile test piece $-(\partial W/\partial A) = kltU$ and $(\partial A/\partial l) = 2t$, Equation (2.8) becomes,

$$2klU \geq G_c \quad (2.9)$$

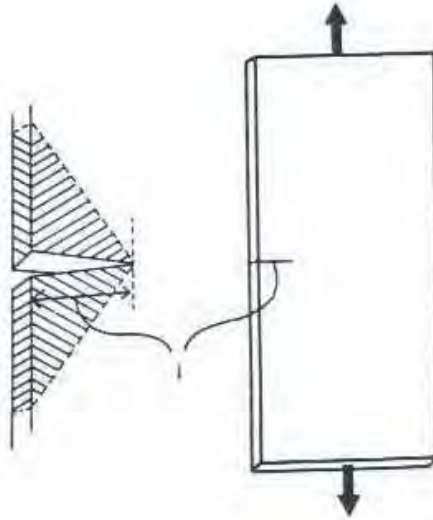


Figure 2.49 Tensile test piece. [12] pg 477

For a material which obeys a linear relationship between tensile stress σ and extension e , the stored energy U is given by $Ee^2/2$ or $\sigma^2/2E$ where E is the Young's modulus. Therefore the stress and extension at break is given by,

$$\sigma_b = (G_c E / \pi l)^{1/2} \quad (2.10)$$

$$e_b = (G_c / \pi l E)^{1/2} \quad (2.11)$$

where k is given the value of π appropriate for linear elastic materials.

Further comparison with Equations (2.7) and (2.10), the critical stress intensity factor K_c and the fracture energy, or critical strain energy release rate G_c , the breaking stress at the crack tip can then be represented as,

$$K_c^2 = EG_c = (\pi/4)\sigma_t^2 r = (\pi/2)U_t Er \quad (2.12)$$

where U_t is the strain energy density at the crack tip. Hence,

$$G_c = (\pi/2)U_t r \quad (2.13)$$

It is stated by Mark et al. [12] that the fracture energy G_c is therefore a product of the energy required to break a unit volume of material at the crack tip in the absence of nicks, external flaws, and the effective diameter of the tip. Where U_t is an intrinsic strength and r is a characteristic roughness or bluntness of a developing crack.

An SEM study on the fracture topography of rubber surface was investigated by Pandey et al. [26]. The study included 4 different rubber formulations each resulting in different observations. These included natural gum rubber, mica, silica and carbon black reinforced rubbers. The tensile and elongation at break properties can be seen in Figures 2.50 and 2.52. Upon SEM analysis of the tensile failed surface of gum vulcanisate, slip lines are present, which is an indication of microductile fracture. The formation of small microcraters/pits was also observed and can be seen in Figure 2.51. The SEM analysis of the tensile failed surface of the mica filled vulcanisate showed different fracture properties. The fractured surface shows detachment of the mica flakes most likely as a result of poor polymer filler adhesion [55]. Deep cracks and grooves were also observed through the SEM and can be seen in Figure 2.53. Figure 2.54 illustrates the SEM photograph of the tensile failed surface of silica filled vulcanisate, as it can be seen that there is comparatively better polymer-filler interaction with silica than mica. Carbon black is suggested by the author to be seen in Figure 2.55 as an agglomeration of particles.

Upon review of this paper, the reliability of the results and observations in the SEM study by Pandey et al. [26], may not be good due to a number of unclear aspects. Firstly, the some of the SEM photographs are out of focus, contrast is too high as a result of electron charging on the surface of the material, fillers are labelled on each photograph without validation methods included such as EDS (energy dispersive spectroscopy) spectra indicating the elements.

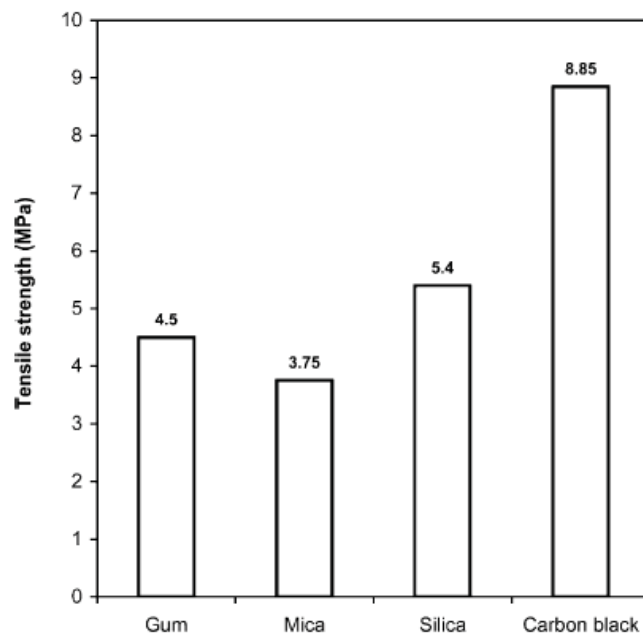


Figure 2.50 Tensile strength of different vulcanisates. [26]

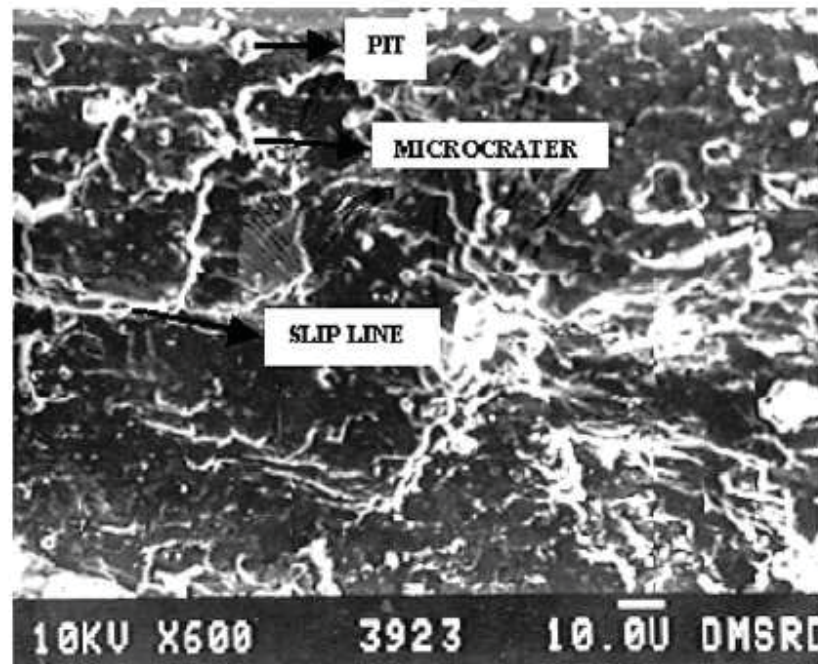


Figure 2.51 SEM photograph of tensile failed surface of gum vulcanisate. [26]

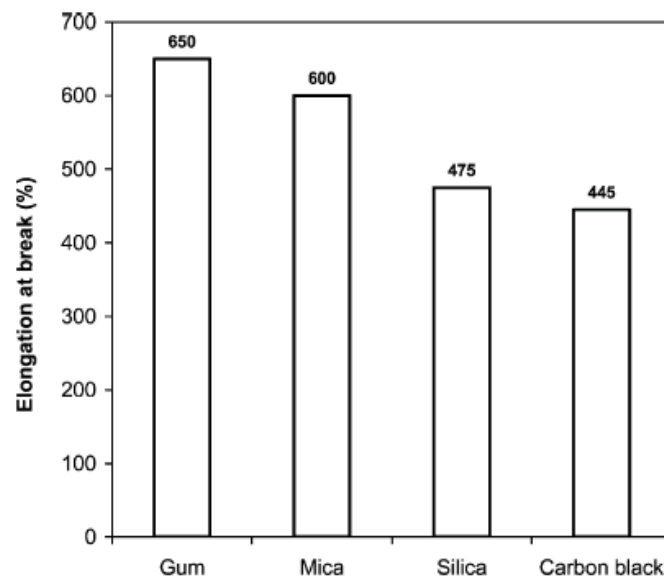


Figure 2.52 Elongation at break of different vulcanisates. [26]



Figure 2.53 SEM photograph of tensile-failed surface of mica filled vulcanisate. [26]

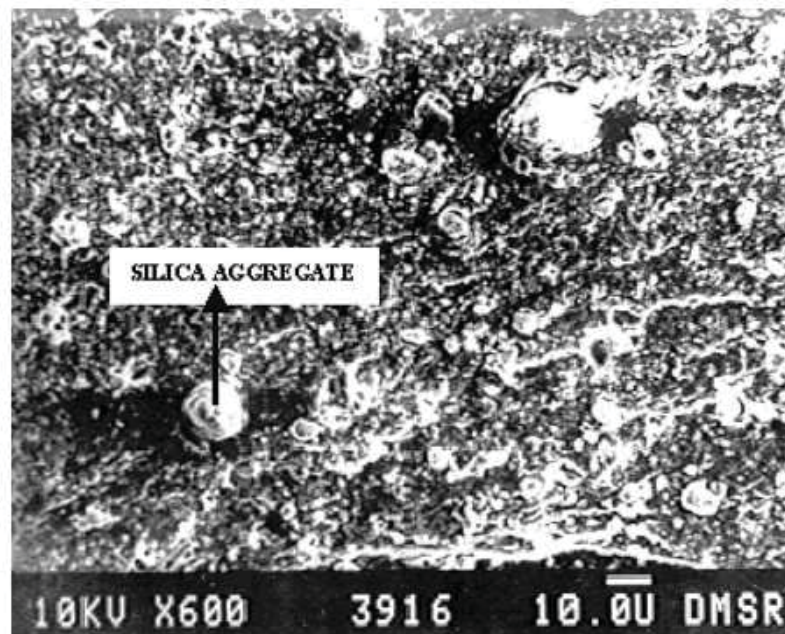


Figure 2.54 SEM photograph of tensile-failed surface of silica filled vulcanisate. [26]

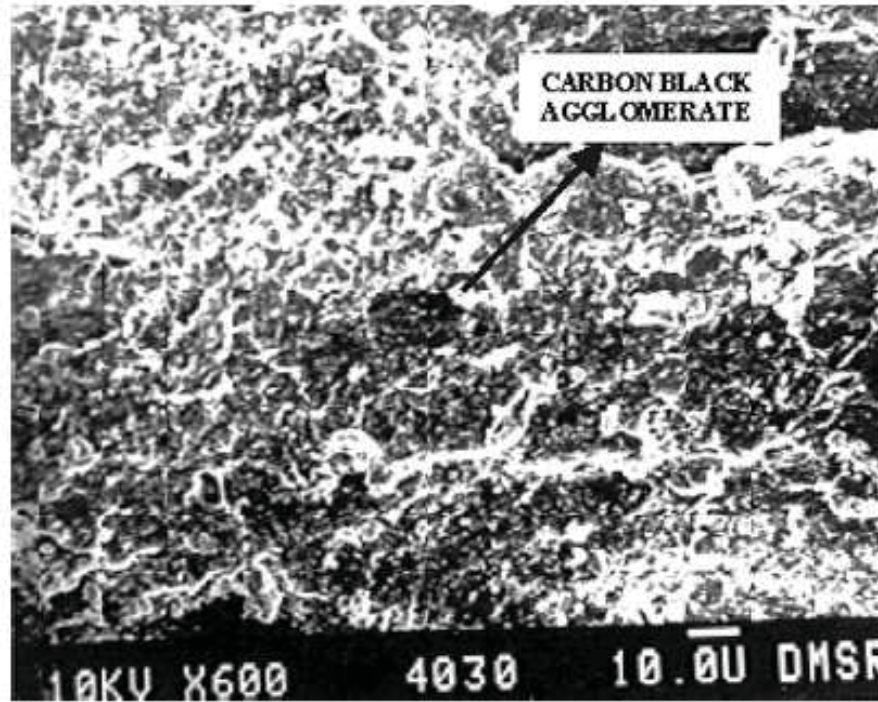


Figure 2.55 SEM photograph of tensile-failed surface of carbon-black filled vulcanisate. [26]

2.6.2.4 Tear test piece

The tear test piece is moulded into a shape that is rectangular in shape with a slit through the centre to the midpoint of the piece (similar to a pair of jeans). Figure 2.56 shows the tear test piece with regions allocated in the testing process. Region I refer to the arms of the sample and are tested in simple extension while region II is left virtually undeformed. The work of fracture $G_c \Delta A$ is then provided directly by the applied force F acting through a distance $2\Delta l$, where Δl is the distance torn through [12]. The corresponding area torn through is $t\Delta l$, where t is the thickness of the sheet. Mark et al. [12] considered the work required for tearing using the Griffith fracture criterion Equation (2.8),

$$F \geq G_c t / 2 \quad (2.14)$$

Since the tear force is independent of the elastic properties of the material and of the length of the tear and a direct measure of the fracture energy G_c , this test piece is suitable to be used in the study of the effects of composition and test conditions [56]. However, it is important to note that the fracture energy G_c is not a constant value for a particular material it strongly depends on the temperature and rate of tear.

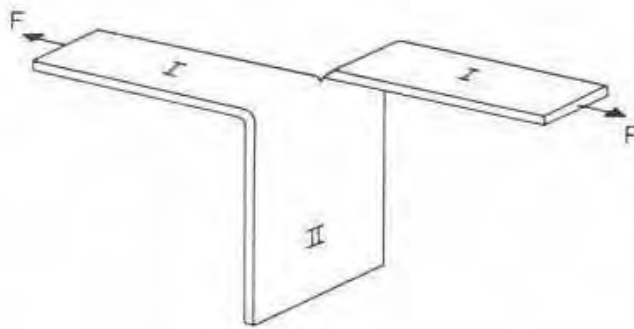


Figure 2.56 Tear test piece. [12] pg 478

Pandey et al. [26] also investigated the tear failure using the SEM. Figures 2.57 – 2.59 show the tear-failed surface of gum, silica filled, mica filled and carbon filled rubber respectively. Tear strength as mentioned earlier is dependant on the addition of fillers to the rubber matrix. Carbon black reinforcement results in higher tensile strength which will then impart higher tear strength on the rubber formulation. Tearing of rubber can be defined as a two stage process; (1) deformation of the crack tip, (2) growth of the cut. The development of high strength is a result of stress dissipation through viscoelastic properties of the rubber near the crack tip. Upon further addition of fillers, additional stress dissipation occurs through reinforcement and as a result giving higher resistance to failure by deflecting or arresting growing cracks within the rubber. Pandey et al. [26] states that several unrestricted tear paths and also the formation of cracks induce poor tear strength seen in Figure 2.57. However, no clear paths can be seen in Figure 2.58 where the mica tends to show signs of pullout from the matrix with the presence of deep cracks and grooves. Figure 2.59 illustrates the benefits of using silica as a filler since the tear lines/paths are short and randomly distributed and do not propagate through the material. The carbon black filler

exhibits much the same behaviour as the silica filled rubber composition such that the tear paths are hindered by the carbon black particles due to the high level of polymer-filler interaction. This extensive tear branching can be seen in clearly in Figure 2.60.

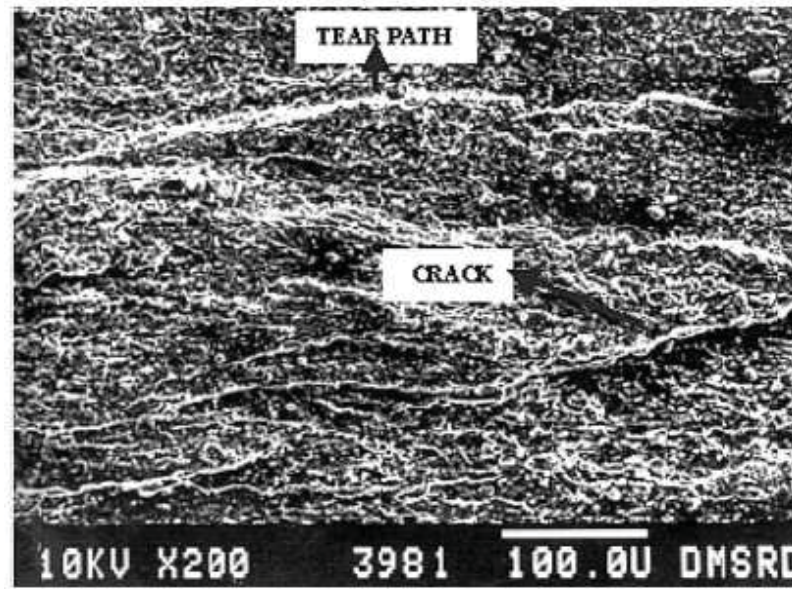


Figure 2.57 SEM photograph of tear-failed surface of gum vulcanisate. [26]



Figure 2.58 SEM photograph of tear-failed surface of mica filled vulcanisate. [26]

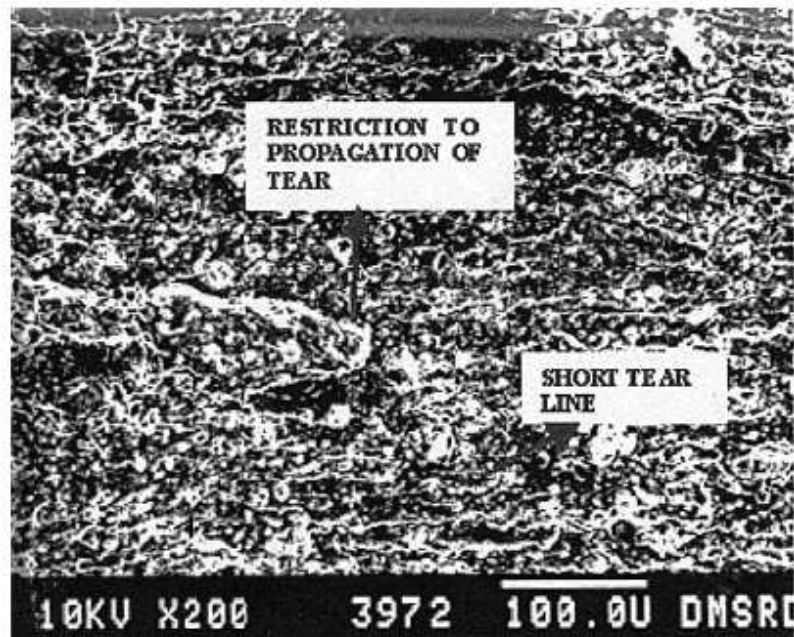


Figure 2.59 SEM photographs of tear-failed surface of silica filled vulcanisate. [26]

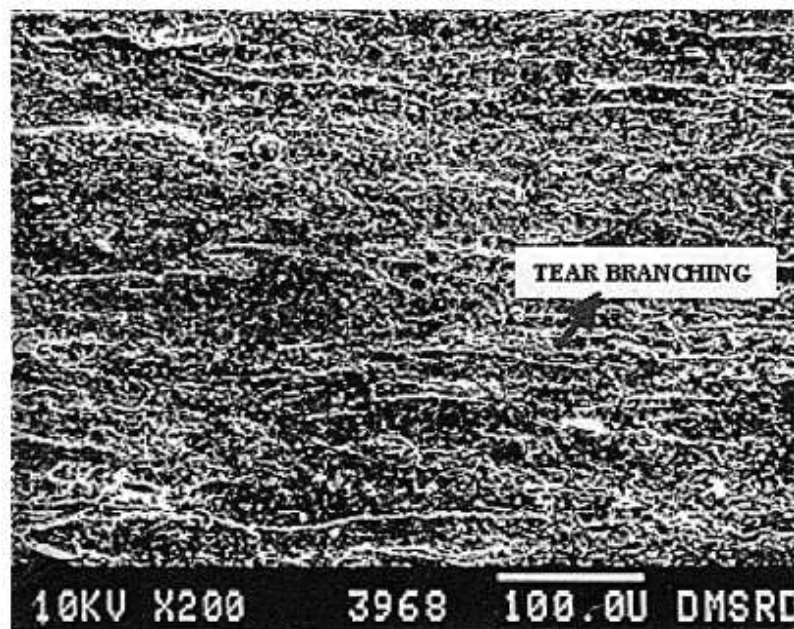


Figure 2.60 SEM photograph of tear-failed surface of carbon-black filled vulcanisate. [26]

2.6.2.5 Relationship between the tear and tensile strength of rubber materials

An extensive study was carried out by Persson et al [53] in relation to crack propagation in rubber-like materials. The study involved investigation into the contribution viscoelastic deformations have to the crack propagation energy (per unit area) G in front of the propagating crack tip. In building a relationship between tear strength, tensile strength, and internal friction, one must consider their significance and definition. Tear strength is determined by the energy per unit area G , to propagate a nick or a crack in a rubber sample. Tensile strength is determined by the stress σ_c needed to break a rubber sample exposed to uniaxial stress [53]. And finally, the internal friction is determined by the loss tangent $E_2(\omega)/E_1(\omega)$ at a given frequency ω . It can be seen in Figure 2.61 that tensile and tear strength is highly dependent on the cross-link density of the rubber.

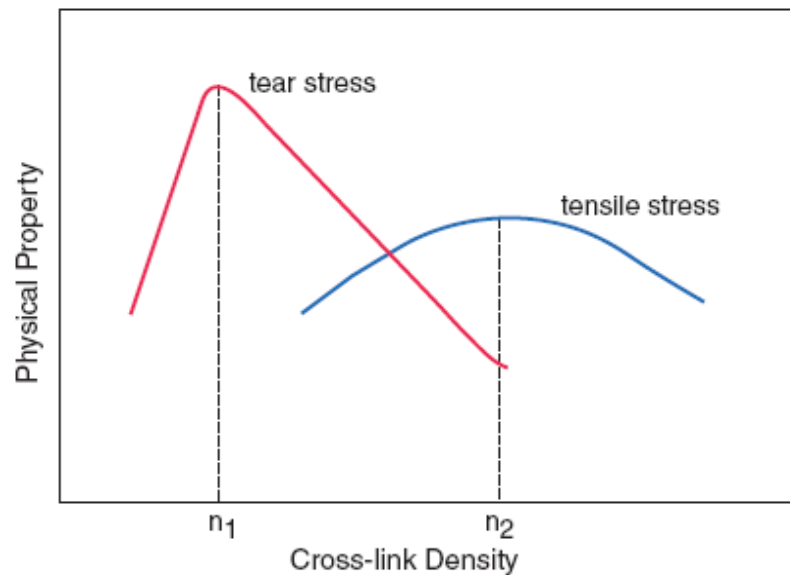


Figure 2.61 The dependence of the tear strength and the tensile stress on the cross-link density. [53]

Crosslink density is defined as the number of crosslinks per unit volume, which is inversely proportional to the average molecular weight of polymer chain between crosslinks [57]. A rubber that is crosslinked will exhibit different behaviour to one that is not. The applied

stress to a crosslinked material will be distributed relatively evenly on the crosslinks, therefore the average tensile force acting on the crosslink will decrease as the crosslink density increases [53]. The fracture behaviour of the crosslink bonds will be dependent on the tensile yield stress σ_c since the bond will not break until the tensile yield point is reached. As a result of this behaviour, the tensile yield stress σ_c will increase with increasing crosslink density. However, it is important to note that too high crosslink density will have an adverse affect on the beneficial elastomeric nature of the rubber for the following reason. Very high crosslink density will result in a brittle-like material that leads to strong stress concentrations occurring in the vicinity of the broken bond. This leads to further bond breaking, even higher stress and crack like defects propagating rapidly across the rubber specimen [53]. It is often favourable to have the crosslink density not too high for the reason above and also for the reason that the stress concentration at the point of the broken bond will be reduced by the rubber surrounding it. It should be noted that the above discussion assumes that the rubber sample does not have any flaws such as cracks, voids or defects to begin with. If these defects are present in the rubber sample, the tensile strength will decrease and will be dependent on the tear strength of the rubber.

2.6.3 Crack Propagation

Crack propagation is different to the initiation of fracture in that the propagation of a crack is widely different for a range of elastomers whereas the initiation of fracture seems similar for all processes. The three basic patterns of crack propagation or tearing are listed by Mark et al. [12] according to the three characteristic types of elastomeric compounds:

1. Amorphous elastomers (e.g. SBR).
2. Elastomers (e.g. NR and Neoprene) that crystallise on stretching.
3. Reinforced elastomers containing large amounts of finely divided reinforcing particulate filler such as carbon black (about 30% vol.).

The first category will be explained first, once fracture has been initiated, a tear propagates at a rate dependant on two principle factors: the strain energy release rate G and the temperature T . The rate at which strain energy can be converted to fracture energy as the crack advances is defined by using Griffith's analogy,

$$G = -2(\Delta W / \Delta A) \quad (2.15)$$

where: W – the total strain energy of the specimen
 A – the surface area (which increases as the crack increases)

For a tensile strip with an edge cut the strain energy release rate is defined as,

$$G = 2\pi lU \quad (2.16)$$

therefore for a tear test piece,

$$G = 2F/t \quad (2.17)$$

In relation to strain-crystallisation elastomers, it can be seen in Figure 2.62 that the tear strength is greatly enhanced over the range of tear rates and temperatures at which crystallisation occurs on stretching at the tear tip. However, this behaviour is only observed in a narrow range temperature as high temperatures will result in the hindrance of crystallisation and low temperatures will not result in reorganisation of crystallines in the short times of stretching as the crack tip advances. It is stated by Mark et al. [12] that the high strength of strain-crystallising materials are attributed to pronounced energy dissipation on stretching and retraction associated with the formation and melting of crystallites under non equilibrium conditions.

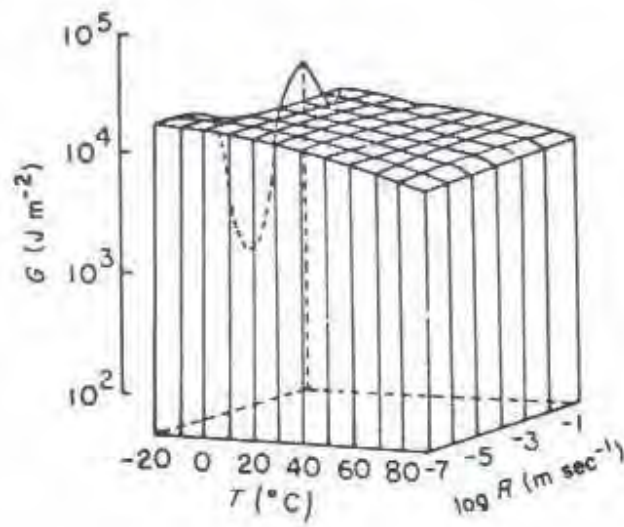


Figure 2.62 Fracture energy G for a strain-crystallising elastomer, natural rubber, as a function of temperature T and rate of tearing R . [12]

The third characteristic refers to the reinforcement of elastomers with large amounts of fillers. This is known to increase the tensile and tear strength of the elastomer remarkably [58]. Figure 2.63 shows this trend, however much like the strain-crystallisation behaviour, the strengthening action is restricted to a specific range of rates of tearing and temperature of the test. These ranges will depend on the type of elastomer and the type of filler used in the composition. Outside this range, the addition of fillers will not enhance the strength of the rubber product.

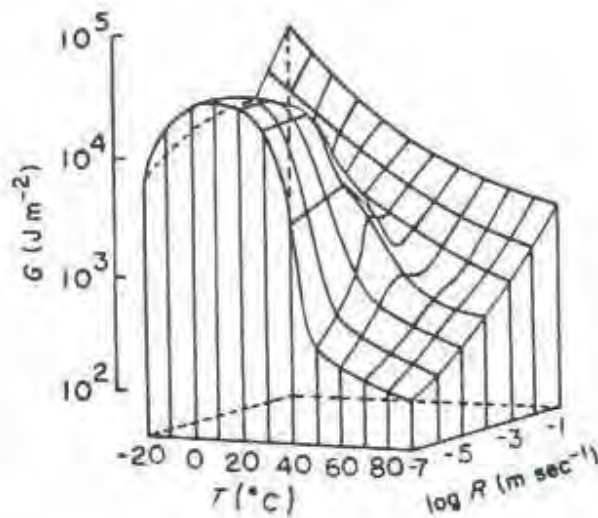


Figure 2.63 Fracture energy G for an amorphous elastomer (SBR) reinforced with 30% by weight FT carbon black. [12]

With the increase in strength by the addition of fillers to the elastomer, this enhancement can be associated with changes to the character of the tear process. The relatively smooth tearing surface of the torn rubber to a discontinuous stick-slip tearing, where the tearing deviates from a straight path and even turns into a direction running parallel to the applied stress until a new tear initiates [12]. This is often referred to as knotty tearing, and this is illustrated in Figure 2.64.

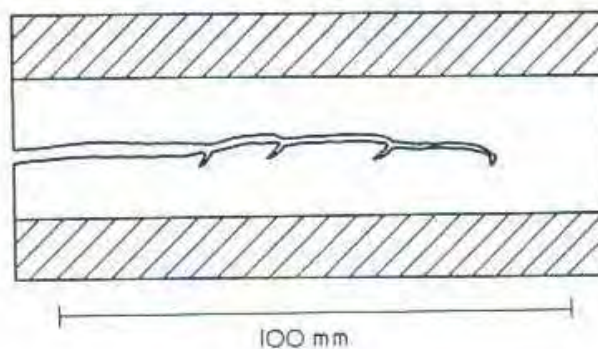


Figure 2.64 “Knotty” tear in a carbon black-reinforced elastomer. [12] pg 493

2.6.3.1 Repeated stressing: Dynamic crack propagation

Amorphous elastomers are found to tear at rates controlled by the available energy for fracture G which is usually steady. Strain-crystallising elastomers do not tear continuously under small values of G of less than 10^4 J/m² e.g. natural rubbers. Nonetheless we will define the crack growth in a stepwise manner by an amount Δl per stress application. Experimentally from Figure 2.65, four distinct growth laws have been observed corresponding to four levels of stressing:

1. $G < G_0$: no crack growth occurs by tearing, but only chemical attack.
2. $G_0 < G < G_1$: the growth step Δl is proportional to $G - G_0$.
3. $G_1 < G < G_c$: the growth step Δl is proportional to G^2 .
4. $G \sim G_c$: catastrophic tearing.

In practice, it is stated by Mark et al. [12] that it is usually possible to approximate crack growth over the whole range of G values by the relation for region 3, represented by the broken line in Figure 2.65,

$$\Delta l = BG^2 \quad (2.18)$$

where the growth constant B is found to be about 10^{-14} m/(J/m²)² per stress application.

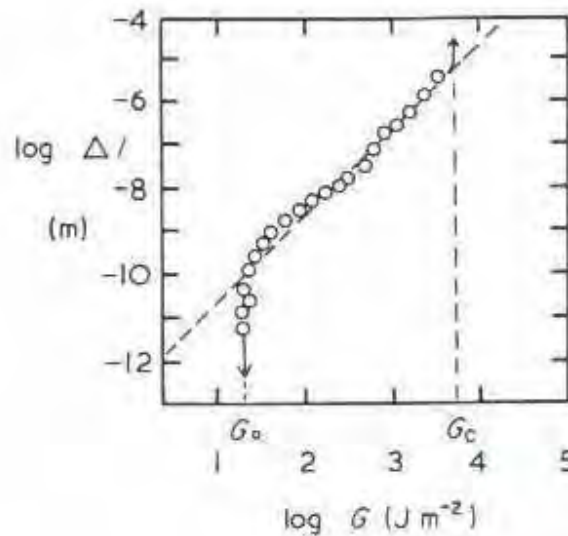


Figure 2.65 Crack growth step Δ per stress application versus energy G available for fracture, for a natural rubber vulcanisate. [12]

2.6.3.2 Crack propagation in rubber

Rubber products used in mining applications are always crosslinked and contain some form of filler reinforcement. It is therefore important to investigate how the rubber properties depend on microstructure, the crosslink density and the concentration of filler particles [53]. Persson et al [53] using viscoelastic analysis of the loss tangent ($\tan \delta$), developed a number of theories and observations in relation to the dependence. Polymers with different side groups are used to obtain the viscoelastic spectra as there is a broad range of molecular mobility in the rubber field. It is stated that large side groups will increase the barrier for local configurational changes to occur within the molecular structure. The result is an increase in relaxation times and a shift in the viscoelastic peak to lower frequencies (at a fixed temperature) or equivalently, to higher temperatures (at a fixed frequency). Figure 2.66 shows the loss tangent at 10 Hz deformation frequency for 3 standard rubber materials. The focus of the 10 Hz deformation is used as it is directly relevant for rubber friction and wear [53]. At temperatures $T > 280$ K the butyl rubber has the highest loss tangent, styrene-

butadiene rubber and then natural rubber. It is also noted that this order also relates to the ranking of these 3 rubbers with respect to friction at typical sliding velocities in tyre applications. The experiments were performed at room temperature and at low crack-tip velocities ($\sim 10^{-5} \text{ms}^{-1}$). The expected crack propagation energy for butadiene rubber is low in comparison to the styrene-butadiene rubber. The experimental results for butadiene rubber (without filler) $G \approx 86 \text{ J m}^{-2}$ (at $T = 120^\circ\text{C}$, $G \approx 59 \text{ J m}^{-2}$), while for styrene-butadiene rubber (without filler) $G \approx 2100 \text{ J m}^{-2}$. For styrene-butadiene copolymer rubber with 54% carbon black the crack propagation energy was even higher, $G \approx 30\,000 \text{ J m}^{-2}$.

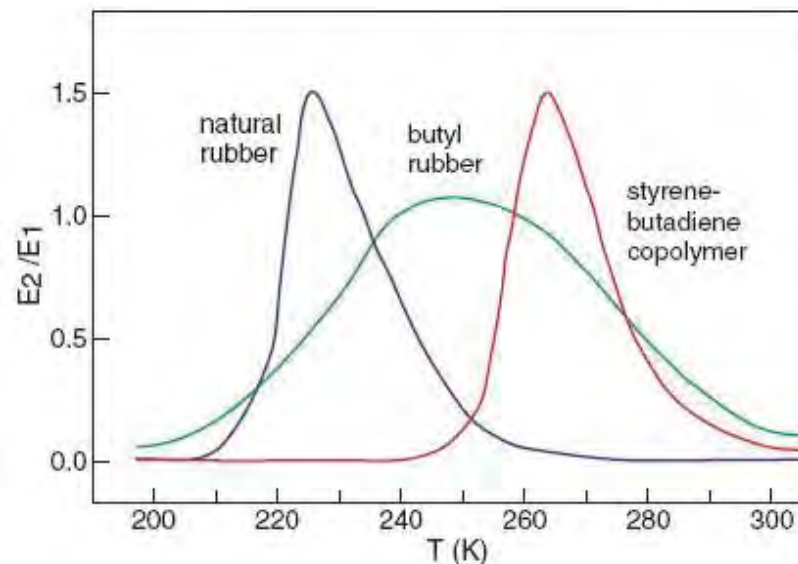


Figure 2.66. The loss tangent E_2/E_1 as a function of temperature for the deformation at frequency 10 Hz. [53]

Crosslink density is can also be shown using the loss tangent method. Figure 2.67 shows the loss tangent for an unfilled styrene-butadiene rubber as a function of sulphur concentration at 10 Hz deformation frequency. Crosslinks are expected to increase with increasing concentration of sulphur, as these crosslinks are formed by sulphur bridges. The loss tangent can be clearly seen to shift at higher temperatures as the sulphur concentration increases. As a result, it is stated by Persson et al [53] that the activation barriers for motion of polymer segments increase with increasing crosslink density which. This motion of the polymer segments is then severely limited due to the crosslinks. The following statement can then be made with reference to the shift in loss tangent. Shift in loss tangent (as a

function of temperature, to higher temperatures) is equivalent to a shift in loss tangent (as a function of frequency, to lower frequencies) [53]. This will ultimately result in an increase in both frictional and tear strength of the rubber material.

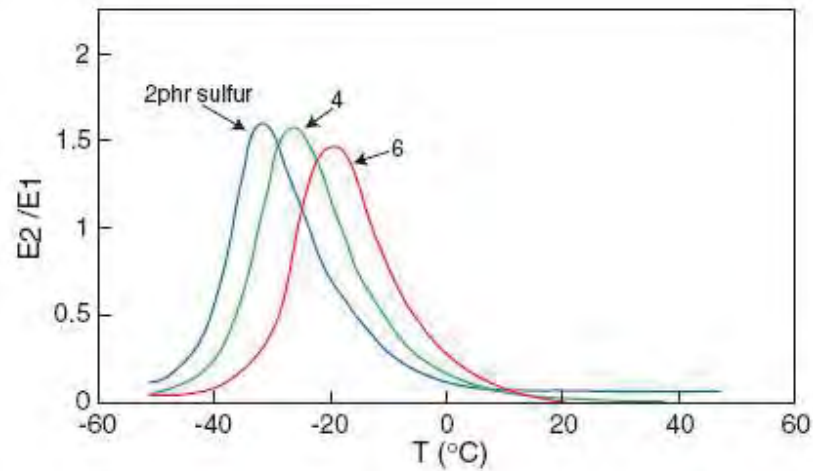


Figure 2.67. The loss tangent E_2/E_1 as a function of temperature for the deformation frequency 10 Hz. [53]

The dependence on filler concentration of the loss tangent is much more obvious as one would expect a lower maximum value of the loss tangent due to lower mobility of the polymer chains. Figure 2.68 shows the dependence of loss tangent on the carbon black filler concentration. It can be seen from this figure that as the filler concentration increases, the maximum value for the loss tangent decreases. Persson et al [53] attributes this behaviour as a result of decreased mobility of the layers of hydrocarbon chains bound to the surfaces of the filler.

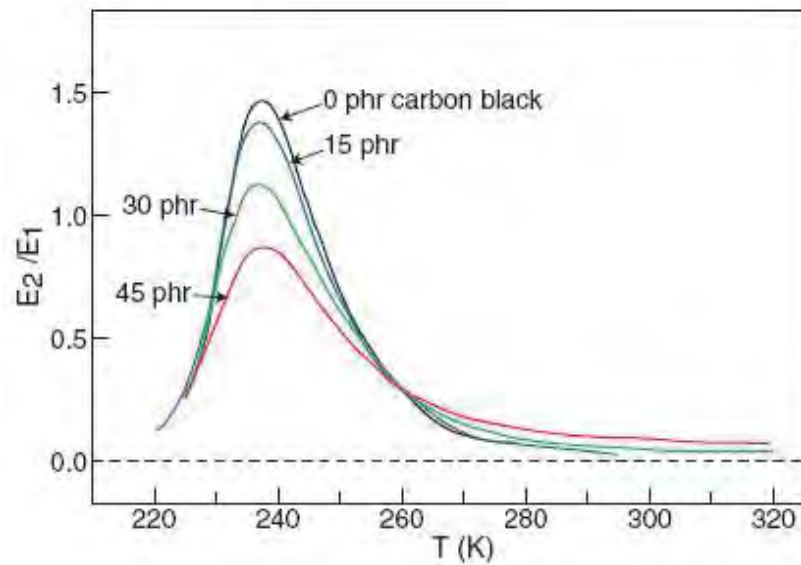


Figure 2.68. The loss tangent E_2/E_1 as a function of temperature for the deformation frequency 10 Hz. Results from several concentrations of carbon black filler particles. [53]

2.7 *Dynamic Mechanical Properties of Rubber*

2.7.1 Introduction

The dynamic mechanical properties of rubber are important in the slurry pump applications. In this application, the rubber undergoes rapid cyclic deformations at a certain frequency over a wide range of frequencies. In a previous study [3], wear was defined as similar to rapid cyclic deformations and this was simulated using the Rubber Process Analyser (RPA) with set conditions i.e., temperature, frequency and time. The elastic modulus G' and the viscous modulus G'' was determined and correlated with wear results. The dynamic properties of rubber are highly dependant on temperature, frequency, the presence of fillers, and the extent of deformation [12]. However, for extremely small deformations the properties are found to be independent of the magnitude of the deformation (linear viscoelasticity), and temperature-frequency superposition can be applied in order to predict the dynamic response over a wide frequency range [61]. It is also important to note that the dynamic mechanical properties of different unfilled amorphous elastomers are quite similar

when the proper reference state is used [12]. The reference state is usually the glass transition temperature; however a better reference state can be formulated in terms of the frequency for the onset of the transition zone at a given temperature (rubbery to glassy zone). Another difference can be seen in the chemical structure of elastomers, here the change in the location of the dynamic response curve on the frequency scale do not change the overall shape of the frequency dependence appreciably. Whereas the dependencies of the dynamic mechanical properties on molecular weight, molecular weight distribution, and crosslinking are similar for different elastomers. Only the elastic response is defined by Mark et al. [12] and characterised by the plateau modulus G_N^0 varies considerably from one elastomer to another as defined earlier in this thesis.

2.7.2 Terminology

Dynamic mechanical properties are generally defined by Mark et al. [12] as responses to periodically varying strains or stresses. Figure 2.69 shows the deformation of a sample confined between two parallel plates which is defined by the strain γ . Strain is defined as the tangents of the angle by which the cubical element is deformed or the displacement of the top surface divided by the height of the sample. The stress σ is defined as the tangential force per unit area resulting in deformation [12].

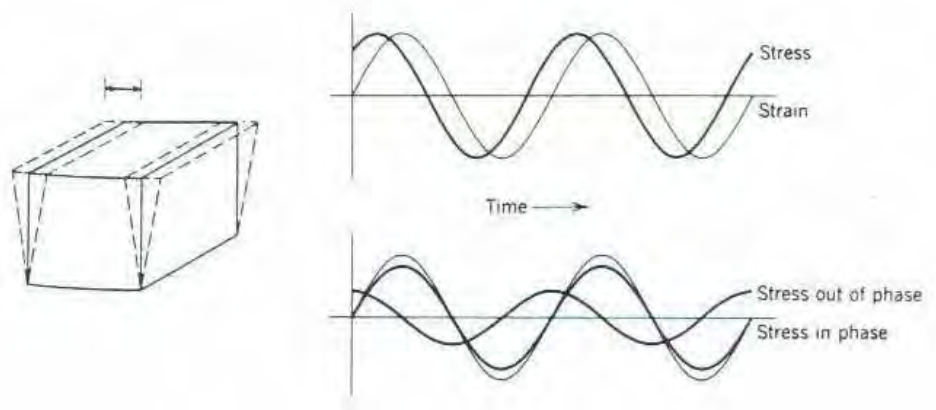


Figure 2.69 Sinusoidally varying simple shear: strain and stress decomposed into in-phase and out-of-phase components. [12]

When a sample is subjected to oscillatory shear deformations, the strain γ varies sinusoidally with time as,

$$\gamma(t) = \gamma_0 \sin \omega t \quad (2.19)$$

Where: γ_0 – the strain amplitude (peak strain)
 ω – the angular frequency ($2\pi \times$ frequency in hertz)
 t – time

The phase shift for the stress which will also oscillate sinusoidally with angular frequency is given by the phase angle δ , resulting in,

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta) \quad (2.20)$$

By combining the stress into a component in phase with strain proportional to $\sin \omega t$ and another component 90° out of phase proportional to $\cos \omega t$ shown in Figure 2.69, the total stress can then be expressed as defining two shear moduli, $G'(\omega)$ and $G''(\omega)$,

$$\sigma(t) = \gamma_0 [G'(\omega) \sin \omega t + G''(\omega) \cos \omega t] \quad (2.21)$$

The elastic modulus G' is a measure of “elastic” energy stored and recovered in cyclic deformation. The viscous modulus G'' is a measure of energy that is dissipated as heat. The ratio of G''/G' is $\tan \delta$, also referred to as the loss tangent.

2.7.3 Zones of Dynamic Viscoelastic Behaviour

2.7.3.1 The plateau zone

The plateau zone is explained extensively by Mark et al. [12] and will be discussed briefly in this thesis. Figure 2.70 shows the zone of viscoelastic behaviour of plots of G' and G'' against angular frequency for uncrosslinked poly(n-octal methacrylate) at 100°C, molecular weight 3.6×10^6 . It can be seen in the plateau zone that G' changes little with frequency and G'' passes through a minimum. This behaviour is interpreted by the “entanglement coupling” concept. The tangled, contorted macromolecules form a temporary network in which the molecules act in some respects as though they were coupled at widely separated points (usually in the order of a few hundred coupling chain atoms apart along each molecule). Within the period of oscillation in this frequency range, there is plenty of time for the network strands between coupling points to rearrange their configurations and store more elastic energy through an entropy change. There is not enough time for the much more complicated molecular rearrangements that would enable widely separated portions of a molecule to change their relative positions, as these processes would involve complicated snaking motions through the entanglements [12]. Therefore, at this particular frequency the material behaves as if it was crosslinked yet always more energy dissipated than in a vulcanised gum rubber at low frequencies. A fall in this zone on the frequency scale will always be dependant on the chemical nature of the polymer, temperature and other variables.

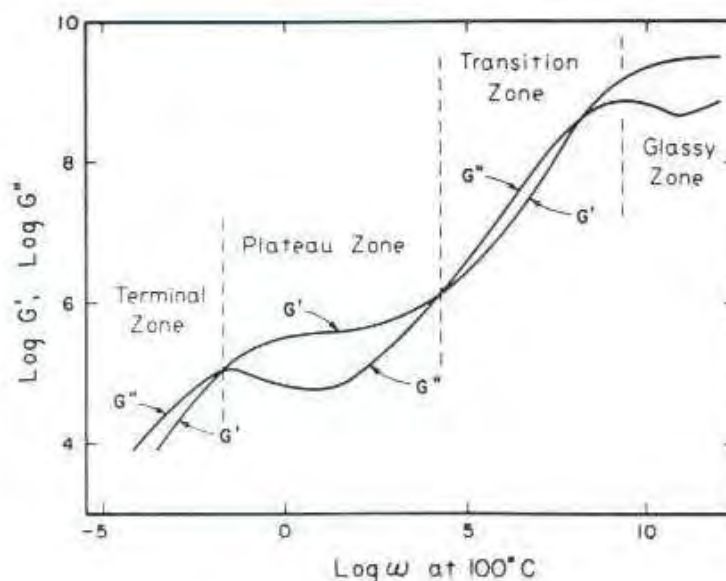


Figure 2.70 Zones of viscoelastic behaviour illustrated by logarithmic plots of G' and G'' against angular frequency for uncrosslinked poly(n-octal methacrylate) at 100°C , molecular weight 3.6×10^6 . [12]

2.7.3.2 The transition zone

The transition zone can also be seen in Figure 2.70 where the frequencies are higher than that in the plateau zone. At these frequencies, the period of oscillation becomes too short to allow all the possible configurational changes of a strand caught between two entanglements. From this, the strain corresponding to the given stress is less resulting in an increase in modulus with increasing frequency. In contrast to the plateau zone, it can be seen that $G'' > G'$, which means that most of the energy of deformation is dissipated as heat because of an increase in friction between the chains. As the name of the zone suggests, this behaviour emphasises the point as G' rises from a low magnitude, characteristic of a soft elastomer, to a high magnitude characteristic of a hard glass [12]. As frequency increases, it can be seen clearly that the polymer is losing its elastomeric properties and becoming first leathery then hard.

2.7.3.3 The glassy zone

This zone consists of very high frequencies, that at which no configurational rearrangements of polymer chain backbones occur within the period of oscillation, except for very local motions [12]. In this zone, the strain in response to a given stress is very small and corresponds to a elastic modulus G' of the order of 10^9 N/m^2 , much like a hard glasslike solid. There is less lag between the stress and strain in comparison to the transition zone and the $\tan \delta$ is of the order of 0.1 whereas the transition zone $\tan \delta$ is typically greater than 1. It must not be forgotten that the $\tan \delta$ of a gum rubber at low frequencies is of the magnitude of 0.01.

2.7.3.4 The terminal zone

This zone is situated at very low frequencies and can often replace the plateau zone. The period of oscillation is long enough to allow the molecules to snake through their entanglement constraints and completely rearrange their conformations [12]. It should be noted that the viscoelastic behaviour in the terminal zone is reflected also by the processing and molding operations at elevated temperatures of the elastomer.

2.7.4 Dynamic Properties in Large Deformations

Pure gum rubber is rarely used as the end product because the introduction of fillers to the elastomer usually improves the properties. Reinforcing fillers such as carbon black and silica will increase the modulus significantly which leads to the improved resistance of the failure properties such as tensile strength, tear resistance, and abrasion resistance [62]. It is important to note that the dynamic mechanical properties are only defined in small-amplitude deformations. In large-amplitude sinusoidal deformations, the resulting stress will no longer be sinusoidal and as a result Equation (2.21) cannot be used to define G' and G'' . In order to define the dynamic moduli at large static deformations, small-amplitude oscillations can be superimposed on the static deformation; however the dynamic moduli obtained does not describe the dynamic properties of rubbers in large-amplitude oscillatory deformations.

2.7.4.1 Effect of strain amplitude

The low-strain elastic modulus is increased significantly with the addition of carbon black to the elastomer [12]. Figure 2.71 shows the effects of filler content and strain on the storage shear modulus for butyl rubber containing HAF carbon black. It can be seen from this figure that the elastic modulus of pure butyl rubber is essentially independent of strain amplitude; however the magnitude decreases significantly going from small to large strain. It is also important to mention the transition from linear to nonlinear dynamic properties that occur at decreasing strain amplitude with increasing filler content.

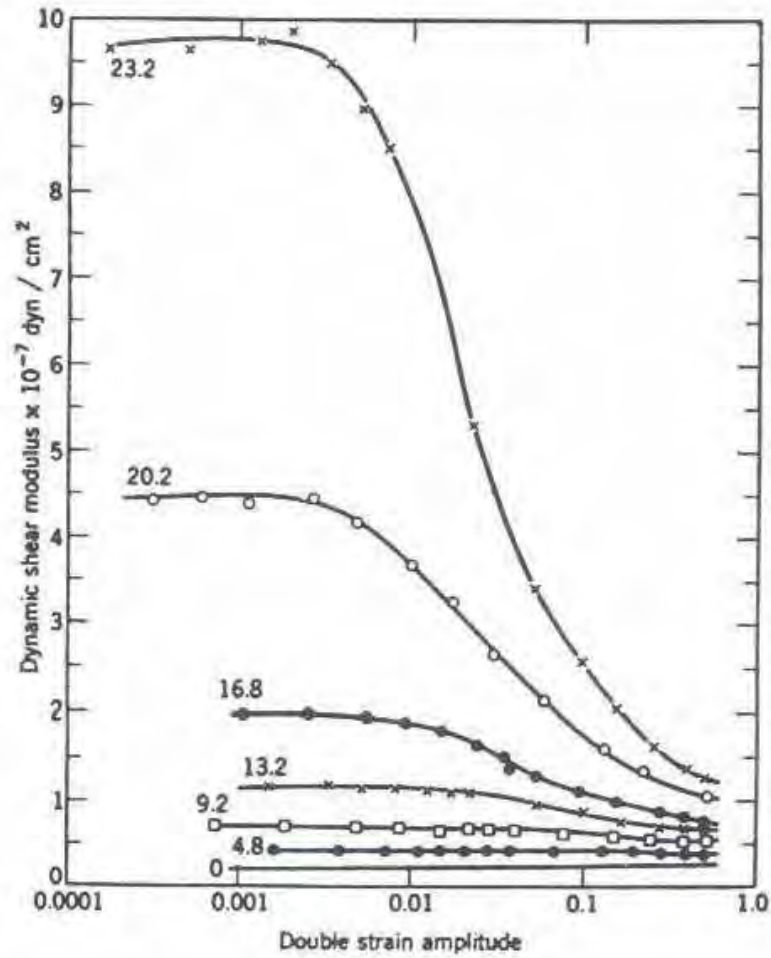


Figure 2.71 Dependence of storage shear modulus on double strain amplitude $2\gamma_0$ at 0.1 Hz for butyl rubber containing various concentrations up to 23.2 vol% HAF carbon black. [12]

The elastic modulus shows limiting values at both strains $G'(\omega)$, and high strains $G'_\infty(\omega)$. It is stated that $G'(\omega)$ depends on the carbon black content, the carbon black structure, particle size, and the degree of dispersion, whereas $G'_\infty(\omega)$ depends primarily on the carbon black structure [12]. It is also stated that the difference between the two limits $|G'_0(\omega) - G'_\infty(\omega)|$ represents structure breakdown in that the carbon black aggregates separate with strain. The dependence of loss shear modulus on strain amplitude can be seen in Figure 18. The maxima in the viscous modulus will decrease as a result of decreasing strain amplitudes with increasing filler content in the region of strain where the elastic

modulus changes most rapidly [12]. The observed strain dependencies of G' and G'' make the maxima in the loss tangent ($\tan \delta = G''/G'$) fall at strain amplitudes which are approximately one order of magnitude higher than for the viscous modulus as seen in the comparison of Figures 2.72 and 2.73.

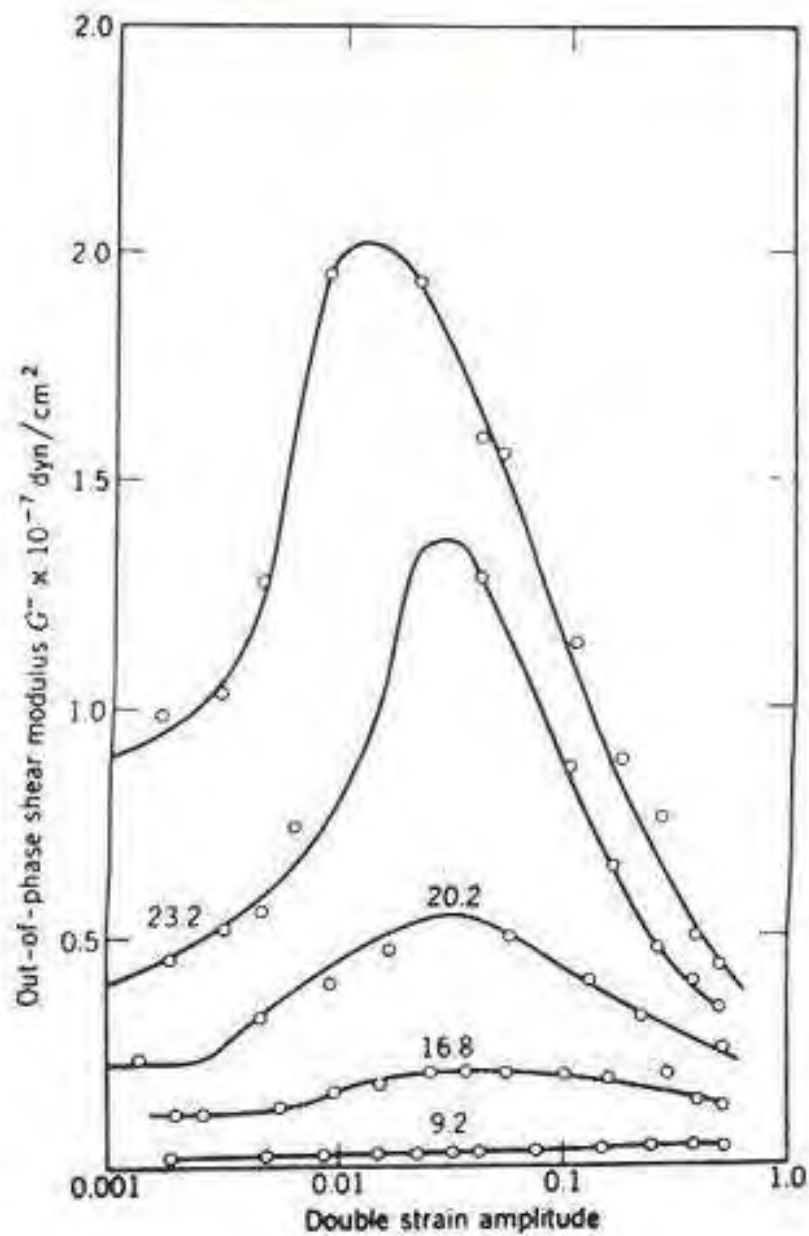


Figure 2.72 Dependence of loss shear modulus on double strain amplitude $2\gamma_0$ at 0.1 Hz for butyl rubber containing various concentrations up to 28.8 vol% HAF carbon black. [12]

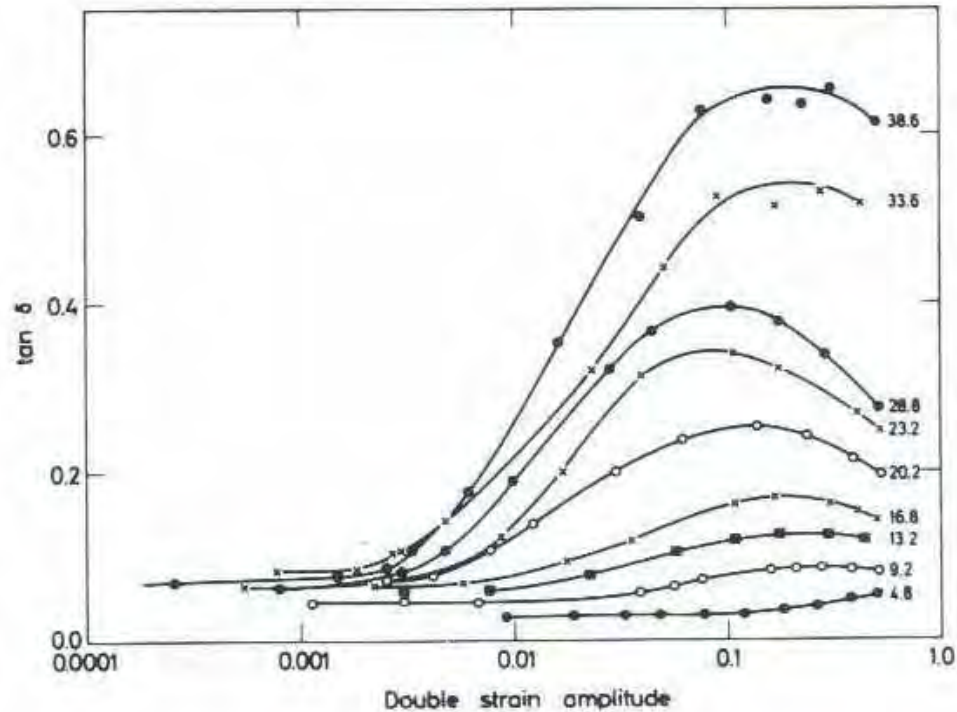


Figure 2.73 Dependence of loss tangent on double strain amplitude $2\gamma_0$ at 0.1 Hz for butyl rubber containing various concentrations up to 38.6 vol% HAF carbon black. [12]

2.7.4.1.1 Effect of static strain

Static strains are also often present and affect the end elastomeric product in addition to the oscillatory motion. Figure 2.74 shows the elastic modulus measured at small strain amplitudes as a function of static strain for SBR pure gum and 2 HAF carbon black filled SBR vulcanisates. The increase in carbon black initially shows a decrease in dynamic elastic modulus followed by a strong increase with increasing static strain.

It is mentioned by the literature that the decrease in E' is a result of a disruption of the filler network and the subsequent increase in E' is a result of higher elongations due to the limited extensibility of the elastomer chains [12].

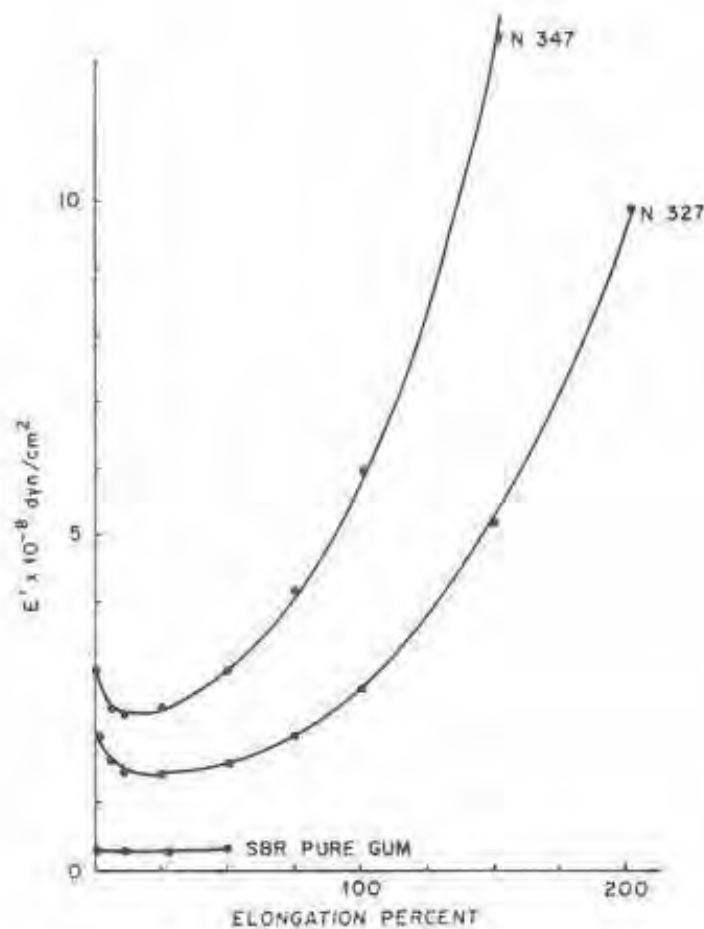


Figure 2.74 Small-amplitude oscillations superimposed on a static elongation. The plot shows dependence of dynamic elastic modulus (Young's) on static elongation for SBR pure gum and two SBR vulcanisates containing HAF carbon black (50phr), at 30°C. Oscillations at 11 Hz and amplitude 1.58×10^{-3} . [12]

2.7.4.1.2 Effects of frequency and temperature

An increase in frequency results in a reduction in the configurational changes which the polymer molecules in the elastomer matrix can respond within a cycle of deformation [12] . This leads to an increase in elastic modulus since Figure 2.75 shows an increase in elastic modulus over four decades in frequency for silica-filled SBR at different elongations.

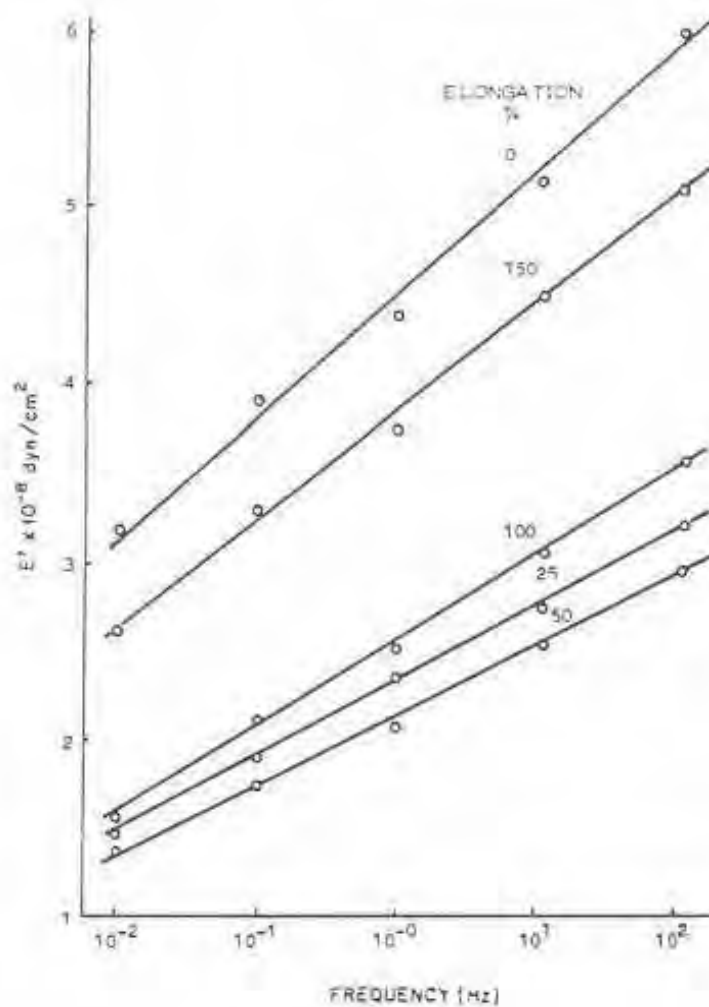


Figure 2.75 Elastic modulus (Young's) plotted against the logarithm of frequency at different elongations for SBR containing silica (50 phr), at 30°C, amplitude 1.58×10^{-3} . [12]

A decrease in temperature results in an increased resistance to molecular motion which leads to an increase in elastic modulus [12]. The effect of temperature on natural rubber can be seen in Figure 2.76. An increase in temperature from 20 to 90°C decreases the elastic modulus at small strain amplitudes, whereas the elastic modulus at high strain amplitudes is independent of temperature.

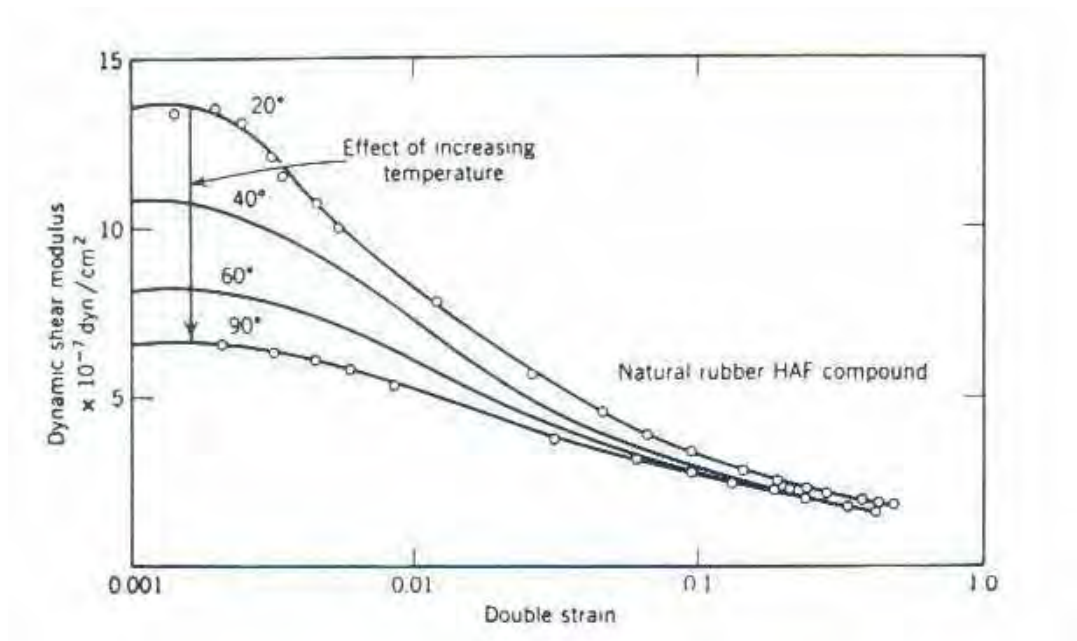


Figure 2.76 Variation of elastic modulus with double strain amplitude $2\gamma_0$ as a function of temperature at 0.1 Hz for natural rubber containing 32 vol% HAF carbon black. [12]

2.8 Chemistry of Rubber

2.8.1 Introduction

The chemistry of rubber is of the utmost importance in the design and development of new materials for rubber pumps since it dictates the physical and elastic properties of that material. During the operation of a slurry pump, different operating conditions and variables must be taken into account during the formulation stage of rubber development. For example, a slurry that contains fine abrasive particles would require a high resilient rubber to minimise the wear [3]. However, this may not always be the case where unexpected poor performance of material will occur that leads to premature failure of the slurry pump. This chapter will introduce an in depth review on the chemistry of elastomers and its properties that make the material unique from others used in the slurry pump industry.

Natural rubber is the prototype of all elastomers, it is basically the backbone or starting point for elastomers to be built on [35, 57, 63-65]. It is important to note the special feature of its structure, as this account for special properties. Due to the repeat structure of the repeat unit in polyisoprene, a number of configurations are possible. The possible isomers that can occur in a polyisoprene chain can be seen in Figure 2.77.

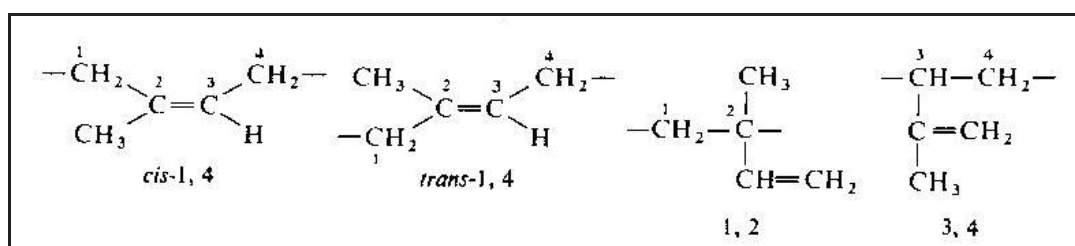


Figure 2.77 Possible isomers in a polyisoprene chain. pg 12 [65]

The natural rubber polymer is nearly 100% *cis*-1,4 polyisoprene. The numbers 1,4 refer to the structure in that the carbon atoms 1 and 4 are attached to adjacent units forming the chain. The terms *cis* and *trans* refer to the position of the various carbon atoms with

reference to the carbon-carbon double bond. The double bond tends to prevent the rotation of attached atoms, therefore the atoms or groups of atoms may occupy positions on either side of this double bond. In the *cis* 1,4 structure, the carbon atoms 1 and 4 are on the same side of the double bond, while in the *trans* 1,4 structure, these carbon atoms are on opposite sides of the double bond. When the chain units in a macromolecule all consist of the same isomer, the polymer is said to be stereoregular. As a result of this regularity, the natural rubber chains can attain a high degree of regularity, especially when the rubber is stretched. Hence natural rubber crystallises on stretching, resulting in high gum tensile strength. The physical properties of natural rubber will be discussed further in the next section.

2.8.2 The Physical Behaviour of Rubber

A large number of polymers exist as partly crystalline solids at normal temperatures [57, 63, 65, 66]. Some macromolecular chains have the ability of crystallising under the right conditions. This plays a very important role in the properties of rubber. These macromolecular chains may or may not be capable of crystallising on stretching, depending on their chemical structure and regularity. Natural rubber has a very regular chain structure, therefore can undergo a high degree of crystallisation on stretching. This produces a fibrillar structure where oriented chains crystallise into elongated crystals, containing bundles of rigid chains at high elongations. This results in a high tensile strength [65]. However, the inter-chain forces cannot maintain this strain-induced crystallisation once the applied force is removed, so that the fibre-like crystals “melt” and the rubber chains retract to their normal configuration.

The physical properties of a rubber, such as tensile strength are controlled by this short-term crystallisation. The tensile strength can vary depending on whether the polymer does or does not undergo crystallisation in stretching. If an elastomer has the ability to crystallise on stretching, the elastomer may also crystallise, at least partially, at some low temperature without stretching. This temperature is known as the crystalline melting point, T_m , and is usually below room temperature; otherwise the rubber will crystallise on storage and

harden. Another phenomenon exhibited by elastomers at lower temperatures is the glass transition temperature, T_g [65]. This occurs regardless of whether or not the polymer is capable of crystallisation and results in transforming the elastomer into a rigid plastic (Natural rubber $T_g = -72^\circ\text{C}$). Degrange et al. [24] investigated the tribological behaviour of NBR, where it was found that rubber with high T_g resulted in a higher resistance to wear in contrast to rubbers with low T_g .

Since elastomers are defined as viscous-elastic liquids, at high temperatures they can easily flow, due to the ability of entangled long-chain molecules to slip past each other under a distorting force [63, 66]. If an elastomer is to behave as a truly elastic material i.e., to exhibit a high degree of elastic recovery and a low degree of “set”, the polymer chains must be fixed to each other. This is done via vulcanisation, where crosslinks are introduced between the long-chain molecules to obtain a continuous network of flexible, elastic chains. Vulcanisation will therefore produce optimum properties for the elastomer.

The properties of elastomers depend very largely on the details of vulcanisation, reinforcement, compounding, and processing. Table 2.5 can only be used as a guide of the physical properties that elastomers exhibit.

For elastomers the major physical parameters that affect wear are:

- Modulus of elasticity
- Tensile strength
- Tear resistance
- Elongation at break
- Resilience
- Hardness

Table 2.5 Typical properties of commercial elastomers. pg 519 [66]

Property	Natural Rubber		Chlorosulfonated Polyethylene			Epichlorohydrin		Fluorinated Rubbers
	SBR	Acrylate	Butyl	EPDM	EPDM	EPDM	EPDM	
Tensile strength (psi)	4000	2200	3000	3000	2800	2500	2400	
Elongation (%)	700	400	700	300	500	400	400	
Modulus (psi, 300-400% elongation)	2500	--	1000	--	--	--	250	
Dynamic properties	Good	Good	Poor	--	--	--	Poor	
Permanent set	Low	Low	Moder.	--	--	--	High	
Tear resistance	Good	Fair	Excel.	Good	Good	Good	Fair	
Abrasion resistance	Good	Good	Good	--	--	--	--	
Adhesion	Excel.	Good	Good	Excel.	Excel.	Fair	Good	
Electrical properties	Excel.	Poor	Excel.	Excel.	Fair	Fair	Excel.	
Gas permeability	High	Low	Low	--	--	--	--	
Upper use temperature (°C)	80	150	100	150	120	120	230	
Lower use temperature (°C)	-50	-20	-50	-40	-50	-45	-40	
Weather resistance	Fair	Excel.	Excel.	Excel.	Excel.	Good	Excel.	
Ozone resistance	Poor	Excel.	Excel.	Excel.	Excel.	Good	Excel.	
Oil resistance	Poor	Excel.	Poor	Poor	Good	Good	Excel.	
Gasoline resistance	Poor	Fair	Poor	Poor	Fair	Good	Excel.	
Water swelling	Excel.	Poor	Excel.	Excel.	Excel.	Good	Excel.	
Adhesion to metal	Excel.	Good	Good	Excel.	Excel.	Excel.	Excel.	

2.8.3 Chemical Composition of Rubber

Quantitative and qualitative chemical analysis methods are often used to determine low molecular weight organic compounds. For example a qualitative chemical analysis technique can be used to determine the composition by the combustion of a sample using thermogravimetric analysis (TGA) and gas chromatographic analysis. The basic composition of rubber compounding consists of the following: (1) Base polymer – natural, polyisoprene, butyl, nitrile, polybutadiene, etc; (2) Fillers – carbon black, silica, calcium carbonate; (3) Plasticisers – process oils, ester plasticisers, waxes, steric acid; (4) Vulcanising agents – Sulphur, peroxides; (5) Other additives – colorants, tackifiers, antioxidants, antiozonants, releasing agents. The carbon, hydrogen, and nitrogen can be determined on small samples by complete combustion (TGA) followed by gas chromatographic analysis of the gas evolved. Others such as sulphur and halogens can be determined by titration methods whereas parts per million (ppm) levels of metals can be determined quantitatively by X-ray techniques.

As mentioned earlier in this literature review, non-destructive techniques that are used to analyse what the polymer comprises of involves the use of the infrared and Raman spectrograph. Various atoms in the polymer will absorb and emit radiation at characteristic frequencies depending on the structure. This amount of absorption or emission will then indicate the skeletal bond transitions of the polymer. For the basic information, the infrared spectroscopy is the most accessible technique, due to its ease of operation both solids and liquids can be analysed using the FT-IR. The Raman spectra is used in a similar way in that many vibrations which are infrared inactive are Raman active, therefore giving a much enhanced spectra. The carbon-sulphur bonds in particular are detected easily, and as a result these spectra can be used to determine crosslinked specimens.

In a previous study in the erosive wear of rubber pump lining materials, three different types of rubber compounds used in similar applications were considered [3]. The rubber composition will dictate its physical properties and hence the erosive wear behaviour of the rubber material. However, the composition alone does not constitute the final rubber

product; the process of fabrication is a complicated process which includes the mixing and curing of the rubber which can affect the physical properties. These mixing and curing systems are confidential information from the accommodating company and cannot be reproduced in this paper.

Extensive erosion testing for three rubber compounds were undertaken with the following descriptions; A1 a natural rubber consisting of pure gum rubber, A3 a polymer blend of natural rubber and poly-butadiene reinforced with granulated silica, and B1 a natural rubber reinforced with precipitated silica. Each rubber has a different composition that results in different physical properties. The chemical composition of A1 is made up majority of natural gum rubber. Figure 2.78 shows an ESEM picture of an unworn A1 rubber sample. The EDS analysis (Figure 2.79) provides the chemical elements present in the A1 rubber mix. By having the majority of the composition made up of natural gum rubber, the physical properties will favour low erosive wear loss. It is stated that the higher the value of elastic modulus (G''), will result in higher wear loss. Since A1 is made up of natural gum rubber, which is known to have low elastic properties [67], the elastic modulus (G') will be low (Figure 2.80). The elastic modulus dictates the amount of energy from the attacking particle that is reflected or rebounded off the surface as a result of the material's stiffness.

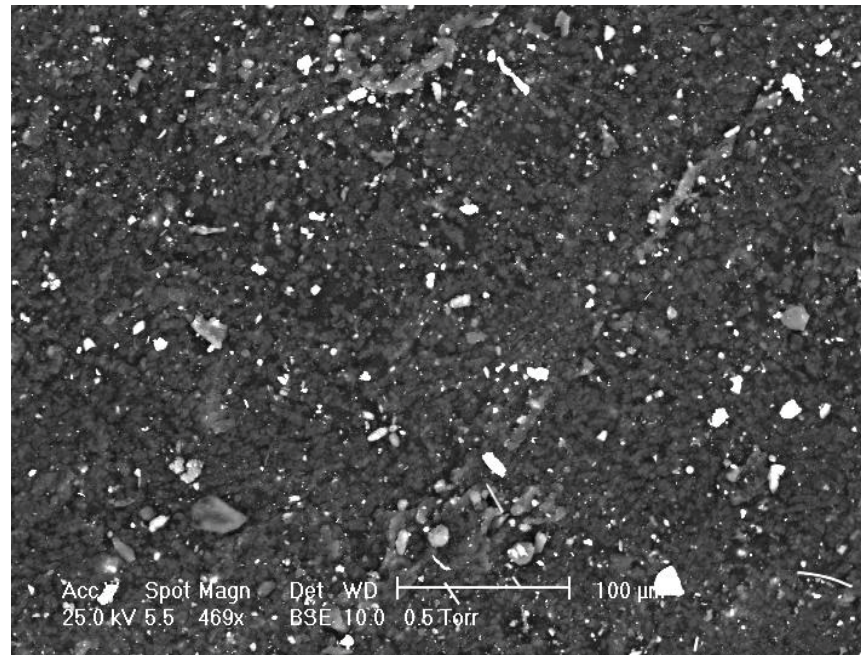


Figure 2.78 ESEM picture of unworn A1 rubber using BSE detector at magnification 469x. [3]

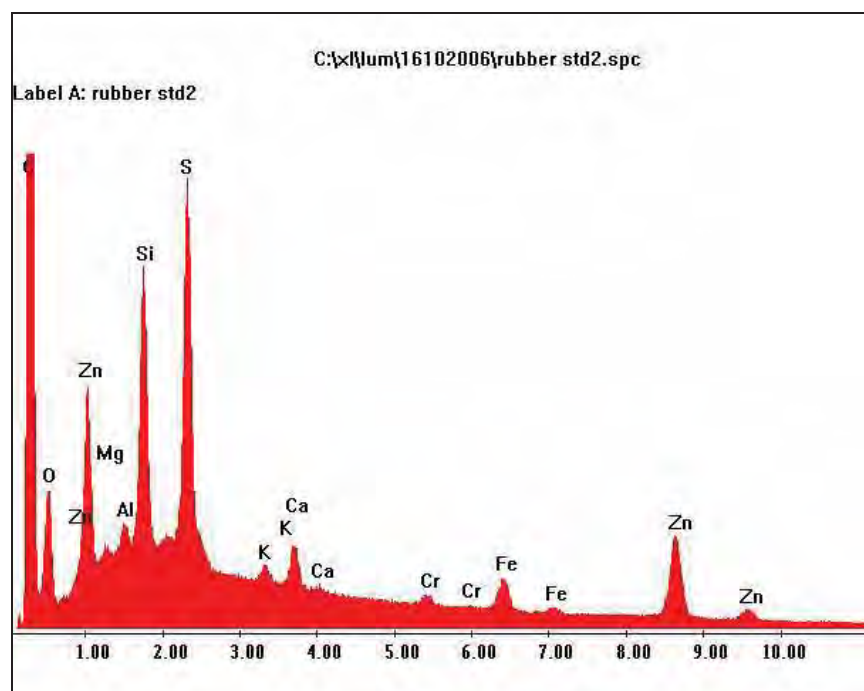


Figure 2.79 EDS analysis on the A1 standard rubber (unworn). [3]

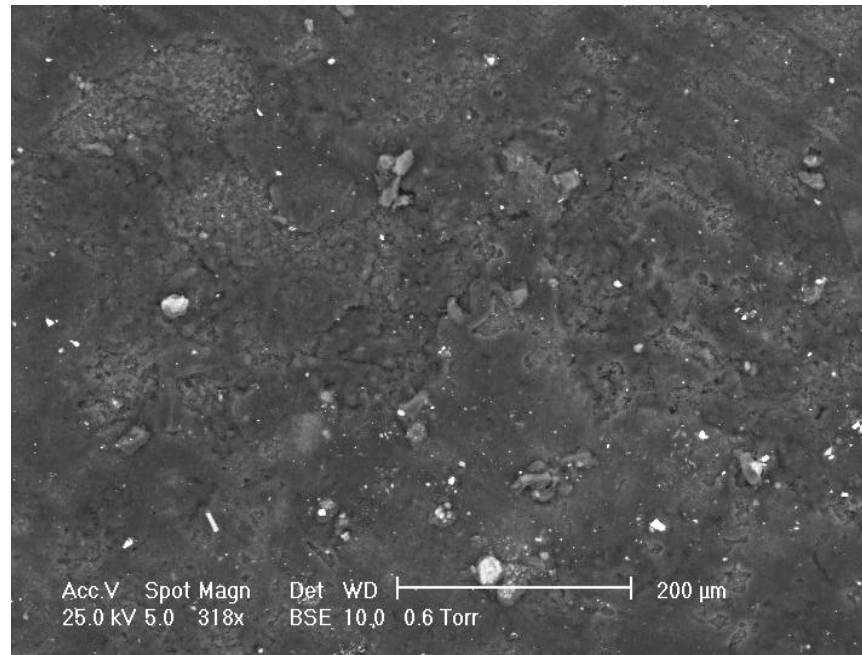


Figure 2.80 ESEM picture of unworn A3 rubber using BSE detector at magnification 318x. [3]

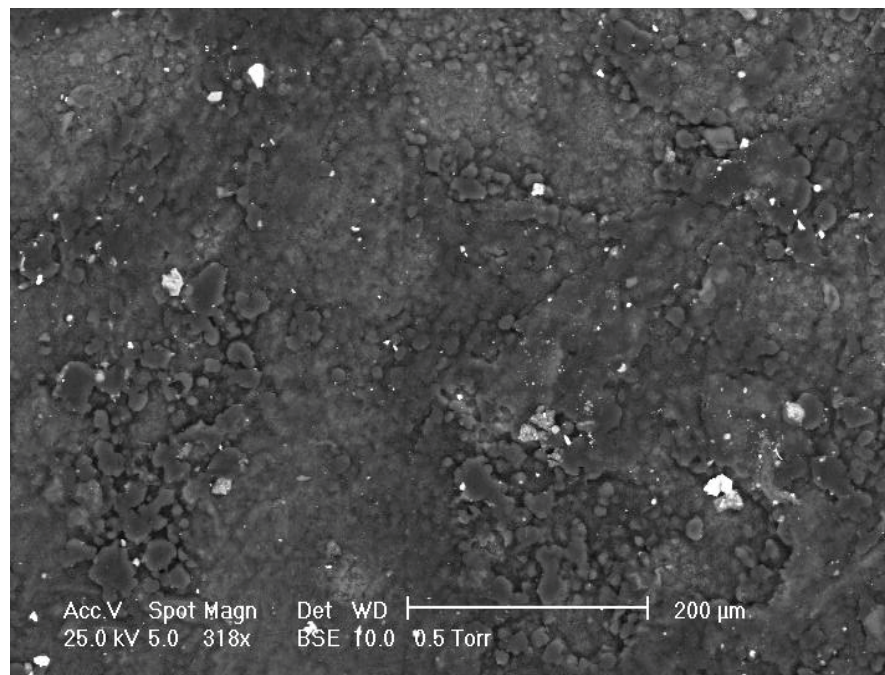


Figure 2.81 ESEM picture of unworn B1 rubber using BSE detector at magnification 318x. [3]

A3 has a different chemical composition than the other rubbers investigated in that it is a polymer blend. This blend consists of natural rubber and polybutadiene rubber reinforced with granulated silica. Figure 2.81 shows the coalescence of the natural rubber and the polybutadiene, where the natural rubber particles are now covered by the more even surface structure of polybutadiene. This reinforcement will provide the rubber with increased hardness and lower wear loss with larger sized impacting particles. Figure 2.82 shows the average wear loss in all conditions for the 3 materials investigated. It can be seen that A3 has the lowest combined average wear loss most likely due to its reinforcement with polybutadiene. The physical properties are affected by the reinforcements and will be discussed later on in this thesis.

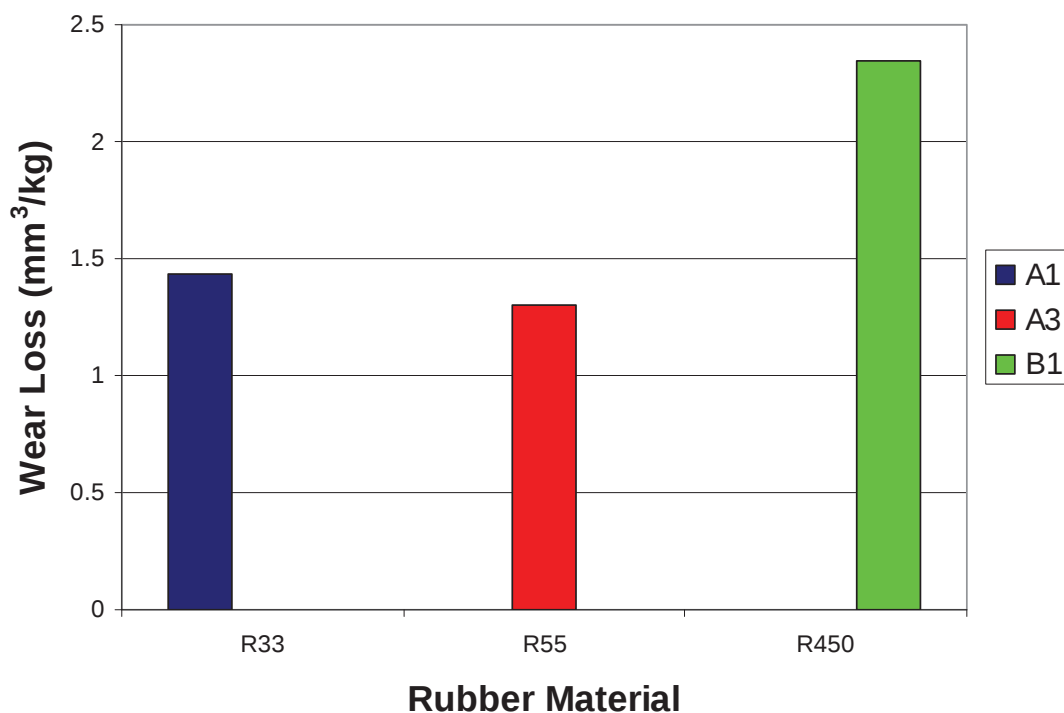


Figure 2.82 The combined average wear loss for all conditions vs. rubber material. [3]

The chemical composition of B1 is of great interest as it resulted in the highest amount of wear loss as shown in Figure 2.82. B1 is a natural rubber reinforced heavily with precipitated silica, approximately 20 percent of the total weight. Figure 2.81 illustrates the

blending of natural rubber with precipitated silica. It can be seen from the ESEM picture that there are dark and light regions. The dark regions tend to have larger, more defined particles showing, as a result they can be assumed to be rubber particles. Whereas in the light regions, there does not seem to have any large particles showing. This is an example of the precipitated silica fully dispersed into the rubber structure. With a high percentage of filler, it is expected that the rubber will be much stiffer than the other 2 rubbers, resulting in high values of G' and G'' . Figure 2.83 and Figure 2.84 substantiate the previous statement, and as mentioned earlier a high value of G'' results in a high level of energy absorbed by the rubber. This high level of energy absorbed will then lead to higher wear loss as shown in Figure 2.82. In relation to G'' , the elastic modulus G' will also increase as a result of the increase in B1's stiffness as shown in Figure 2.83.

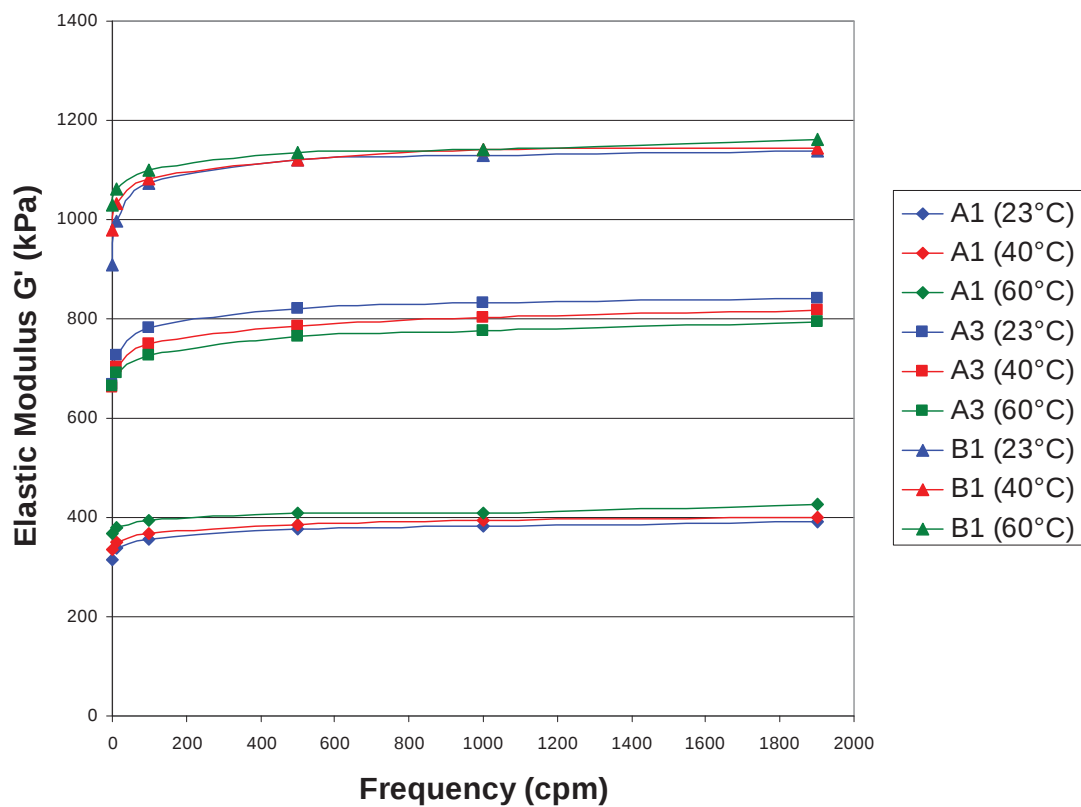


Figure 2.83 The variation of elastic modulus G' as a function of frequency for A1, A3 and B1 at temperatures 20°C, 40°C and 60°C. [3]

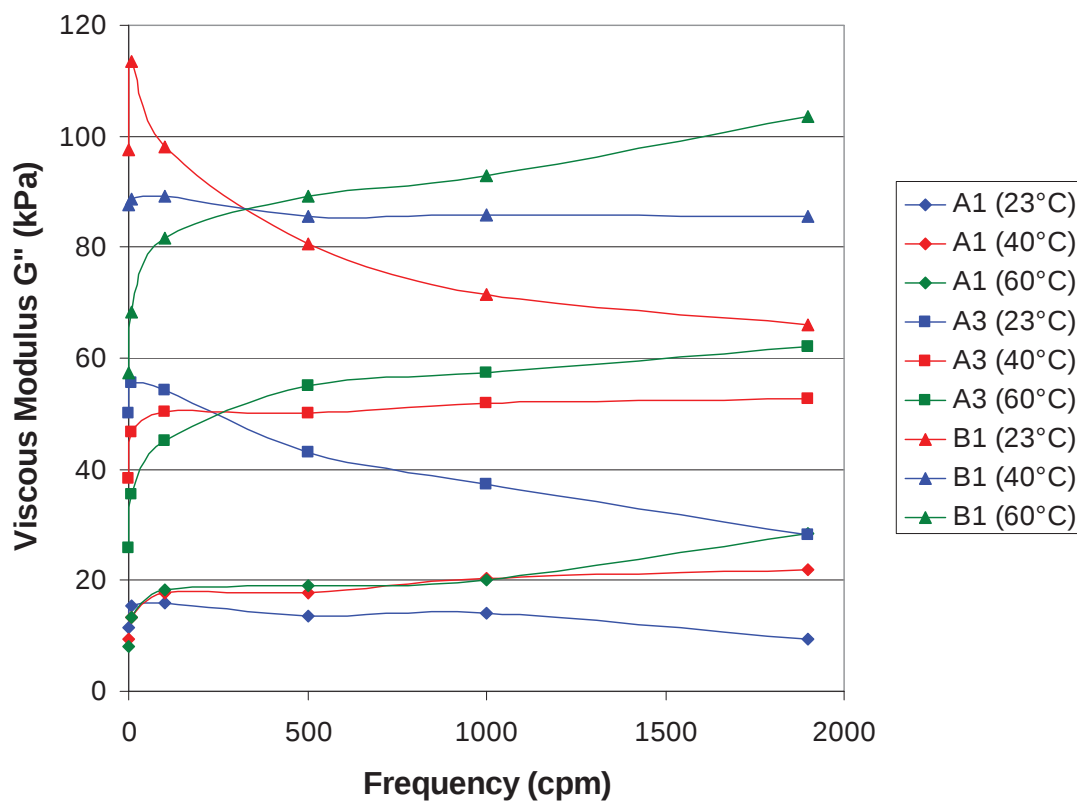


Figure 2.84 The variation of viscous modulus G'' as a function of frequency for A1, A3 and B1 at temperatures 20°C, 40°C and 60°C. [3]

X-ray photoelectron spectroscopy (XPS) was not considered in the earlier study [3], although this can be used to identify the combination of elements on the surface of the rubber material. Degrange et al. [24] used the XPS to chemically analyse the surface (S) of the rubber, the bulk (B) of the material and finally the wear trace (T) of the material. The XPS provides similar measurements as the EDS in that information on elements are presented upon the top atomic layers of the material. This can be a useful tool in determining the chemistry of the rubber including the carbon bonds (C-C or C-H) also the constitutive links between carbons from the polybutadiene found in the A3 material.

2.8.4 Molecular Weight Distribution

It is well known from the literature that the chemical and stereochemical nature of the repeat unit has a profound effect on the polymer properties. However, for a polymer to be classified as an elastomer, the repeat unit must be chosen so that the glass transition temperature $T_g \leq -30^\circ\text{C}$, and the degree of crystallinity f_c remains below a fraction of ~ 0.3 [12]. If the T_g is too high, the polymer will be too leathery and not give the desired rubbery property of being rubbery. However, if the T_g is too low, the crystallinity f_c will be too high and the modulus will be too high leading to the material exhibiting too much permanent set after being deformed. It is stated that at processing temperatures, f_c is usually zero and thus the viscoelastic response is determined basically by the weight-average molecular weight M_w , long-chain branching, and molecular weight distribution of the polymer [12]. The chain ends present in the elastomer are often the cause of defects in the vulcanised network, and thus depends on the number-average molecular weight M_n . Other causes of defects in the vulcanised network include closed chain loops and non-uniform distributions of crosslink density. Figure 2.85 shows frequently observed MWDs in elastomers.

According to Mark et al. the molecular weight distribution is usually presented as a plot of the mole fraction, or of the percentage (number) of molecules of a given molecular weight $N(M)$, vs. the molecular weight M , or as the weight of molecules of a given molecular weight $W(M)$ vs. M [12]. From figure 2.85, it can be seen that the distribution seems continuous, whereas on a molecular scale they are actually separate because the molecular weight must increase in jumps of monomer unit molecular weight.

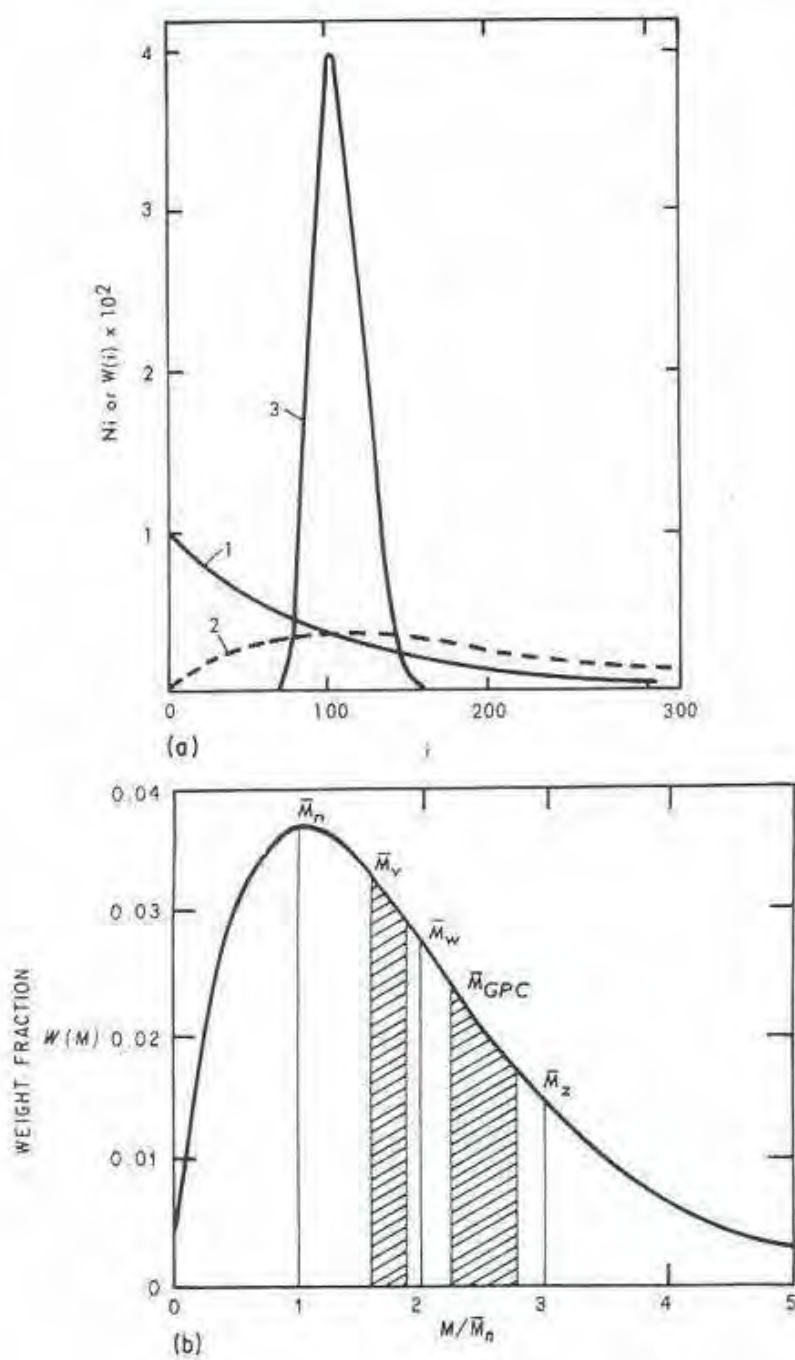


Figure 2.85 Molecular weight distribution. (a) Differential number and weight distributions for a polymer with a number average of 100 units per chain. Curve 1, most probable number distribution; curve 2, most probable weight distribution; curve 3, Poisson number distribution. [12] pg 106

2.8.5 Crystallinity, Morphology and Entanglements

The moduli of a polymer are usually determined by the amount of crystallinity which will increase the mechanical performance as well as the polymer strength. Amorphous polymers have large recoverable extensibility at low stresses above T_g , this is often referred to as “Rubberiness”. Many rubbers contain crystallites embedded in the elastomeric matrix for reinforcement. These crystallites are known as filler particles and physically crosslink the unvulcanised semicrystalline rubber to support stress indefinitely. As mentioned in an earlier chapter, crystallisation can be induced by stress, producing a state in which the stress-induced degree of crystallinity raises the strength of the rubber. Natural rubber is said to be the premier example of a material that has a low modulus and small strain with tensile strength of tens of mega Pascals after crystallisation at high strain [12]. It is important to mention in terms of this research that polybutadiene elastomers possess significant degrees of crystallinity at ambient temperatures, whereas natural rubber crystallise significantly only when stressed. Crystallinity of polymers is still an active field in terms of research, and a number of models have been proposed for a wide variety of states of semicrystalline polymers. A polymer is often considered as a two-phase system of crystalline and amorphous domains, each phase has its own characteristic of the pure phase and are undisturbed by the other. As mentioned earlier, the degree of crystallinity is described as a weight (W_c) or a volume fraction (f_c). Typically, the structure of crystal lattices is studied by X-rays, but this is often hard to perceive as the degree of crystallinity in elastomers is so low and the long range order in the crystal is so poor that only a few maxima can be viewed. As a result, determination of the crystal structure is difficult, therefore often the most intensive maxima from a particular geometry that is observed is used to assume that the particular crystal structure is that of the polymer of the same repeat unit which has crystallised more completely under other conditions.

The morphology of a material is stated by Mark et al. as its organisation on a supermolecular scale, i.e., the form, size and orientation of its crystallites, domains, the structure of groups of molecules in the specimen and of their boundaries, and the degree of

crystallinity. In terms of crystals, the area of concern relates to how the polymer chains are incorporated and form links between the crystals. In the presence of filler particles or other components, size, dispersion, and distribution has a major effect on the physical properties of the final material. There is also interest in the morphology of mixtures of two or more polymers, otherwise known as a polymer blend. Most blends are heterogenous, and the sizes and shapes of the phase domains control mechanical and transport properties [12]. The measurement of interfacial tension is also important as this controls the phase separation and growth, thus the morphology.

It is well known that elastomers will recover its original shape after it has been extended and the stress released. The elastomer will exhibit this property to some degree whether chemical crosslinking is present or not. If the elastomer is not crosslinked, the material will no longer recover to its original shape if it is held long enough in its deformed state. The elastic response of the uncrosslinked polymer behaves much like a crosslinked polymer as the polymer chains cannot pass through one another until they have had time to flow in a direction along their contours, until ends pass the constraint of neighbouring chains. The elastic response is defined by Mark et al. [12] and characterised by the plateau modulus G_N^0 .

$$G_N^0 = \nu_e RT \quad (2.22)$$

Where: ν_e – apparent number of crosslinks
 R – is the universal gas constant
 T – absolute temperature

The characterisation concentration of physical links can also be determined by using a molecular weight $M_e = \rho / G_N^0$ between the links. These physical links will determine the structure of the polymer and dictate the rubbery property. Therefore, it can be said that the magnitude of G_N^0 and ν_e will have a profound affect on the performance of an elastomer in its application.

The chemical composition will dictate its physical properties and hence the erosive wear behaviour of the rubber material. The composition alone does not constitute the final rubber product, the process of fabrication is a complicated process which includes the mixing and curing of the rubber.

2.9 *Aging of Rubber*

2.9.1 Introduction

Rubber compounds with good aging properties will dictate the acceptable service life of the rubber material [57]. Baranwal also states in general, a high level of antidegradants in the rubber compound will result in better aging properties. Rubber compounds that do not have antidegradants are more vulnerable to oxidation and ozonisation effects which lead to premature aging and failure of rubber products. With the ever increasing need for wear resistant materials in the mining industry, aging becomes an important avenue for research. In slurry pump applications of rubber, environmental aging does not play a large role in the operation of the pump, since the rubber is enclosed in a metal casing. However, where it does have an affect on the rubber are in storage situations. Often is the case in mining companies and locations where shipping is difficult and time consuming, the company will purchase a number of spare parts for storage. Depending on the weathering conditions, the rubber spares can be affected by sunlight, rain and wind. As to the degree at which these weathering conditions affect the properties of the rubber is unknown. During the operation of the pump, the rubber is exposed to slurry that consists of abrasive particles and liquid, usually water. The water may have an affect on the rubber which essentially reduces the wear life of the material in operation. The operating temperature of the pump may also dictate the wear life of the material as heat aging will have a negative affect on the rubber. From a previous study, temperatures of 70°C and above will degrade the rubber at an increased rate. However, since the slurry is a mixture of abrasive sand and water and continuously replenished, the temperature will not reach 70°C. Therefore the temperature will be more in the range of 40°C - 50°C.

The aging of rubber can be considered as a chemical change to the rubber. This chemical change can be a result of oxidation and/or ozonisation. Oxidation is a process of free-radical mechanisms that leads to chain scission and crosslinking [57]. Chain scission is the process where free radicals attack the polymer backbone causing degradation. Baranwal suggests that heat, UV light and the presence of transition metals accelerate the oxidation process [68]. Heat is a major concern with rubber aging, as this can lead to chain weakening and premature failure. One must not exclude the mechanism of flexing and its affect on rubber. Flexing has not only a mechanical fatigue affect on rubber, but heat is also generated accelerating the aging process. Ozonisation involves chain scission at the double bond of the unprotected rubber resulting in decomposition products such as ozonides, polymer peroxides, hydroperoxides, aldehydes, and ketones [57]. In this paper, it is of interest to investigate the affects of aging on rubber pump lining materials before and after use when exposed to weathering conditions. In particular, at a microscopic level if the chemical structure of the rubber is strengthen/weakened by the aging affect.

2.9.2 General Aspects of Polymer Degradation

2.9.2.1 Polymer life phases and degradation

Rubber oxidation is extensively reviewed by Li and Koenig. The aging of rubber is stated as being caused by oxidative degradation that leads to the deterioration in the physical properties of vulcanised rubbers [52]. Polymer degradation is a result of chemical bond scission reactions that occur in the macromolecules [69]. The various modes of initiation of chemical degradation are as follows; thermal, mechanical, photochemical, radiation chemical, biological and chemical degradation of polymeric materials. Degradation is an unavoidable process throughout a polymer's engineering life cycle. The quality of the rubber product can be affected in all 3 stages of rubber life i.e., synthesis, processing, and finally in use [70]. During the synthesis of polyisoprene or any base polymer rubber, most additional polymerisation reactions are exothermic. Li and Koenig suggest the free energy

of polymer per monomer unit decreases as the temperature is raised during the synthesis [52]. Therefore, at a certain temperature the optimum polymerisation reaction will occur and at temperatures about this point, long chain polymers is no possible. As a result, premature polymer degradation will occur.

The processing stage of the base polymeric material results in an increase in thermal and mechanical stresses on the polymer chains. Processing of rubber requires mastication that results in a shearing action. The energy generated by this shearing action is then converted into heat which is responsible for the temperature rise during mixing [71]. This rise in temperature may be a cause for polymer degradation and lead to various defect formation that can have an adverse affect on the subsequent service life of the rubber material. Finally, the most obvious polymer degradation will occur when the product is in use. Depending on the application of the rubber product, the chemical structure will be attacked by chemical, thermal and mechanical processes. Many additives are used in the formulation of rubber to protect it from these degrading processes such as antioxidants, antiozonants, waxes, etc. These additives will be discussed further in a later chapter in this thesis.

2.9.2.2 Chemical structures and polymer stability

The chemical structure and composition of the materials are significant with respect to its stability [52]. Chemical bonds, stereochemical organisation, and topological arrangements are decisive factors given that the chemical composition of the material affects the service life. In particular, when discussing chemical bonds there are different bond energies that relate to the nature of the chemical groups to which the atoms belong. Li and Koenig states, in polymers consisting only of primary and secondary carbon atoms (e.g. PVC), the presence of tertiary or allylic bonds are undesirable as they form weak chemical sites that are susceptible to attack. The bond dissociation energies of various single bonds can be seen in Table 2.6.

Table 2.6 Bond dissociation energies of various single bonds [52] pg 357

Bond Broken	Bond Dissociation Energies (Kcal/Mol)	Bond Broken	Bond Dissociation Energies (Kcal/mol)
C_2H_5-H	99	$C_6H_5-CH_3$	94
$n-C_3H_7-H$	98	$C_6H_5CH_2-CH_3$	72
$t-C_4H_9-H$	91	CH_3-Cl	84
$CH_2=CHCH_2-H$	82	C_2H_5-Cl	81
C_6H_5-H	103	$CH_2=CHCH_2-Cl$	65
$C_6H_5CH_2-H$	83	CH_3-F	108
$C_2H_5-CH_3$	83	C_2H_5-F	106
$n-C_3H_7-CH_3$	83	$HO-OH$	51
$t-C_4H_9-CH_3$	81	$t-C_4H_9O-OH$	36

Table 2.7 Bond dissociation energies of some CH_3-R bonds [52] pg 357

Bond Broken	Bond Dissociation Energies (Kcal/Mol)
CH_3-R	88.4
C_2H_5-R	84.5
$n-C_3H_7-R$	84.9
$n-C_4H_9-R$	84.7
$i-C_3H_7-R$	83.8
$t-C_4H_9-R$	80.5
$CH_2=CHCH_2-R$	72.3
C_6H_5-R	94
$C_6H_5CH_2-R$	71.9

The presence of certain additives or polymer blend components may also result in chemical instability; however they are added to improve the physical properties. These additives or components are typically not chemically bonded to the polymer.

The extent of degradation is determined by the bond dissociation energy of the various bonds in the polymer. Degradation is a process that begins with the scission of the weakest available bond or in some cases a chemical attack at this bond. Other factors that have an affect on the chemical structure which leads to degradation include steric factors, stability of the intermediates, and the possibility of resonance stabilisation. Table 2.7 shows the

effect of steric factors and resonance stabilisation on bond dissociation energies of some $\text{CH}_3\text{-R}$ bonds.

Aging and chemical degradation occurs in the rubber components of high impact polystyrene due to their unsaturated bonds [52]. A compromise is usually set in the formulation of products such as high impact polystyrene where improvements in physical properties comes as a cost of lower resistance to UV light or oxidation. Chemical modifications of polymers in improving stability are being increasingly used to prevent degradation. The most common is the elimination of weak sites or substitution of labile groups with stable groups by grafting. This modification can have the added benefit of improving other properties that can be useful for the application of the final product.

The physical and morphological factors may also influence polymer stability [52]. Physical factors such as oxidation in polymers are primarily initiated in the amorphous phase of semi-crystalline polymers. Oxidation propagates into the crystalline phase as a result of the destruction of the crystalline order. Therefore it can be said that the relative crystallinity is an important characteristic of the polymer in terms of oxidative stability. The morphology of the polymeric materials in relation to degradation can be related to the diffusion conditions. A compact material will be more stable against oxidation than a flexible material because the diffusion of oxygen will be more difficult. However, this may not always be the case using the example of the easy diffusion of HCL evolved from PVC with a flexible morphology. The flexible morphology reduces the autocatalytic character of the degradation which may lead to a catastrophic destruction in the case of compact dense materials [52].

2.9.3 Simple Model Predicting Heat Aging

2.9.3.1 Property deterioration relationship

A simple model for predicting heat aging of ethylene-propylene-diene monomer (EPDM) rubber is made known in a paper by Pauglis [72]. The loss of both tensile strength and elongation, can be described by the factor of fractional strain energy at break (FSEB). This concept of FSEB was introduced and notated by Bergstrom as $(TE)f^2$ and is defined in Equation (2.23). FSEB is a useful dimensionless parameter used to compare materials with different initial properties on the same relative basis [72]. FSEB has also been used in other studies to characterise property deterioration of materials.

$$(TE)f = \frac{(T_b \times E_b)_{aged}}{(T_b \times E_b)_{unaged}} \quad (2.23)$$

Where: T_b - tensile strength
 E_b - elongation at break

Based on the FSEB expression, Paeglis [72] developed an empirical expression to quantitatively describe the observed deterioration of properties. This empirical expression is represented by Equation (2.24).

$$[1/(TE)f - 1/a'] = k't \quad (2.24)$$

Where: $(TE)f$ – fractional strain energy
 t – fractional strain energy aging time
 k' – effective rate coefficient
 T – effective rate coefficient temperature
 a' – intercept factor

A regression analysis of experimental data using the slope of $1/(TE)f$ vs. time at specific temperatures can determine the value of k' .

2.9.3.2 Temperature dependence of degradation rate

Using the Arrhenius Equation a relationship for the variation in reaction rate in a thermally activated molecular process to temperature can be represented in Equation (2.25).

$$\ln k = -(E_a/RT) + \ln A \quad (2.25)$$

Where:

- k – reaction rate
- E_a – activation energy
- R – gas constant
- T – absolute temperature in °K
- A – pre-exponential factor

Paeglis states, if the stress-strain properties degrade with consistent activation energies, an Arrhenius relationship can be used to predict changes at different temperatures and times. The use of Arrhenius relationships have been used in previous studies for elastomeric and plastic materials.

2.9.3.3 Relationship to service conditions and limitations of model

The various mathematical models for heat aging stated above are of interest to actual service conditions and lifetimes of elastomeric and plastic products. However, one must bear in mind that these are models only, and may not be applicable to real life applications. In real life applications other factors relating to heat aging such as polymer chemistry (i.e. Mw, Mw/Mn, ethylene content and diene), compounding ingredients, curative ingredients and the migration of these additives content may influence the performance of the product

in a laboratory or field test. Mathematical models are only used to provide guidance as to what the approximate service life of the product will achieve.

2.9.4 Storage Time of Raw Natural Rubber (NR)

2.9.4.1 Introduction

The storage of natural rubber (NR) at room temperature is of great interest in the mining industry and in particular the spare parts industry. Mining locations are often far from civilisation and access to these areas is often difficult or limited. The purchase of spare parts is common and stored onsite for a number of days, months even years before use. Due to this storage time, there is a need for research into the area of degradation and temperature aging of the rubber product. The effect of the environment such as light, heat, and oxygen causes the NR molecules to degrade and as a result leads to depolymerisation [73]. The resulting rubber part is left as in a nonelastic state affecting the performance of the rubber product. A study in 1975 by the International Rubber Conference in Kuala Lumpur describing smoke sheet stored for 50 years under Japanese climate conditions still possessed satisfactory performance characteristics. Literature reviewed in this paper indicated studies up to this point in regards to effective storage life of vulcanised rubber and rubber products only. Due to the large difference in molecular structure of raw/green natural rubber and vulcanised rubber, this will result in different storage life.

During storage, oxidative depolymerisation reaction occurs in the molecular chain of the raw NR. This is a result of light, heat and oxygen that causes a decrease in the plasticity value. However, it is known that at lower temperatures (near T_g) the polymer chains lose mobility as a result increasing the stability of NR therefore becoming more crystalline [74]. The lower the storage temperature, the more crystallisation will occur to the NR molecules which will prolong the effective storage life [73]. Hot-air aging and differential thermal analysis (DTA) methods were used to predict and evaluate the effective storage life of raw NR in comparison to the control samples of required storage life.

2.9.4.2 Principle method

The heat aging life equation [73] is similar to the Arrhenius Equation a relationship for the variation in reaction rate in a thermally activated molecular process to temperature can be represented in Equation (2.25). The heat aging life equation of the high molecular weight materials is usually as follows:

$$\log \tau = a + \frac{b}{T} \quad (2.26)$$

Where: a – constant, the intercept of aging life line

b – constant, the slope of aging life line, $b = \frac{E}{2.303R}$,

E – activation energy of oxidation

R – gas constant ($R = 8.314$)

T – ambient temperature, K

τ – time needed when the properties of high molecular weight materials reaching at the out-of-service index, d .

At ambient temperatures T_1 and T_2 , Equation (2.26) can be written as follows:

$$\log \tau_1 = a + \frac{b}{T_1} \quad (2.27)$$

$$\log \tau_2 = a + \frac{b}{T_2} \quad (2.28)$$

Subtracting (2.28) – (2.27),

$$\log \tau_2 - \log \tau_1 = \frac{b}{T_2} - \frac{b}{T_1} \quad (2.29)$$

Rearranging gives,

$$\log \tau_2 = \log \tau_1 + \frac{E}{2.303R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (2.30)$$

By solving for τ_2 the aging life of the material at temperature T_2 can be calculated.

2.9.4.3 Hot-air aging test of NR

The ISO standard for heat aging testing of raw NR is outlined in ISO 2930:1995 Rubber, raw material – Determination of plasticity retention index (PRI). The PRI is determined using a ratio between rapid plasticity before and after heating 30 minutes at 140°C. This is expressed in the following equation:

$$PRI = \frac{P_{30\min}}{P_0} \times 100 \quad (2.31)$$

Where: PRI – plasticity retention index
 $P_{30\min}$ – rapid plasticity after 30 mins of heating
 P_0 – rapid plasticity before heating

Zhang et al. [73] made alterations to this equation to meet their testing needs as the heating temperature at 140°C was too high causing a violent aging reaction. Therefore the test was carried out at 70°C with a longer testing time and the sample taken out at certain intervals with its plasticity determined. Hence, Equation (2.31) becomes:

$$PRI' = \frac{P_i}{P_0} \times 100 \quad (2.32)$$

Where: i – is number of days

The acceptable PRI value according to the International Standard ISO 2000:1989 for Standard Rubber 50 is 30 ($PRI \geq 30$). When the PRI for the rubber is less than this number, the NR is then rendered out-of-service. The results from the testing and the relative PRI' value can be seen in Tables 2.9 and 2.10.

Table 2.8 Test results of heat aging of NR [73] pg 4115

Code	Item	Aging time at 70°C (days)					Regression equation	Correlation coefficient	τ -value PRI' = 30 (days)
		0	5	10	15	16			
A-1-1	P_i	44.0	39.5	38.0	37.0	34.5	$PRI' = 79.96 - 0.807 \tau$	0.9560	62.0
	PRI'	100	89.8	86.4	84.1	78.4			
A-1-2	P_i	43.5	38.0	34.0	31.5	30.5	$PRI' = 53.76 - 0.546 \tau$	0.9896	43.5
	PRI'	100	87.4	78.2	72.4	70.1			

A-1-1, acetic acid coagulation; A-1-2, natural coagulation of 7 days.

Table 2.9 Test results of heat aging of NR [73] pg 4116

Code	Item	Aging time at 70°C (days)						Regression equation	Correlation coefficient	τ -value PRI' = 30 (days)
		0	4	8	12	16	20			
A-2	P_i	26.0	36.5	33.0	30.0	27.5	23.0	$PRI' = 105.0 - 1.885 \tau$	0.9718	39.8
	PRI'	100	101.4	91.7	83.3	76.4	63.9			
B	P_i	54.0	51.0	43.0	33.5	28.0	21.5	$PRI' = 103.2 - 3.186 \tau$	0.9933	23.0
	PRI'	100	94.4	79.6	62.0	51.9	39.8			
C	P_i	56.0	53.5	51.0	47.5	45.5	41.0	$PRI' = 100.7 - 1.309 \tau$	0.9947	54.0
	PRI'	100	95.5	91.1	84.8	81.2	73.2			

A-2 and C, acetic acid coagulation; B, biological coagulation.

2.9.4.4 Determination of oxidation temperature of NR

Oxidation data of natural rubber at room temperature is difficult to obtain as NR will oxidise very slowly [73]. Zhang et al. discussing the determination of the oxidative exothermal peak of NR by using a TG-DTA thermoanalyser. It can be seen in Figure 2.86

that by accelerating the oxidation process due to temperature increase will reflect on the TG and DTA curves. The first exothermal peak of NR sample under air atmospheric conditions appears on the DTA curve at 185-205°C, however this peak does not appear on the curve under a nitrogen atmosphere. The TG curve is also unchanged, in the form of a straight line indicating the heat generation of NR within the scope of this temperature is an oxidative heat generation process.

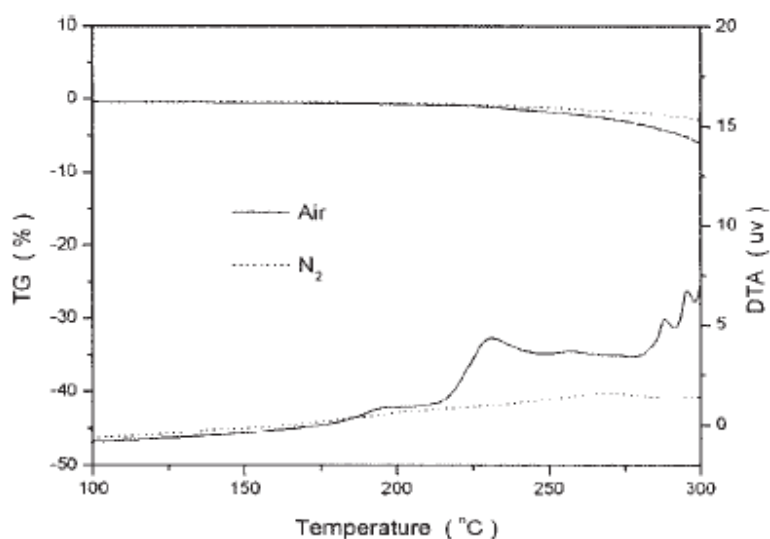


Figure 2.86 TG–DTA curves of acetic acid-coagulated rubber sample under air and nitrogen atmosphere with a heating rate of 6°C/min. [73] pg 4116

2.9.5 The Effects of Thermal Aging on Fracture Performance of Polychloroprene

2.9.5.1 Introduction

The tensile and tearing resistance of polychloroprene have been measured as a function of aging time and temperature [29, 75, 76]. A steady increase in stiffness was observed in this study, which indicates crosslinking is the dominant reaction that occurs during the aging of CR. During the early stage of aging, the tensile strength and tearing energy increases due to

the optimised balance between the strength enhancement from the crosslink network and the network capability in dissipating energy [77]. However, extending this aging time results in a gradual decrease in strength and tearing energy. Ha Anh and Vu-Khanh [29] used the superposition principle between aging time and aging temperature to determine the activation energy controlling the change of tearing energy in thermal aging. This activation energy was found to be the controlling factor in the variation of not only the tearing energy but also the strain energy density to break. Oxidation is once again a contributing factor to the aging and degradation of rubber as mentioned by a number of authors [29, 52, 72, 73], where the change in tearing energy is controlled by chemical reactions in relation to the amount of oxygen consumption dissolved in the material.

This study by Ha Anh and Vu-Khanh aims to reveal the understanding of the variations in tearing behaviours of polychloroprene rubber (CR) caused by thermoxidative aging. The major limitations in using CR is its poor aging resistance, although it does demonstrate reasonably good oxidative aging resistance at temperatures of up to 80°C, however at temperatures of 100°C and above, degradation becomes more apparent leading to brittle fracture.

2.9.5.2 Effects of aging on tear behaviour

The effects of aging on tear behaviour in relation to various temperatures from 100 to 160°C can be seen in Figure 2.87 [29]. It was observed for temperatures below 150°C, the tearing energy first increases to a maximum value at a given time before decreasing with aging time. There is also a general trend where at higher aging temperatures results in a drop in tearing energy. Previous studies have suggested, the fracture energy is the sum of the threshold energy expended in the rupture of the chemical bonds and a dissipation term which is many times larger [29]. Crosslinking is a major contributor to the tearing behaviour of rubber. At high aging temperatures, the amount of crosslinking increases restricting the mobility of the polymer chains resulting in a network incapable of

dissipating much energy. This behaviour leads to the elastomer failing in a relatively brittle manner with low elongation and tearing energy.

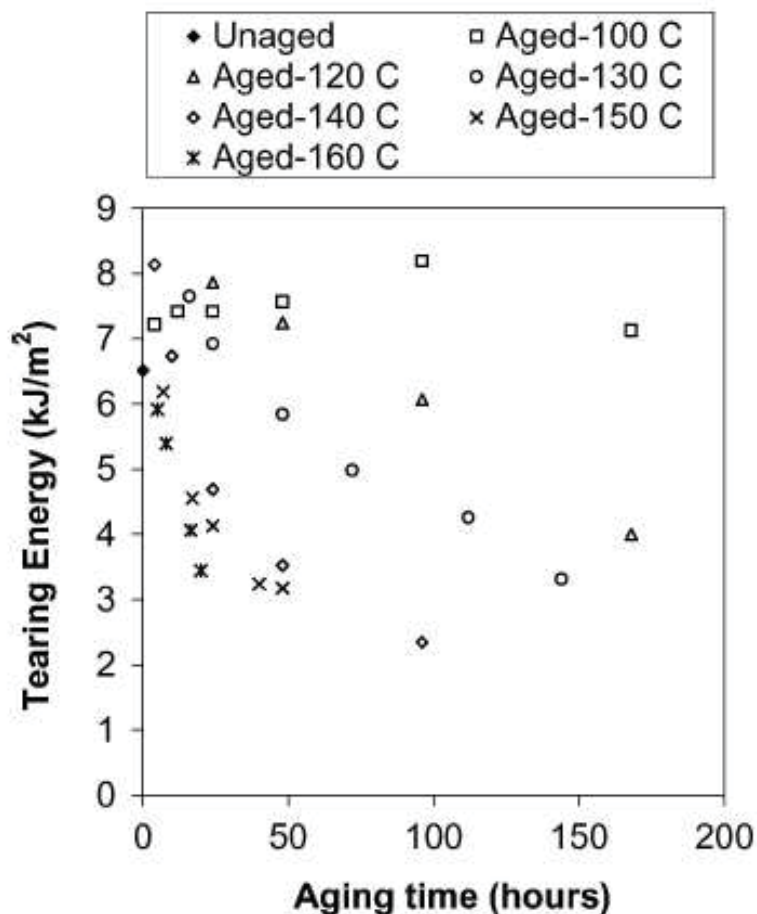


Figure 2.87 Variation of tearing energy of CR with aging time at various aging temperatures. [29] pg 5244

Oxidation as mentioned earlier in this literature review is a degradation process that involves a number of complex chemical reactions that yield an effective reaction rate constant with an effective activation energy. Figure 2.88 shows the variation of tearing energy of CR with the logarithm of aging time at various aging temperatures. Ha Anh and Vu-Khanh [29] have suggested that the effective activation energy may remain unchanged throughout the experimental temperature range. In accordance to the Arrhenius, Equation (2.25), the temperature dependence of the rate of a chemical reaction is proportional

to $\exp(-E_a/RT)$. As suggested, the effective activation energy is constant within the temperature range; therefore the rate will only be increased by the Arrhenius factor. From this, the time to reach a certain amount of damage, t_c , is given by,

$$t_c = \text{const.} e^{\frac{E_a}{RT}} \quad (2.33)$$

Taking the logarithmic of both sides gives,

$$\log(t_c) = \frac{E_a}{RT} \log(e) + \text{const.} \quad (2.34)$$

Where: t_c – life time of the material according to given criterion

By choosing 60, 70 and 80% of the original value of tearing energy of unaged CR samples as failure criteria, the corresponding life time to reach these limits are presented in Table 2.10. Using these results, Anh and Vu-Khanh [29] used Arrhenius plots of the logarithm of the aging time to reach 60, 70 and 80% of the initial value of tearing energy of unaged CR samples versus $1000/T$. Figure 2.89 clearly shows relatively linear and parallel plots suggesting the change in tearing energy during aging is controlled by an Arrhenius behaviour, which has a constant activation energy in the range of experimental tests. By calculating the average slope of these straight lines, a global activation energy of 93.9 kJ/mol can be obtained using Equation (2.34). In other studies covered by the authors in this paper, in particular Wise et al. [73], it was found that the degradation of the CR more of an oxidation cause rather than a dehydrochlorination reaction. Activation energies of 91 ± 8 kJ/mol were obtained by measuring the dependence of O_2 consumption rate, CO_2 formation rate and CO formation rate on the degree of thermal degradation. A direct correlation can therefore be made with the change in tearing energy controlled by chemical reactions with the change in oxygen consumption or carbonyl formation in the material and can be predicted with aging time and aging temperature.

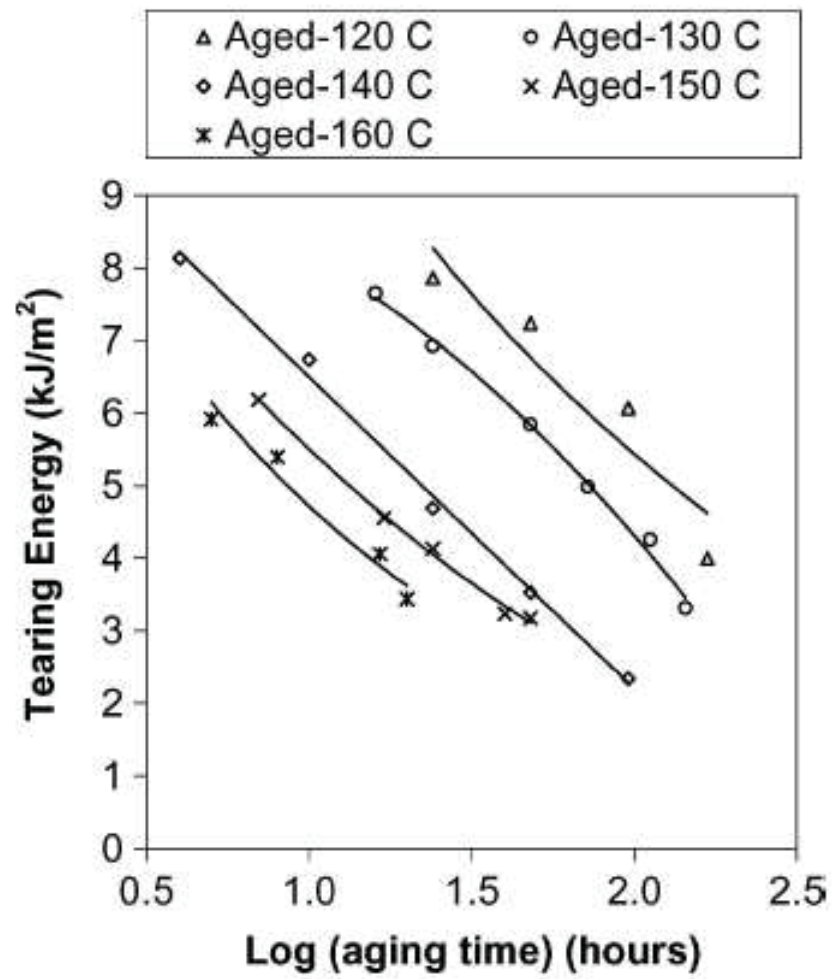


Figure 2.88 Variation of tearing energy of CR with logarithm of aging time at various aging temperatures.
[29] pg 5245

Table 2.10 Aging times necessary for the aged CR samples to reach the 60%, 70% and 80% of the original value of tearing energy of unaged CR. [29] pg 5245

Aging temperature ($^{\circ}\text{C}$)	$1000/T$ (K^{-1})	$t_{60\%}$ (h)	$t_{70\%}$ (h)	$t_{80\%}$ (h)
120	2.54		148	126
130	2.48	124	95	66
140	2.42	40	27	20
150	2.36	28	17	13
160	2.31	17	13	9

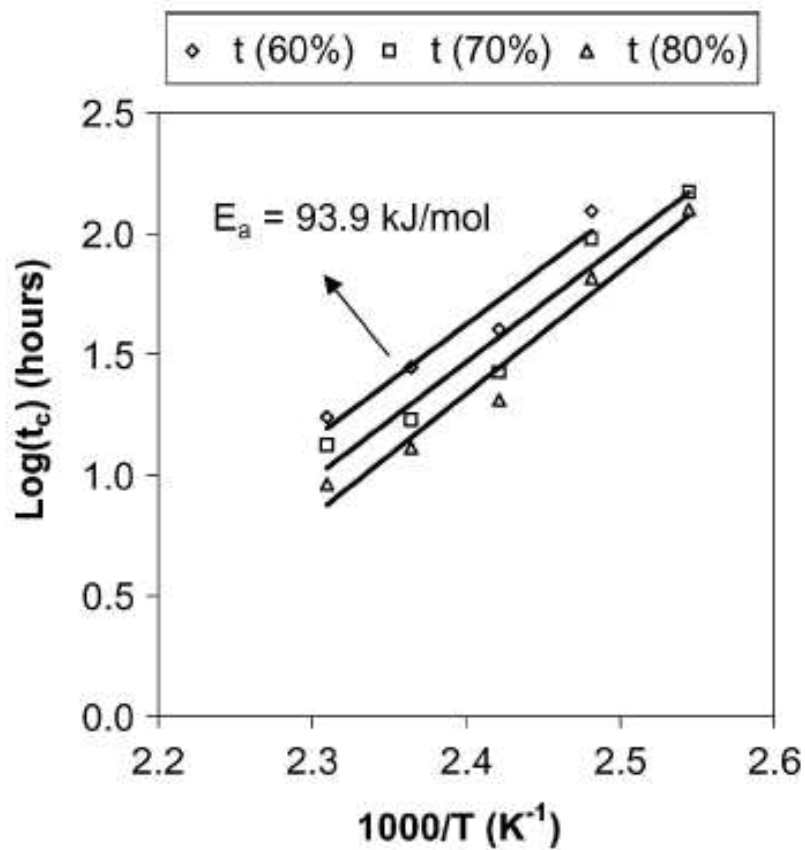


Figure 2.89 Arrhenius plots of the logarithm of the aging time to reach 60, 70 and 80% of the initial value of tearing energy of unaged CR samples. [29] pg 5245

2.9.5.3 Effects of aging on tensile behaviour

The aging effects on the tensile behaviour of CR at different temperatures are similar to the aging effects on the tearing behaviour [29]. Figure 2.90 illustrates the stress-strain curves for CR after aging at 120°C for various times resulting in an increase in modulus. This indicates that crosslinking is the dominant factor during thermal aging. However, this is not the case for tensile strength, where initially increasing to a maximum after 1 day of aging then decreasing. This result was also found for CR thermally aged at different temperatures, as shown in Figure 2.91. In the early stage of aging, both the tensile strength and tearing energy increase rapidly to a maximum value. An assumption made by Anh and Vu-Khanh [29] as to why this occurs is basically an optimisation balance between the strength enhancement from additional crosslinked networks and the network capability of dissipating strain energy. Figure 2.92 shows the Arrhenius plot of the logarithm of the time t_a against the reciprocal of temperature. Where t_a can be defined as the time an elastomer takes to reach its maximum mechanical value that decreases with increasing aging temperature. The activation energy calculated from the slope of this graph is about 95.2 kJ/mol, which is exceptionally similar to the activation energy for the aging time-aging temperature superposition of tearing energy as calculated above. It can then be concluded that the increase in fracture energy of CR would also be controlled by the same chemical reactions of oxidation and changes in oxygen consumption dissolved in the material as the tearing energy discussed earlier.

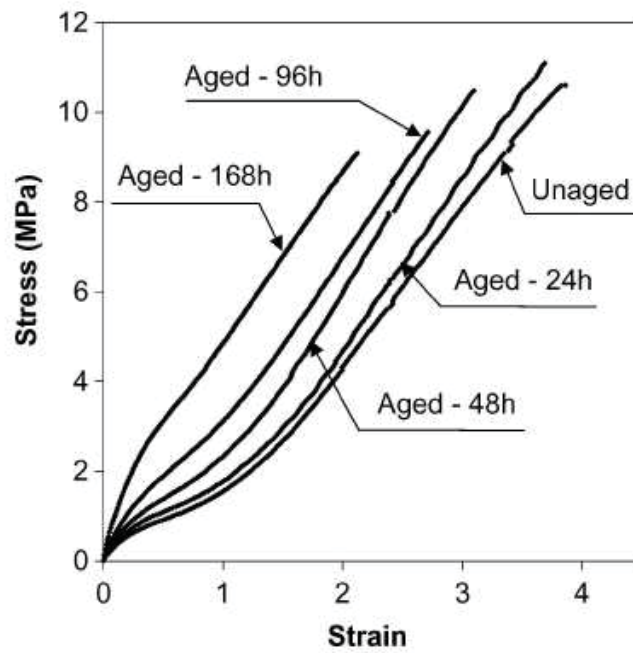


Figure 2.90 Stress-strain curves of CR after various times of aging at 120°C. [29] pg 5246

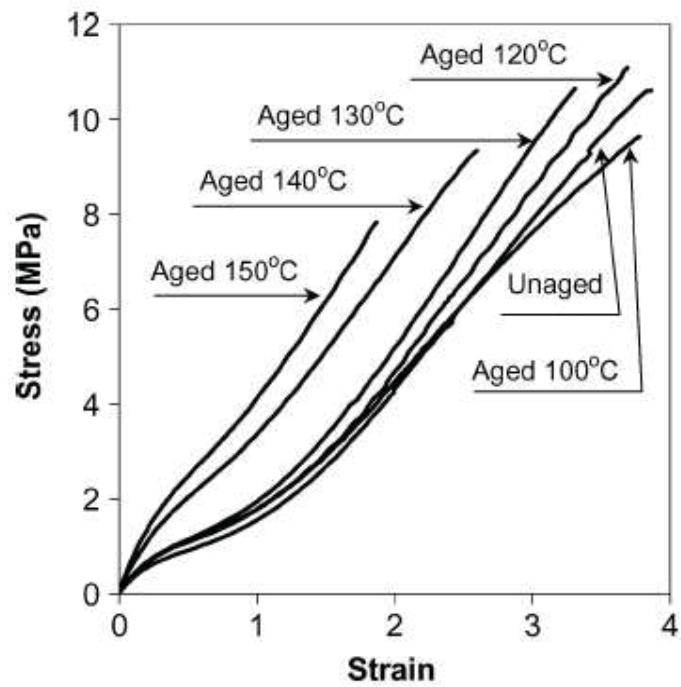


Figure 2.91 Stress-strain curves of CR after aging for 24 h at various temperatures. [29] pg 5246

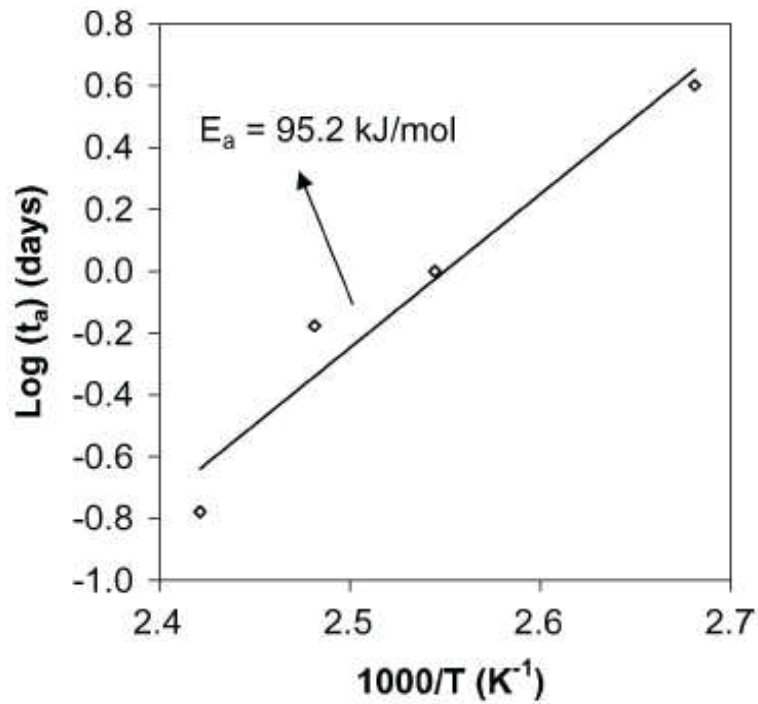


Figure 2.92 Arrhenius plot of the logarithm of the time t_a against reciprocal temperature. [29] pg 5246

The concept of strain energy was also discussed in this paper, where calculations are made in relation to visco-elastic work at the crack tip. Figure 2.93 shows the variation of the strain energy density at fracture of CR as a function of the logarithm of aging time at various aging temperatures. There is once again a similarity with this observation with the tearing energy observations (Figure 2.89). And by using the method of superposition between aging time-aging temperatures, Figure 2.95 represents a similar illustration than both tearing and tensile activation energies. Taking the slope of Figure 2.94, the activation energy $E_a = 92.5$ kJ/mol, is nearly the same as that obtained from tearing tests indicating a strong relationship between the 3 physical properties of the CR.

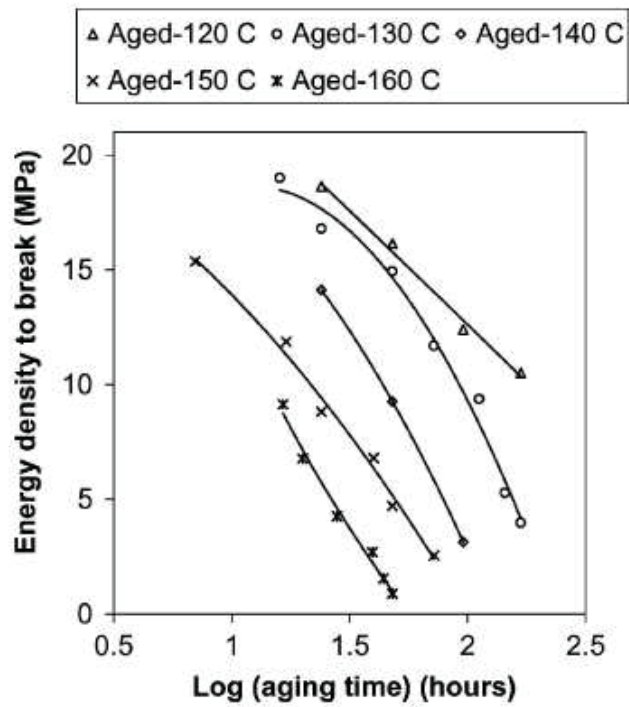


Figure 2.93 Variation of energy density to break (obtained from tensile tests) of CR with logarithm of aging time at various aging temperatures. [29] pg 5247

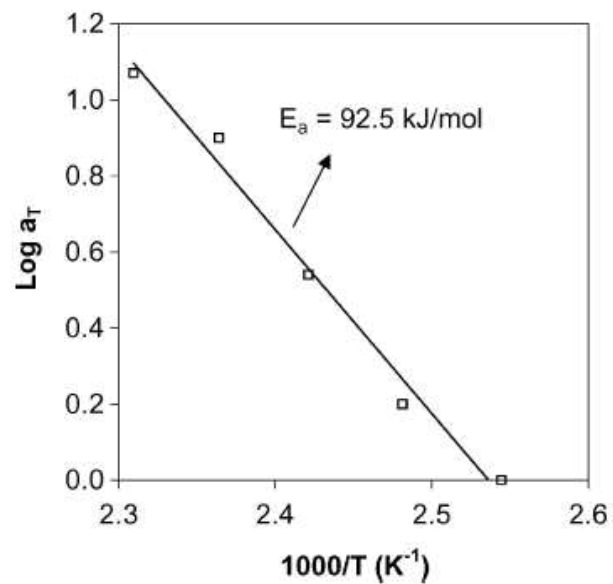


Figure 2.94 Arrhenius plot of horizontal shift factors a_T used to superpose tensile fracture energy data at a reference temperature of 120°C. [29] pg 5247

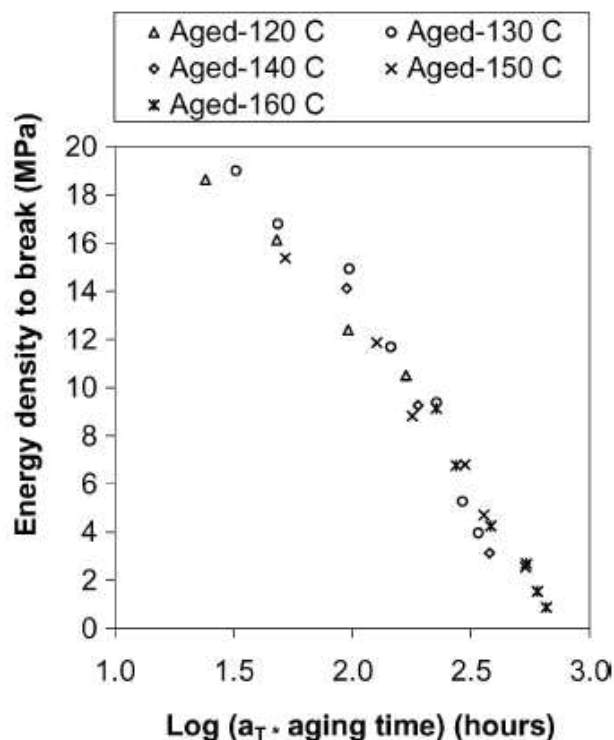


Figure 2.95 Empirical aging time/aging temperature superposition of the tensile fracture energy data at a reference temperature of 120°C using $E_a = 92.5$ kJ/mol. [29] pg 5247

2.10 Raman and Fourier Transfer Infra-red Spectroscopy of Rubber

2.10.1 Introduction

The spectrographic analysis involving the technique of Raman and Fourier transfer infra red (FT-IR) spectroscopy has been made available for over the past half century [14, 80]. It is a useful non-destructive test; however the analysis of rubber has been made difficult due to the problems of fluorescence. With the introduction of the Fourier Transform Raman Spectrometer, many barriers to the application of this technique are solved within a laboratory environment [81]. Infrared spectroscopy is also readily available in the analysis of polymers. This method involves examining the vibrational behaviour of the total molecular structure to indicate the nature and molecular structure of the base polymer,

crosslinking, accelerators, antidegradents, decomposition products from these accelerators and antidegradents, and finally the fillers. However, the use of IR is particularly sensitive to polar bonds (e.g. carbonyl bonds) and only responds to the vibrations that involve dipolar movement. For materials that involve changes in polarisability, the Raman spectroscopy is better suited. A comprehensive scan is required for the analysis of rubber which requires a “complete” vibrational spectrum using both the Raman and IR spectroscopy. Therefore, the FT-Raman is very useful in the study of the structure and vulcanisation of natural rubber (NR) as it incorporates both the Fourier Transform IR as well as the Raman spectroscopy.

Extensive studies have been investigated by a number of researchers in particular Koenig et al. [83]. The structure of NR and synthetic polyisoprenes has been examined with the FT-Raman, in particular the basis for the positions of chemical bonds of interest. The position of the $\nu_{C=C}$ vibration is situated in the 1665 cm^{-1} region, as a result the amount of *cis*- and *trans*- 1,4-isoprene units as well as vinyl units can be determined. The use of near-IR (1064nm or 1337nm) excitation is essential for many NR materials. Without the use of near-IR excitation, the background will greatly be affected by the luminescence deeming the Raman technique useless.

FT-IR spectroscopy is an intriguing area of focus in relation to rubber pump liner wear mechanisms. Wear of rubber is still somewhat a new area of research as to what is occurring to the material e.g. a physical process of the abrasive material attacking the surface of the polymer, a chemical process of the rubber molecules being excited by the thermal energy of the erosive material, or is the process of wear a mechanical phenomenon that can be simply improved by reinforcing the material or engineering design of the process. The FT-IR spectrometer will provide the evidence as to what is occurring to the chemical bonds when the rubber is worn. In particular the carbon-carbon double bond with the wave-number of 1666cm^{-1} which shows up clearly on the typical FT-IR spectra.

2.10.2 Study of Non-catalytic Hydrogenation of Unsaturated Rubbers

Hydrogenation is an important method for improving and modifying the properties of unsaturated elastomers [15]. Samran et al. investigated the effects of hydrogenation on natural rubber and epoxidised rubber. Hydrogenation can be applied to the polymers using two methods, catalytic and non-catalytic. For catalytic hydrogenation, high pressure hydrogen and a suitable metal catalyst such as Ni or Rh are needed for the reaction to occur, whereas in non-catalytic hydrogenation, an organic molecule which can generate a diimide intermediate is introduced. This diimide molecule can then provide a hydrogen molecule to the carbon-carbon double bonds without the use of a catalyst. In relation to the rubber pump liner wear, hydrogenation is not applied to the rubber compounds used in this study. However the spectroscopy test data from Samran et al. can be used to identify characteristic chemical bonds in the rubber pump liner rubbers of interest.

2.10.2.1 Fourier Transfer Raman analysis

Natural rubber consists of a high *cis*-1,4-polyisoprene structure shown in Figure 2.96. The term “saturation” is often referred by chemists describing the macromolecular structure of the polymer. A polymer is deemed “saturated” when it does not contain any double bonds in its structure for example polyethylene, polypropylene, polystyrene, etc. A polymer that is “unsaturated” applies to those that have double bonds in its macromolecular structure such as polyisoprene (NR) [84]. Samran et al. used Raman and FT-IR spectroscopy to analyse the carbon-carbon double bond with success. Figure 2.97 shows a FT-IR spectra of NR and hydrogenated NR. It can be seen that there are two characteristic peaks, one at 1665 cm^{-1} and the other at 836 cm^{-1} [15, 81]. The first peak refers to the $\nu_{\text{C}=\text{C}}$ vibration and the second peak refers to the $\delta(\text{CH}_3)$. During hydrogenation, the first peak will decrease as the carbon-carbon double bond is being broken and hydrogen is substituted into the molecular structure. This is clearly shown in Figure 2.97 as the diimide reacts with the carbon double bonds of the polyisoprene units. The plan of this thesis is to determine if the wear of rubber

pump lining materials is a result of carbon-carbon double bond breakage. Using the FT-IR will give a good indication of whether or not this statement is true.

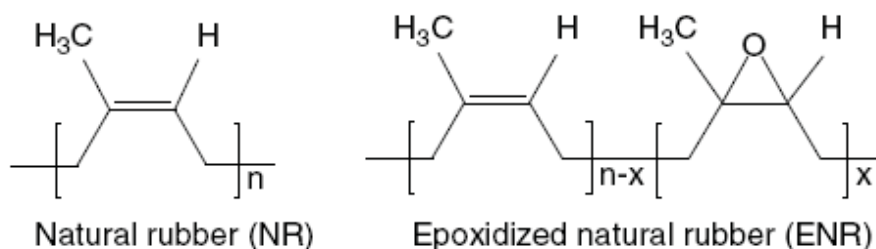


Figure 2.96 Structures of natural rubber and epoxidised natural rubber. [15] pg 1074

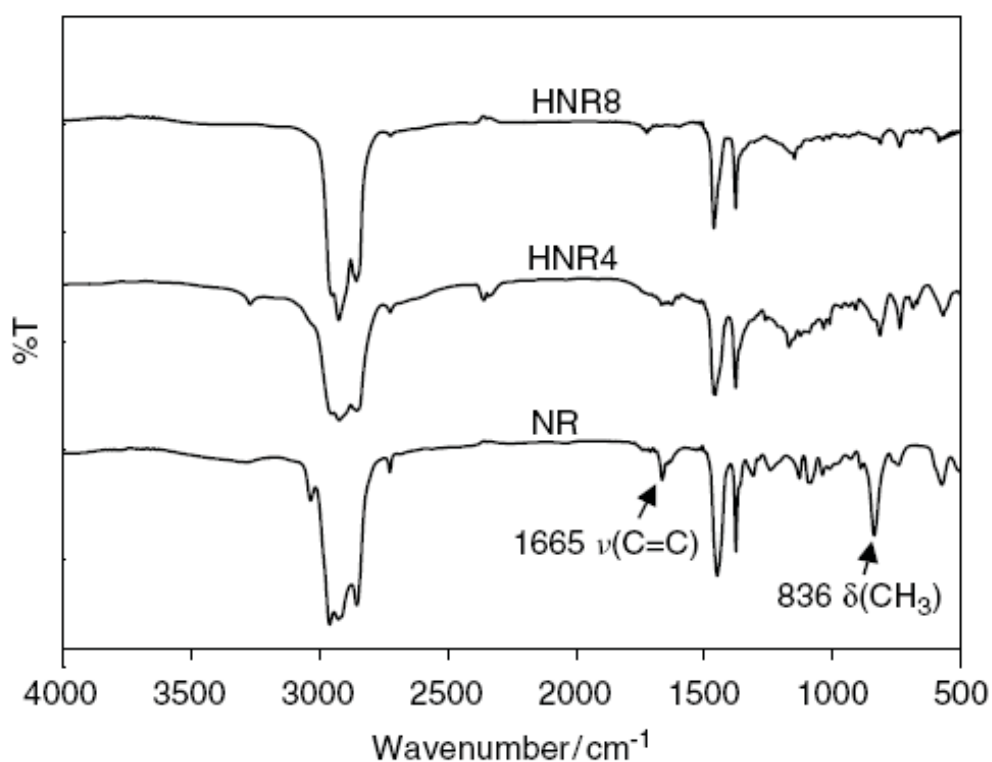


Figure 2.97 FT-IR spectra of NR and hydrogenated NR after reaction times of 4 h (HNR4) and 8 h (HNR8). [15] pg 1075

The theory behind Raman spectroscopy refers to the structure of the natural rubber. It is well known that NR possesses a highly regular structure, entirely composed of linear sequences of *cis*-1,4-polyisoprene units [15, 29, 81, 85]. Since the *cis*-1,4-polyisoprene unit

possess a low symmetry point group, this point group was then used to analyse the number of vibration modes in NR. A typical Raman spectrum of NR is shown in Figure 2.98. The $\nu_{(C=C)}$ vibrational peak is distinctive in comparison to the FT-IR spectrum. Samran et al. [15] compared the Raman spectra of NR and hydrogenated NR samples taken at various times. It can be seen in Figure 2.99, that the intensity of the 1664 cm^{-1} $\nu_{(C=C)}$ vibrational peak decreases with increasing hydrogenation process. In previous studies, the literature and experimental, the wavelengths (cm^{-1}) and assignment bands observed in the Raman spectrum of natural rubber can be seen in Table 2.11. These values are of interest as they can be used to identify which bonds are present in the macromolecular structure of the rubber.

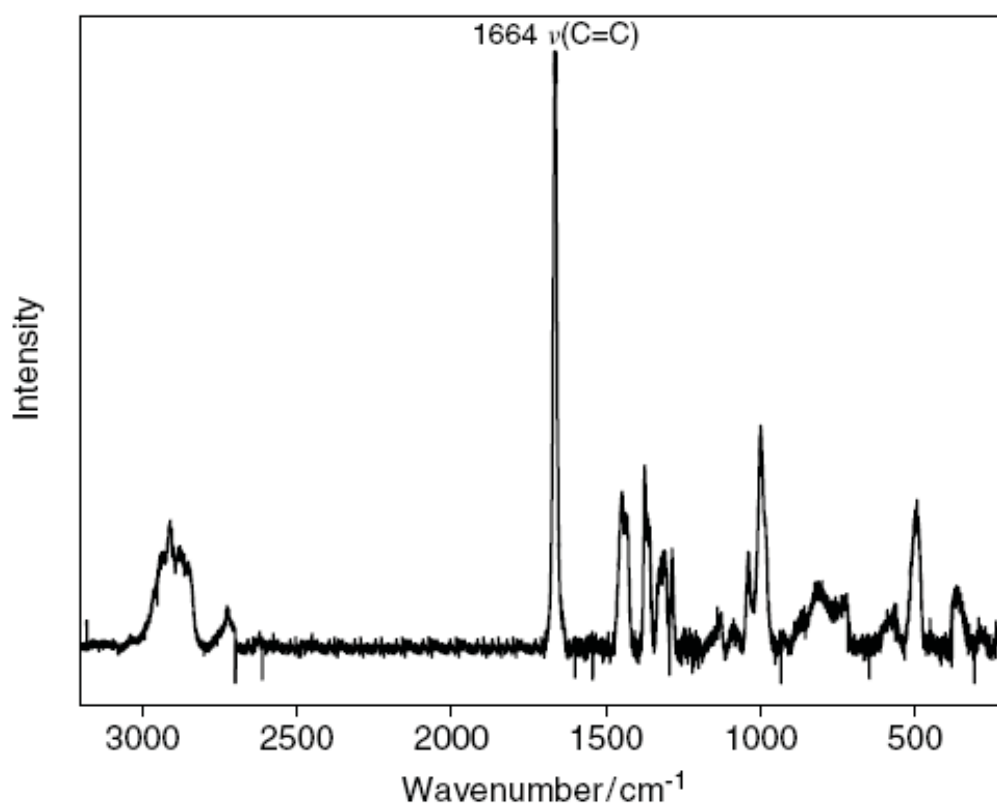


Figure 2.98 Typical Raman spectrum of NR. [15] pg 1076

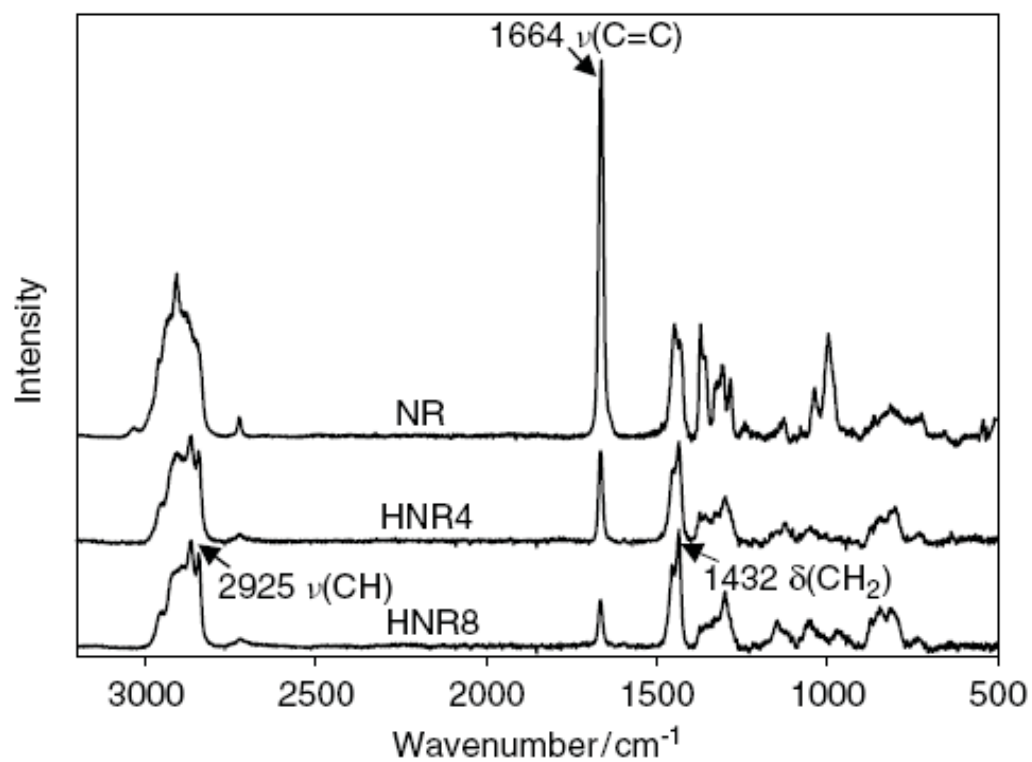


Figure 2.99 Comparison between the Raman spectra of NR and hydrogenated NR samples taken at 4 h (HNR4) and 8 h (HNR8). [15] pg 1078

Table 2.11 Wavenumbers (cm⁻¹) and assignment of bands observed in the Raman spectrum of natural rubber
[15] pg 1077

Literature ^{11-13,16,17}	Experimental ^a	Assignment
3032	3033 vw	=C-H stretching
2962	2965 m	CH ₃ asymmetric stretching
2931	2940 m	CH ₂ asymmetric stretching
2912	2911 s	CH ₃ symmetric stretching
2885	2881 m	— ^d
2854	2850 m	CH ₂ symmetric stretching
2727	2725 vw	— ^d
1666	1664 vs	C=C stretching
1452	1452 m	CH ₃ asymmetric stretching
1440	1432 m	CH ₂ deformation
1375	1371 m	— ^d
1363	1357 m	CH ₂ deformation
1325	1327 m	=C-H in-plane deformation
1311	1314 m	CH ₂ twisting
1287	1286 m	CH bending
1243	1243 w	CH ₂ twisting
1208	— ^c	=C-H in-plane bending
1143	1147 vw	C-H out-of-plane of <i>cis</i> -C(CH ₃)=CH wagging
1131	1130 w	CH ₂ wagging
1040	1039 m	CH ₃ rocking
1000	1000 m	C-CH ₂ stretching
— ^b	983 m	C-CH ₃ stretching
— ^b	840 w	=CH out-of-plane bending
820	815 m	CH wagging
— ^b	788	CH ₂ rocking
— ^b	759 m	CH ₂ rocking
724	729	— ^d
— ^b	596 w	C-C in plane bending
572	569	— ^d
492	491	=CC ₂ rocking and scissoring
428	— ^c	CC ₂ rocking
367	372 w	CC ₂ rocking
— ^b	223 vw	CH ₃ torsion

^a s, Strong; m, medium; w, weak; v, very.

^b Not mentioned in the literature.

^c Not detected in this experiment.

^d No assignment in the literature.

2.10.3 Distribution of Elastomers and Silica in Polymer Blends

2.10.3.1 Raman spectra

Zerda *et al.* investigated the distribution of silica filler and elastomer in binary and ternary polymer blends containing *cis*-1-4 polybutadiene (BR), brominated polyisobutylenecoparamethylstyrene (BIMS), natural rubber, and styrene-butadiene rubber (SBR) [82]. By using contour maps, the distribution of elastomer phases and silica within each phase was determined for polymer blends with different compositions. The polymer blends used are listed in Table 2.12 [82]. Unfortunately, due to the poor quality of the paper, the contour maps for the distribution of fillers could not be viewed.

Table 2.12 Composition of Polymer Blends in PHR [82] pg 771

Compound	50/50 BR/ BIMS	40/40/20 BR/ BIMS/NR	30/50/20 BR/ BIMS/NR	30/30/40 BR/ BIMS/NR	30/50/20 BR/ BIMS/SBR	30/30/40 BR/ BIMS/SBR
BR	50	40	50	30	50	30
BIMS	50	40	30	30	30	30
NR		20	20	40		
SBR					20	40
Silica	45	45	45	45	45	45
Silane coupler ^a	2.52	2.52	2.52	2.52	2.52	2.52
Processing aid	12	12	12	12	12	12
Zinc stearate	5	5	5	5	5	5
Trigonox 29 ^b	0.8	0.8	0.8	0.8	0.8	0.8
Accelerator ^c	0.8	0.8	0.8	0.8	0.8	0.8

^a Si69 = Triethoxypropylsilyltetrasulfane.

^b Peroxide = 1,1-di-(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane.

^c 1,3-dibutylthiourea.

The concentrations of elastomers obtained from the Raman that averaged over an area of 10 x 10 μm was observed to be nearly always equal to the theoretically mixed phr concentrations of the elastomers in the blend [82]. The amount of silica present in the polymer blends appeared to be uniformly dispersed in the BIMS enriched regions, with

maximum concentration at the interface with the BR phases. Silica was difficult to distinguish in the BR phases as the Raman peaks overlap with the silica peaks due to the NR. In general, all blends tend to have silica dispersed throughout the specimen, however large silica aggregates were present near the regions enriched in the BIM component [82]. This area of filler and elastomer distribution is essential in the minerals processing industry. The quality of the distribution will dictate the wear behaviour and life of the rubber product. By using the Raman spectroscopy and the research covered by *Zerda et al.* the quality of the rubber can be determined, and also the general trend for wear to occur at specific locations, for example in the enriched aggregated regions of filler.

2.10.4 Applications of Raman Spectroscopy

2.10.4.1 Raman spectra of natural rubber

Hendra and Jackson have extensively studied the Raman spectroscopy and its applications to the analysis of natural rubber [14]. Figure 2.100 shows the FT-Raman and IR spectra of natural rubber loaded with 25 phr SiO₂ (a) and a similar level of CaCO₃ (b). The bands of the filler are clear and sharp and the C=C once again is predominant at 1665 cm⁻¹. The comparison of the IR and Raman spectrums indicates the complementary nature of the two. Materials with strong IR absorptions will often result in weak Raman spectrums and vice versa, therefore by using a FT-Raman the benefits are high in chemical analysis of rubber.

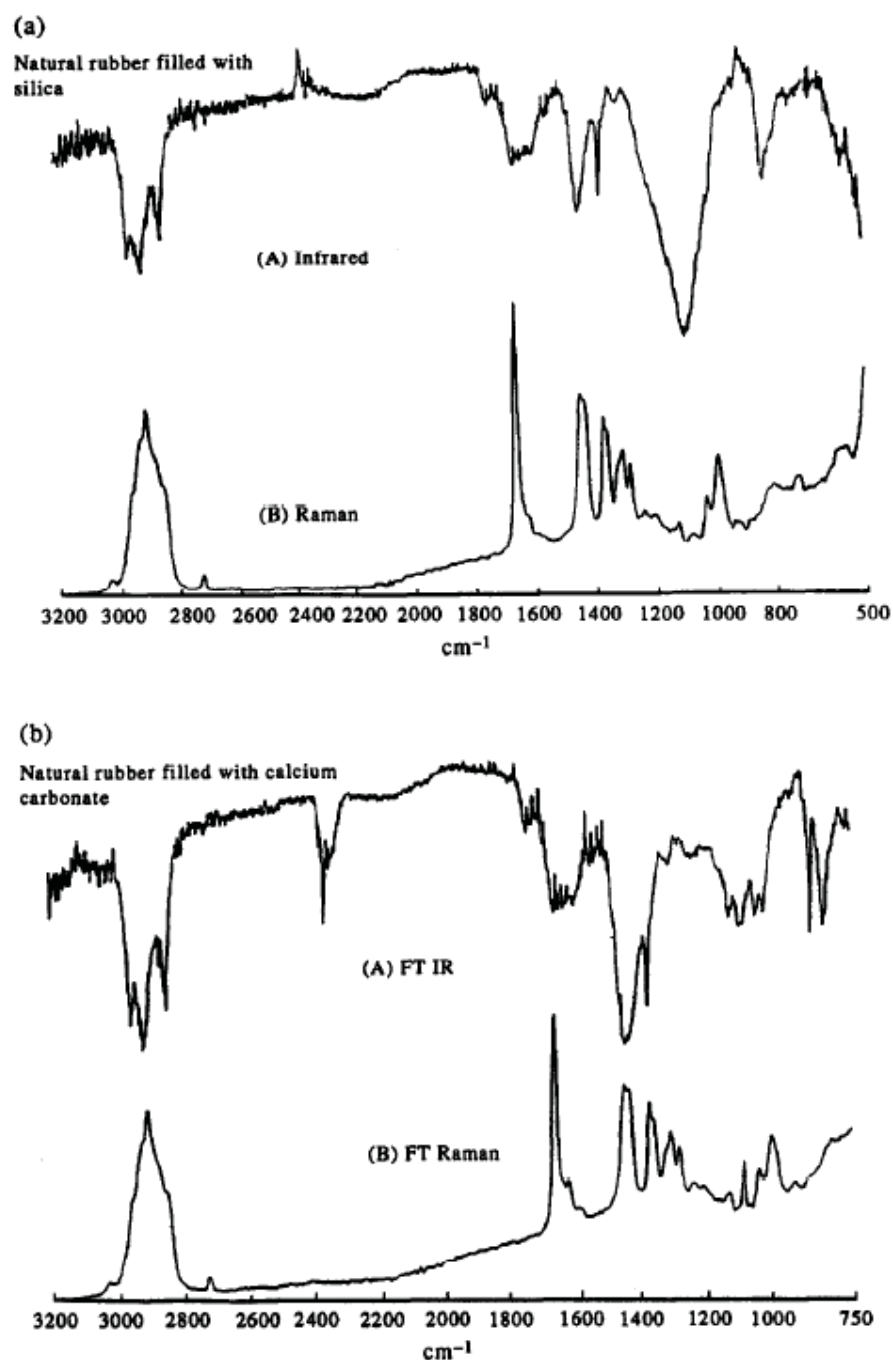


Figure 2.100 ATR FT-IR (A) and FT-Raman (B) spectra of a natural rubber vulcanizate filled with (a) silica (50% by weight) and (b) calcium carbonate (50% by weight). [14] pg 1989

The FT-Raman can also be used for the study of natural rubber crystallisation. Figure 2.101 shows the effects of -20°C storage temperature to raw Standard Malaysian Rubber, Latex

Grade (SMRL) after 3 weeks and 3 months in comparison to a control specimen. Hendra and Jackson also state that the changes induced by strain crystallisation may also be monitored using the FT-Raman [14]. Figure 2.102 shows a sample of SMRL cured with 1 phr dicumyl peroxide, unstretched and extended to 500%. It can be seen clearly the differences in the intensities of the Raman bands for these conditions. The current Raman evidence seems to suggest the morphology of the stress induced crystals, being different from that of the low-temperature-nucleated random crystals.

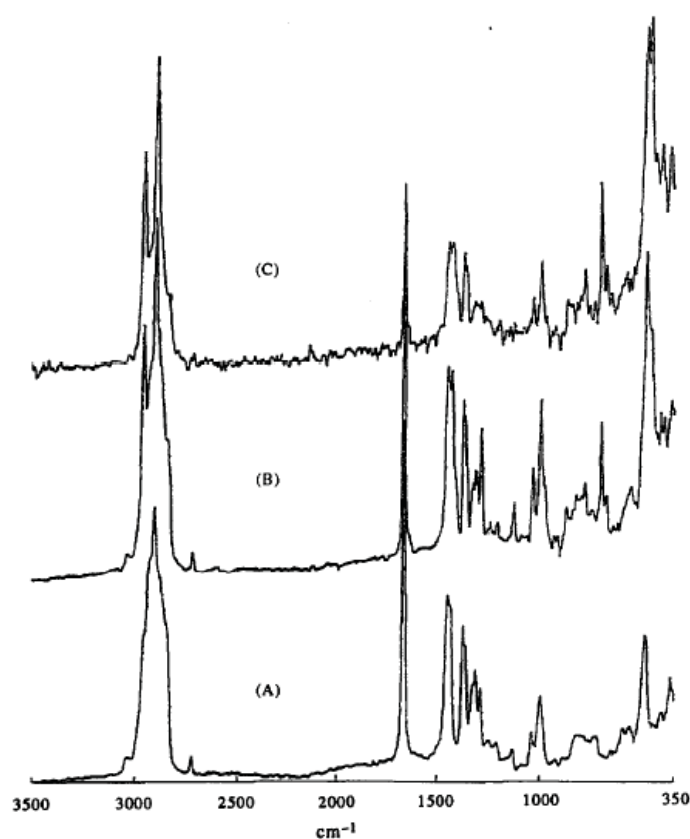


Figure 2.101 FT-Raman spectra of natural rubber as a function of cold soaking time: (A) control, (B) 3 weeks and (C) 3 months. [14] pg 1990

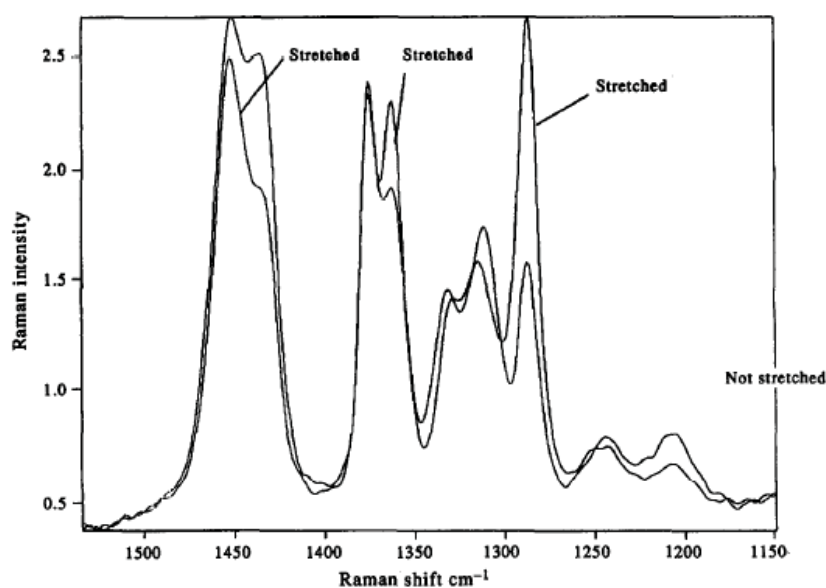


Figure 2.102 FT-Raman spectra of dicumyl peroxide cured natural rubber (stretched by 500% and unstretched). [14] pg 1991

2.10.4.2 Vulcanisation

During the vulcanisation of rubber, many chemical groups are generated during the process. The relative concentrations of these groups depend on the different factors such as relative ratios of sulphur to accelerator, the concentration of activators, and the curing time and temperature for vulcanisation [14, 86]. Hendra and Jackson classified the type of cure into three board groups depending on the sulphur-to-accelerator ratio. These groups are described as “conventional”, “semi-efficient” and “efficient” vulcanising systems. Figure 2.103 shows these groups in comparison to a raw NR spectrum. It can be seen clearly from these bands at 1632, 1609, 1591 and 1582 cm^{-1} that there are much more modifications to the conventional cure system (C) than the other systems.

The degree of crosslinking is attributed to the vulcanising effect and can be observed using the FT-Raman. Hendra and Jackson noticed a greater change in width of the $\nu_{(\text{C}=\text{C})}$ band than other bands in the spectrum with the addition of tetramethylthiuramdisulphide (TMTD). This suggests that crosslinks are produced generating a shift (about -6cm^{-1}) in the

$\nu_{(C=C)}$ band frequency in carbon-carbon double bonds. However, it is also suggested since the number of crosslinks compared with the total unsaturation level is low and consequently no new bands can be expected and broadening will be small and hard to quantify [14].

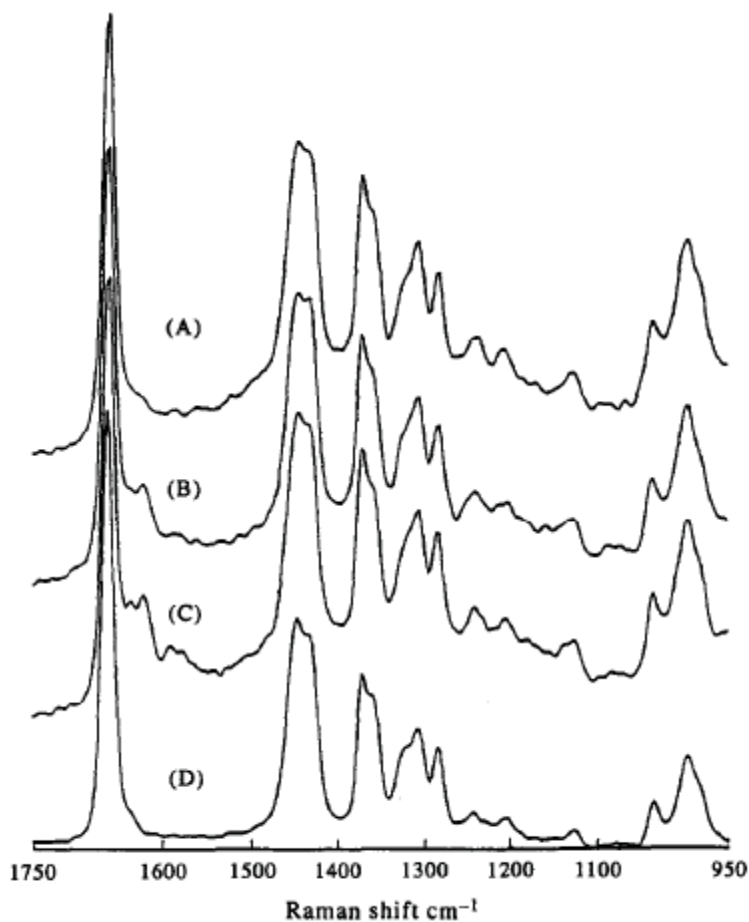


Figure 2.103 FT-Raman spectra of natural rubber vulcanized with an efficient cure system (A), a semiefficient cure system (B), a conventional cure system (C) and raw (D). [14] pg 1993

2.10.4.3 Limitations of the FT-Raman spectroscopy

The FT-Raman provides excellent results in the analysis of elastomers, polybutadienes, ethylene propylene rubbers and terpolymers, styrene butadiene copolymers and silicone

rubbers [14]. However, this is not for all cases as suggested by Hendra and Jackson as carbon black loaded rubber compositions are currently (1993) inaccessible to the Raman experiment as the source laser and Raman scattering are absorbed by the carbon black. This becomes a problem in our research in rubber pump liner wear, as the rubber materials used in this industry are lightly to highly carbon black filled.

2.10.5 Strain-induced and Cold Crystallisation of Natural Rubber

Healey et al. [74] discussed the effect of strain-induced crystallisation and cold crystallisation of natural rubber using FT-Raman spectroscopy. Two rubber samples, cured and uncured were used in the analysis and the room-temperature spectra in both case were recorded as identical. Table 2.13 shows the FT-Raman vibrational mode assignments for the spectrum of natural rubber and also the infra-red band intensity results.

Table 2.13 FT-IR. and FT-Raman vibrational mode assignments for the spectrum of natural rubber. For the infra-red results the band intensities are also shown. [74] pg 4011

Infra-red frequency ^a (cm ⁻¹)	Raman frequency (cm ⁻¹)	Assignment ^b
3292 broad w		
3114 sh. w		
3036 m	3038	$\nu(=\text{CH})$ in $(\text{C}(\text{CH}_3)=\text{CH})$
2996–2855 vs	2962	$\nu(\text{CH}_3)$
	2931	$\nu_1(\text{CH}_2)$
	2912	$\nu_3(\text{CH}_3)$
	2885	
	2854	$\nu_3(\text{CH}_2)$
2726 m	2727	
1663 m/s	1666	$\nu(\text{C}=\text{C})$
1637 sh. m		
1548 w		
1452 broad s	1452	$\nu_a(\text{CH}_3)$
1432 broad s	1440	$\delta_a(\text{CH}_3)$
1376 s	1375	
1362 sh. m	1363	$\delta(\text{CH}_2)$
1324 sh. w	1325	$\delta(=\text{CH})$ in-plane
1309 m	1311	CH_2 twist ^c
1287 w	1287	$\delta(\text{CH})$ bending ^c
1259 m		
1244 sh. m	1243	CH_2 twist
	1208	
	1143	
1128 m	1131	$\nu(\text{C}-\text{C})$ <i>cis</i> or CH_2 wag ^c
1091 broad m		
1038 m	1040	$\gamma_r(\text{CH}_3)$
1015 m		$\text{C}-\text{CH}_2$ stretch ^c
	1000	
985 sh. w		$\text{C}-\text{CH}_3$ stretch ^c
971 sh. w		
930 w		
889 m		CH_3 wag ^c
		CH of $\text{CH}_2=\text{C}(\text{CH}_3)^d$
837 s		CH_2-CH_2 stretch ^c
		$\text{C}-\text{H}$ out-of plane of
		<i>cis</i> - $\text{C}(\text{CH}_3)=\text{CH}^d$
	820	CH wag ^c
799 sh. m		
764 w		CH_2 rock ^c
		$\text{C}(\text{CH}_3)=\text{CH}^d$
741 w		CH_2 rock ^c
		$\text{C}(\text{CH}_3)=\text{CH}^d$
	724	
598 sh. w		
573 m	572	
506 broad m		
488 broad m	492	$\gamma_r(=\text{CC}_2)$, $\gamma_s(=\text{CC}_2)$
	428	$\gamma_r(\text{CC}_2)$
	367	$\gamma_s(-\text{CC}_2)$
	205	

^a Band intensities: vs = very strong, s = strong, m = medium, w = weak, vw = very weak and sh. = shoulder

^b According to Cornell and Koenig¹³ except where noted

^c Saunders and Smith¹¹

^d Binder¹²

The physical properties of an elastomer are dependant on the degree and nature of crosslinking. The surrounding physical environment is often the cause of decreases in these properties. The ability of natural rubber to crystallise under 2 different conditions was investigated, they are: cold crystallisation which involves soaking the rubber material for a period of time (between -40°C and 0°C optimised at -25°C), and stain-induced crystallisation which involves stretching the material. Crystallisation affects physical properties such as tensile tear strength, extension, and modulus.

2.10.5.1 Cold crystallisation

Cold crystallisation was carried out by Healey et al. using $+4$ and -25°C for a total duration of 2 months [74]. The samples at $+4^{\circ}\text{C}$ showed no difference in the FT-Raman spectrum, therefore the results were not included in the study. However, at -25°C a number of changes can be seen from the control sample. The differences can be viewed in Table 2.14 and Figure 2.104 shows the total difference between the 2 spectra (spectrum of untreated NR subtracted from the spectrum of treated NR). The difference in the spectrum is a result of crystallisation. It can be seen from this figure that large differences are observed in the region between 3200 and 2700 cm^{-1} , which can be related to the C-H stretching mode. However, the most significant change is the appearance of a new band at 2948 cm^{-1} . Band 3046 cm^{-1} masks the existing band of 3042 cm^{-1} and the bands at 2843 , 2873 , 2929 and 2969 cm^{-1} have increased in intensity. Unfortunately these observations could not be explained by the authors of this paper due to the complexity of this part of the spectrum, but it is said to be indicative of the alteration in the structure of NR on crystallisation.

Table 2.14 Frequencies of changes observed in the vibrational spectrum of natural rubber due to crystallization. [74] pg 4013

Cold crystallization	Strain-induced crystallization (laser and sample parallel)	Strain-induced crystallization (laser and sample perpendicular)
2969	2965	2965
2948		2945
2929	2930	2932
2904	2901	2906
2873	2873	2874
2843	2839	2841
1668	1671	1672
1453	1454	1454
1425	1429	1427
1377	1374	1374
1363	1360	
1333	1332	
1316		1317
1284	1286	1286
1130	1129	1128
1040	1042	1042
1007	1004	1004
981		981
876		876
848		849
833		
765		763
584		
568		
524		521
490	492	490
456		460
398		
365		

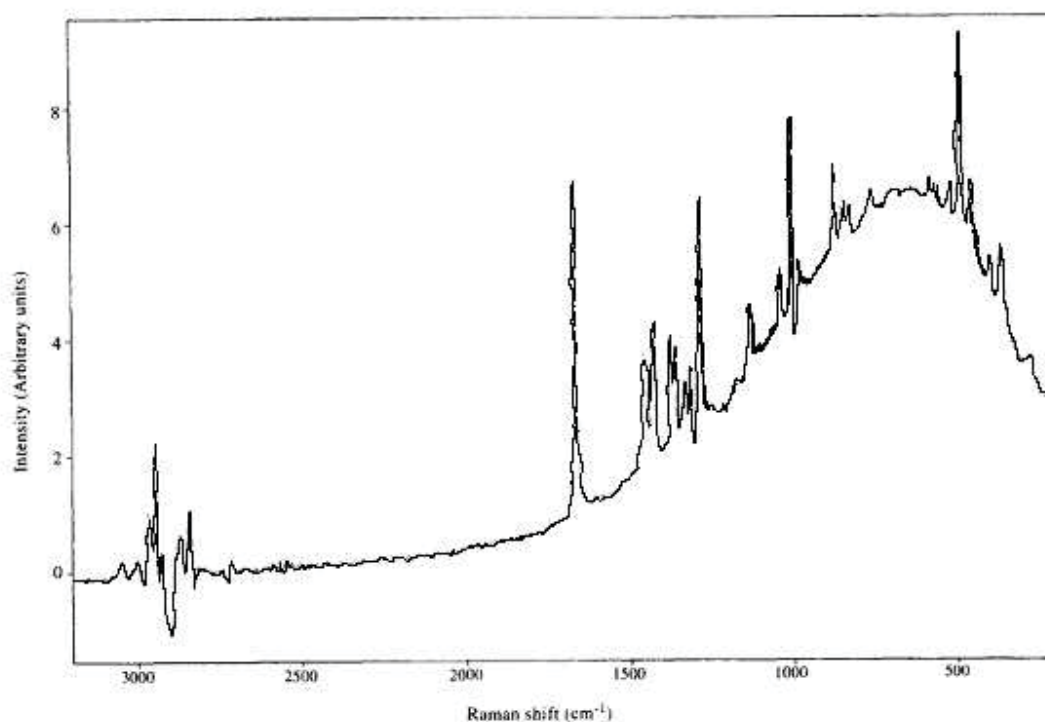


Figure 2.104 Difference spectrum (control spectrum subtracted from cold-soaked spectrum) showing the vibrational modes of natural rubber due to crystallization after cold soaking at -25°C for 2 months. [74] pg 4012

Figure 2.104 shows the characteristic peak of $\nu_{(\text{C}=\text{C})}$ band which undergoes a marked increase in intensity during cold crystallisation. In the region of 1500 to 1000cm^{-1} there are new fairly strong bands at 1316 , 1130 and 1007cm^{-1} . It was proposed that the band 1007cm^{-1} may be assigned as a C-C stretch previously unassigned [74]. The increase in band intensity for the band near 1284cm^{-1} has been assigned as C-H bending mode as has the band at 1040cm^{-1} been assigned as a CH_3 rocking motion. The extra resolution of features near 1440 , 1370 and 1320cm^{-1} are the result of cold soaking and are dependant on the crystallinity of the sample. Cold soaking also results in a number of new bands below 1000cm^{-1} distinctively at 876 and 456cm^{-1} . Finally, small weak peaks can be seen at 848 , 833 , 765 , 584 , 524 and 398cm^{-1} .

2.10.5.2 Strain-induced crystallisation

Three distinct regions exist in a strain-induced crystallised material: (1) distorted amorphous, (2) ordered amorphous and (3) ordered crystalline [74]. *Healey at al.* considered samples stretched to ~500% elongation and it was necessary to consider the strain-induced crystallisation as a function of direction of sample stretch with respect to the laser polarisation [74]. The spectrum taken were as follows: 1) unstretched and heated, 2) stretched and heated so any crystals left over will be melted, and 3) stretched and cooled to study crystallisation effects. It can be seen from table 13, the frequencies of changes observed in the vibration spectrum for cold crystallisation, strain-induced crystallisation (laser and sample parallel) and strain-induced crystallisation (laser and sample perpendicular) are evaluated.

2.10.5.3 Comparison of spectra from strain-Induced and thermal crystallisation in natural rubber

The general observation made by Healey at al. [74] on the spectral characteristics of crystalline NR for the stretched samples is much weaker than the cold soaked samples. The most significant result from this study was the observed band frequencies where they were identical for strain-induced and thermal crystallisation, except for the abnormality of the shifty C=C stretch band at $\sim 1665\text{ cm}^{-1}$ in the stretched cases. All possible spectral changes were able to be viewed in a single spectrum as there was no orientation of the crystallites in the thermal case. Whereas in the stain-induced stretching case, the stretching of the rubber forces the crystallites to have some order, causing the total spectrum to be partially resolved into perpendicular and parallel components. The general trend of the vibrations in both components followed the expectations in that the stretching vibrations were observed in the parallel spectrum and the wags and bends in the perpendicular spectrum. The frequency range for both the parallel spectrum and perpendicular spectrum can be considered as mid-frequency and low-frequency respectively.

When considering the individual bands, the spectral differences due to crystallisation can be considered as those which have changed existing bands and those where new bands are generated. It is important to note that the parallel spectrum shows only changes to the existing bands, and the perpendicular spectrum shows many of the changes to existing bands although at a lesser extent as well as the new bands.

Stable lamellar type crystals are slowly formed as a result of cold soaking [74]. The stretching of natural rubber results in unstable crystallites which are thought to be bundle-like in nature. From this study, it is stated that the spectral changes due to crystallisation of natural rubber is of a similar magnitude whether formed by prolonged cooling or stretching to large extensions. However, in a case where a highly extended sample is analysed the spectral changes are significantly weaker than those resulting from a prolonged cooling, suggesting less crystallisation is present from stretching than from cold-soaking. A reason for this discrepancy in the general nature could possibly be partially explained by the anisotropic nature of the stretched sample or due to the differences in the Raman scattering cross-section between the 2 morphologies [74].

2.11 Fourier Transform Infrared (FTIR) Spectroscopy of Rubber

2.11.1 Introduction

Fourier transform infrared (FT-IR) spectroscopy has been used extensively to study and evaluate the molecular structure of rubber materials [87-90]. It is importantly used as a tool in raw material identification and evaluation of rubber. This method involves examining the vibrational behaviour of the total molecular structure to indicate the nature and molecular structure of the base polymer. A spectrum is produced where strong bond or characteristic vibrations result in large peaks illustrated by the spectrum. FT-IR can also be used to determine the amount of crosslinking, fillers, accelerators, antidegradents, decomposition products from these accelerators and antidegradents. However, the use of IR is particularly

sensitive to polar bonds (e.g. carbonyl bonds) and responds to the vibrations that involve dipolar movement. For materials that involve changes in polarisability, the Raman spectroscopy is better suited as discussed in Chapter 8.

The FT-IR involves the material specimen to be exposed to infrared radiation. The amount of infrared energy that may be absorbed is dependant on the material itself. Whatever that is not absorbed by the material will then be transmitted. This transmitted beam is then passed through a detector which will determine how the beam has changed. Molecules within the material are composed of atoms bonded together. These atoms are always moving or “vibrating” having an intensity of their own. As the infrared radiation is absorbed through these atoms, the intensities of the vibrations will increase. The chemical bonds within the molecules require a precise amount of energy for it to vibrate. However, the radiation is only absorbed by a molecule only if the frequency of the radiation provides energy in the precise amount required by one of the bonds in the molecule. Characteristic vibrations can occur depending on the number of ways the bonds can move (bend, stretch, twist, wag, etc). For example, the double bond between carbon and oxygen (C=O) absorbs energy near 1750 wavenumbers causing a characteristic stretching vibration. Characteristic vibrations in a molecule can also occur by functional groups such as carbon-hydrogen bonds in the CH₂ and CH₃ functional groups. These carbon-hydrogen bonds can also bend a number of different ways. A specific amount of energy is required for each bending motion to occur. Typical molecule absorbance radiation range for this to occur is between 1500 and 1350 wavenumbers. Strong vibrations tend to absorb more energy producing larger peaks in the spectrum. In contrast, where smaller peaks are a result of low energy absorbance which indicates the amount of transmittance is high.

FTIR spectroscopy is an interesting area of focus in relation to rubber pump liner wear mechanisms. Wear of rubber needs to be identified as to what is occurring to the material e.g. chemical processes of the rubber molecules being excited by the thermal energy of the erosive material. The FTIR spectrometer is another tool that will provide the evidence to what is occurring to the chemical bonds when the rubber is worn.

2.11.2 Analysis of Silica filled Natural Rubber

Silica is primarily used in rubber compounds as a reinforcing agent. This reinforcement promotes an increase in tear, flex, abrasion, heat resistance, high modulus and resilience [89]. However, due to silica's highly active surface, it can react with other chemical ingredients used in the rubber compound. For example, silica commonly reacts with the zinc activator, hindering the crosslinking process during vulcanisation. Strong filler-polymer bonds are also difficult to achieve for polar silica molecules and non polar hydrocarbon polymer molecules. Poor filler-polymer bonds results in poor dispersion of and filler agglomeration leading to a decrease in physical properties. Figure 2.105 illustrates the silica filler particles to aggregates to agglomerates matrix. Therefore it is essential to use coupling agents and other additives to control these effects.

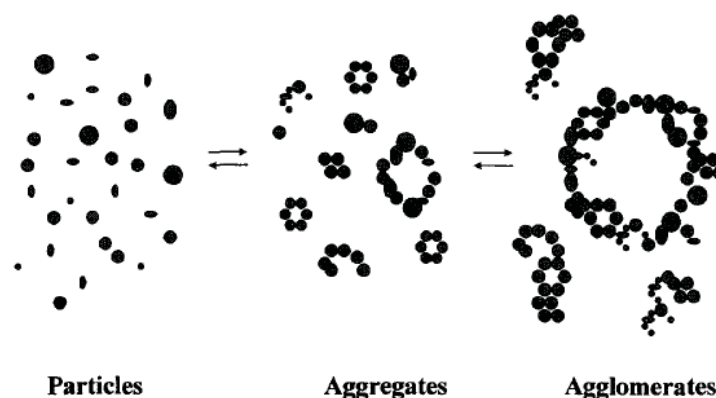


Figure 2.105 Silica filler particle to aggregate to agglomerates matrix [89] pg 308

FTIR spectroscopic analysis of silica filled natural rubber have been reviewed by Kravlevich and Koenig [89]. Interactions of silica filler in zinc activated, sulphur vulcanised *cis*-1,4-polyisoprene (IR) were investigated and characterised. FTIR was used with an Attenuated Total Reflectance (ATR) spectrometer. The aim of this study was to determine the quality of mixing by monitoring the levels of silica present in each batch mix. The silica absorbance region was observed to be in between the wavenumbers of $1000 - 1250 \text{ cm}^{-1}$ [89]. It was also stated that wavenumbers near 1040 and 1017 cm^{-1} are caused by physical

interactions between the silica and the natural rubber. Figure 2.106 shows the effects of increased silica on the asymmetric Si-O-Si stretch in the silica region. It can be seen that clearly that the Si-O-Si band widens as the silica content in the rubber increases. Kraleovich and Koenig [89] suggest the cause of this band widening is the result of surface interactions where species are present on the surface of the silica.

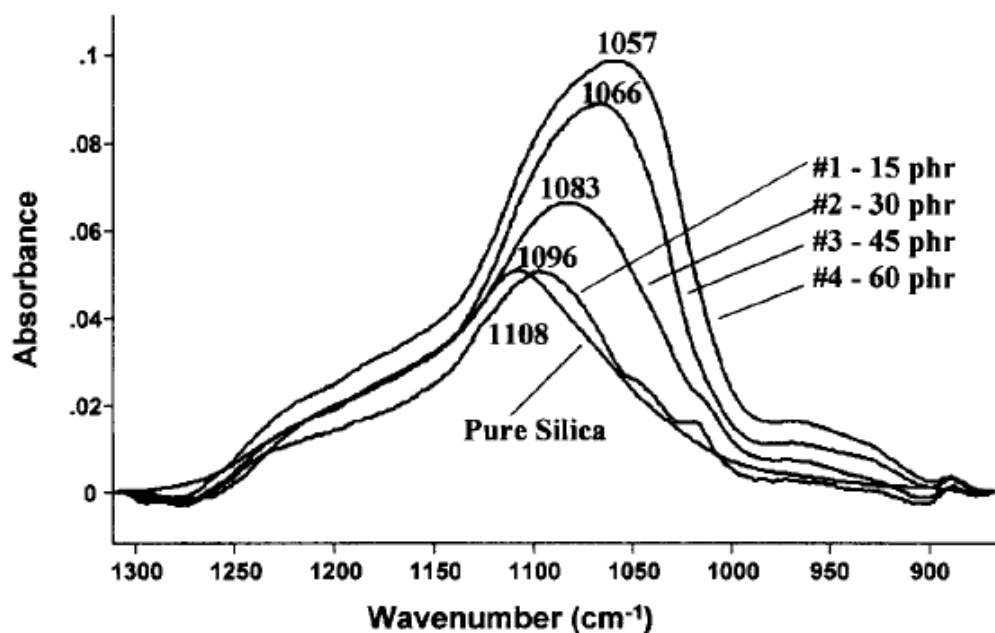


Figure 2.106 Effects of increased silica filler on the asymmetric Si-O-Si stretch in the silica region [89] pg 302

The amount of silica present in the rubber compound also affects the rheometer vulcanisation. Figure 2.107 shows the rheometer curves for silica filled rubber compounds. Each compound has a distinct point of inflection, and at this point the rate is slowed drastically. Kraleovich and Koenig relate this observation with silica adsorption upon heating. It is stated that as heating begins, the silica adsorption process occurs simultaneously with the vulcanisation process [89]. When all the free cure system is adsorbed or used up in the reaction, the rheometer curve will then reach its point of inflection and the silica region of the FTIR spectrum will reach its lowest wavenumber

value [89]. Hence, a delay or waiting time is needed for the cure system to desorb from the silica surface for the rubber to be fully vulcanised.

Figure 2.108 illustrates the spectral results of a poor mix and a normal quality mix of silica filled rubber. A poor mixed sample would result in large agglomerates of silica leading to a wavenumber increase due to a decrease in surface area for reactions to take place. Therefore, poor mixed samples will result in lower absorbance intensity values for functional groups [89]. Areas of interest include the CH_3 bend at 1378 cm^{-1} , silica region of $1000\text{--}1250\text{ cm}^{-1}$, Si-O stretch 965 cm^{-1} , OH region of $3000\text{--}3500\text{ cm}^{-1}$, C=C stretch at 1665 cm^{-1} [87, 89].

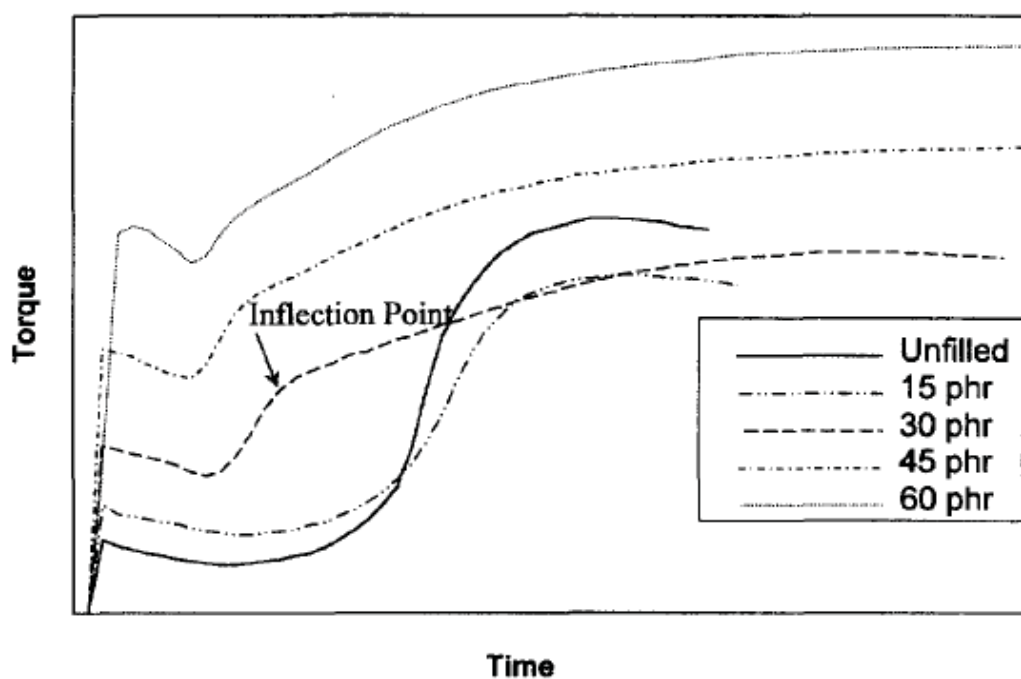


Figure 2.107 Rheometer curves for silica filled natural rubber [89] pg 307

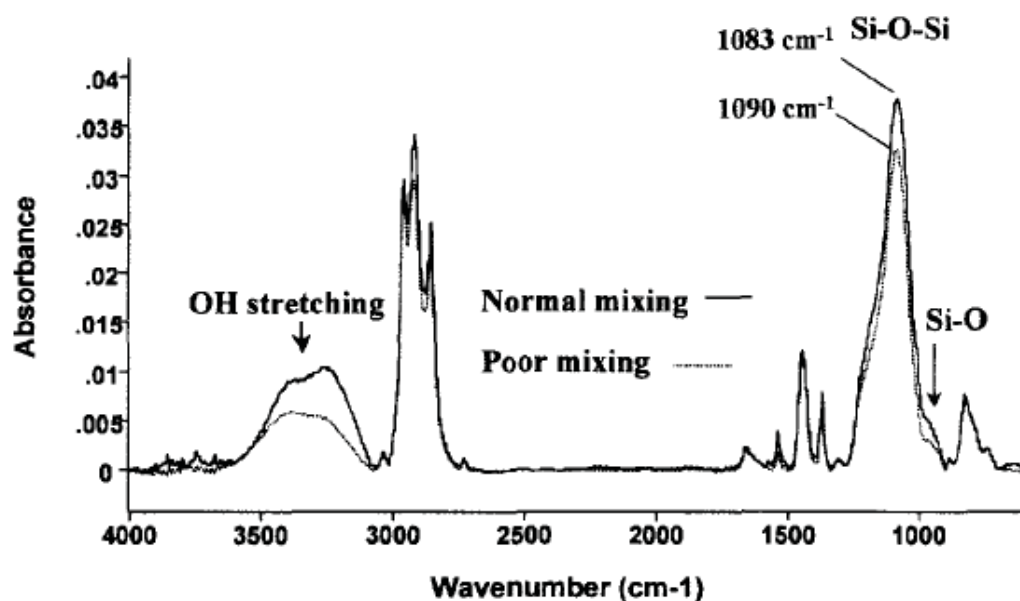


Figure 2.108 Spectral comparisons of normal mixing and poor mixing of silica in rubber compounds [89] pg 308

2.11.3 FTIR Investigation of the Molecular Structure at crack interface of Polyisoprene

Glime and Koenig investigated unfilled and silica filled polyisoprene samples tested to crack formation [87]. The crack tip was then analysed using FTIR to catalogue the changes in molecular structure at this point. Figure 2.109 shows the extracted profile for silica filled and unfilled polyisoprene. Similar to the previous section, it can be seen clearly from the spectra that the silica will have a wavenumber region of 1000-1250 cm^{-1} .

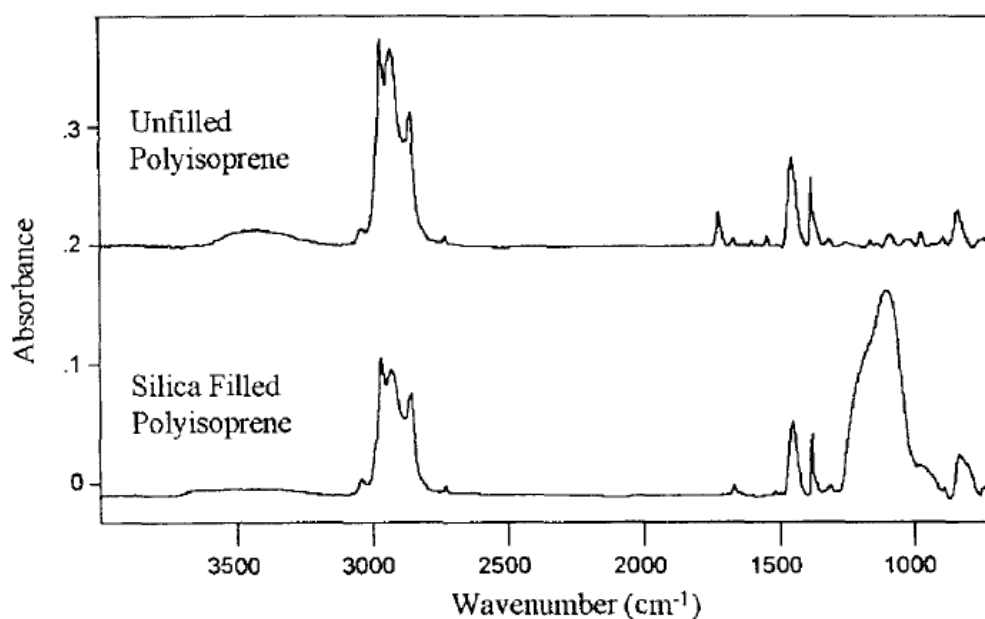


Figure 2.109 Extracted spectra for filled and unfilled polyisoprene [87] pg 49

The absorbance value for the C=C stretch band was found to increase in the region ahead of the crack tip in silica filled samples [87]. The molecules in the plane perpendicular to the incoming energy contribute to the IR absorbance value. Stretching the sample will cause more rubber chains to be aligned in the plane which results in this increase in absorbance. No other changes in absorbance values were observed at a distance from the crack in unfilled and silica filled samples. The intensity of the C=C stretching was also unchanged in unfilled samples [87].

2.11.4 FTIR Spectral Analysis of Rubber Blends

Gunasekaran et al. studied the relationship of FTIR spectral analyses of rubber polyblends [88]. Polyblends are a new family of elastomers, much like a composite material where a specific rubber is blended with another rubber. For example, a natural rubber blended with a nitrile butadiene rubber would be known as a polyblend. In order to analyse the FTIR spectra and physical properties improvement of these polyblends, it is essential to firstly

analyse each rubber material individually. The rubber materials used in this study included the characterisation of natural rubber (NR), styrene butadiene rubber (SBR), nitrile butadiene rubber (NBR) and ethylene propylene diene monomer (EPDM). The FTIR spectra of natural rubber can be seen in Figure 2.110. It is noted that strong asymmetrical ($\nu_{as} \text{CH}_2$) and symmetrical ($\nu_s \text{CH}_2$) stretching of methylene group vibrations present in NR are commonly observed at 2950 and 2853 cm^{-1} [88]. The methyl group also shows two distinct bands occurring at around 2964 cm^{-1} . OH stretching occurs at vibrations of 3470 cm^{-1} which is a characteristic of the polymeric hydroxyl compound. This OH stretching occurs irrespective of the rubber compound and composition. The vibrational band of 1076 cm^{-1} is present in all gum and reinforced elastomers but absent in raw materials. This band represents the symmetric C-S-C group stretching vibrations in the two C-S bonds [88]. During the vulcanisation process, the sulphur breaks the double bonds between the two carbon atoms such that the sulphur atoms bridge the gap between the chains. The spectral difference between the gum rubber and the reinforced rubber is due to the rate of absorption [88]. The theory of absorption was discussed earlier in this chapter.

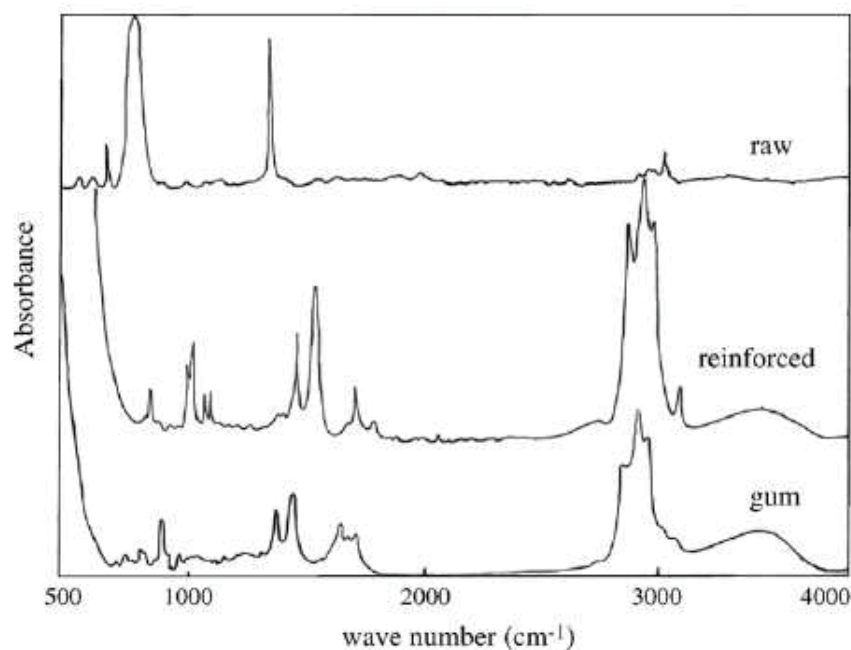


Figure 2.110 FTIR spectra of natural rubber [88] pg 326

The FTIR spectra were obtained for SBR and can be seen in Figure 2.111. Vibrational bands of 756 and 704 cm^{-1} are a result of out of plane bending vibrations of aromatic $=\text{C}-\text{H}$ and $\text{C}=\text{C}$ groups of polystyrene in SBR. Bands at 990 and 902 cm^{-1} are attributed to the out of plane bending vibrations of $\text{C}-\text{H}$ of vinyl groups, while the band at 960 cm^{-1} is attributed to the trans $-\text{CH}=\text{CH}-$ group vibrations of the butadiene [88]. Figure 2.112 shows the FTIR spectra of NBR. The band at 2230 cm^{-1} is the result of alkyl $\text{C}\equiv\text{N}$ stretching vibrations of the acrylonitrile present in NBR. The $\text{C}-\text{H}$ wagging vibrations of butadiene are present at the band 960 cm^{-1} [88]. Figure 2.113 shows the spectra of NR with NBR polyblend. The compatibility of this polyblend is illustrated by the vibrational band at 960 cm^{-1} indicating the $\text{C}-\text{H}$ wagging vibrations of butadiene present in NBR and also the functional groups present in NR. Gunasekaran et al. therefore states that from the spectra analysis, the NBR plays a dominate role in the polyblend since methyl absorption is greater in the gum state which is the case for NBR [88].

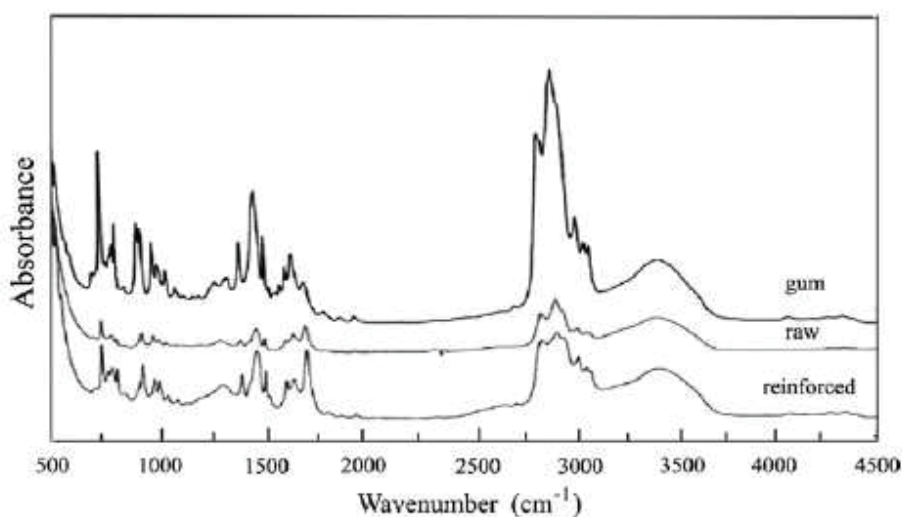


Figure 2.111 FTIR spectra of SBR [88] pg 326

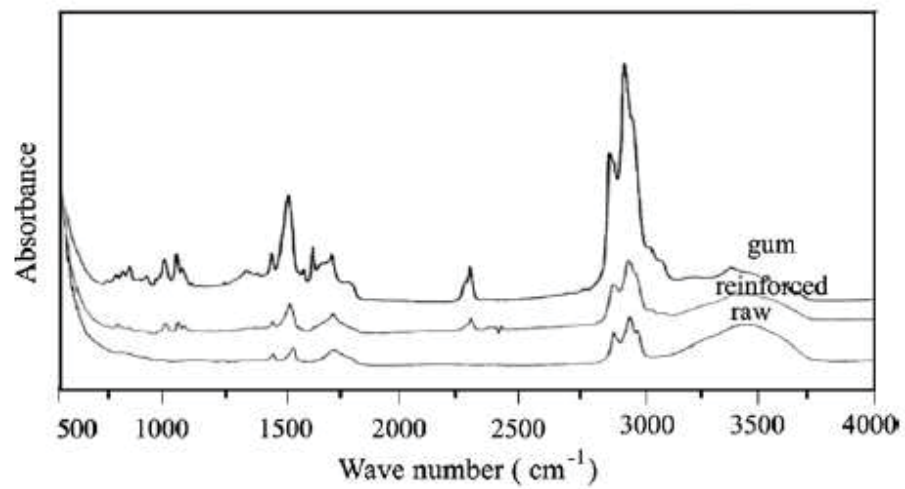


Figure 2.112 FTIR spectra of NBR [88] pg 327

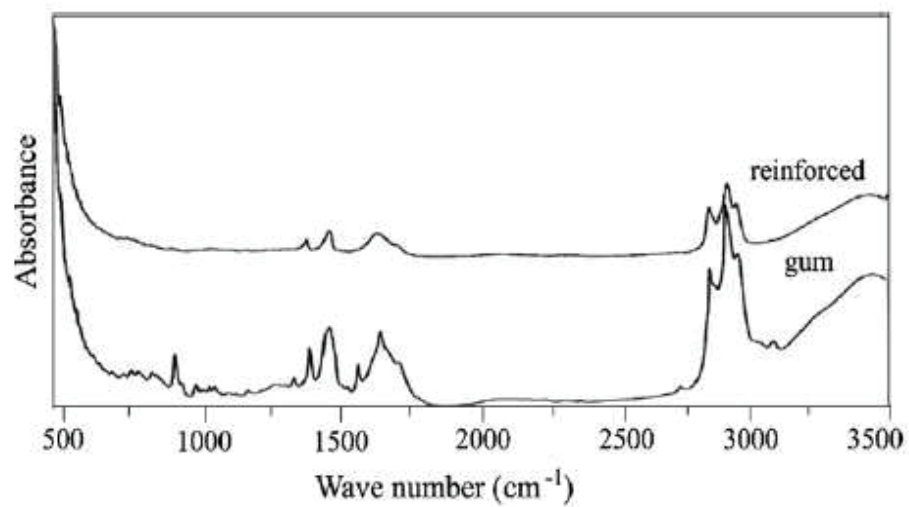


Figure 2.113 FTIR spectra of NR with NBR [88] pg 327

2.12 Summary

The slurry pump is used to transport slurry in minerals processing in mining applications. The centrifugal slurry pump utilises the force generated by a rotating impeller to impart energy to the slurry in order to move it to its desired location. A slurry is defined as a fluid

containing solid particles. As the slurry pump needs to withstand wear caused by abrasive, erosive and often corrosive attack, there are many important material considerations. These include physical, viscoelastic and chemical properties of the material. The erosive wear mechanisms are defined in three main modes of wear. These are as follows: a) sliding bed, b) random impact and c) directional impact. It could be seen in Figure 2.31 that all three of these modes of wear are evident in slurry pump wear. Fourier transfer infra red (FT-IR) has been used extensively to determine the chemistry of natural rubbers. Table 2.13 outlines the characteristic FT-IR band intensities for the natural rubber spectrum. These characteristic band intensities will be important to identify which chemical bonds have broken during the heat aging and erosive wear process. Relationships will be made in this study with erosive wear and these processes.

3 Hypotheses and Approach

3.1 *Introduction*

The purpose of this study is to determine the fundamental process of erosive wear in rubber pump lining materials used in the mining industry. For this study to be successful, appropriate hypotheses must be defined before any testing and analysis is carried out. It is difficult to define wear to one particular condition; it is the collection of variables and conditions the material is exposed to that causes the wear to occur. As identified from the literature survey, the possible failure modes involved with erosive wear are dependant on three distinct areas; (1) the material properties, (2) the environment, and (3) the mechanical stress and strains which are imposed on the material during operation. These areas are the basis of the hypotheses.

The basis of erosive wear during slurry pump operation is unclear as this area has not been extensively studied. However, many authors have used the physical properties of the rubber to correlate with the wear rate and wear mechanisms. This may not be the best method to approach the problem of wear as physical properties are tested under controlled conditions. It is essential to understand the material itself before any approach is taken into account. The variables involved during the wear process must then be defined to determine their affect on the material. The material and the variables involved in the wear process will be broken down individual topics to develop a number of hypotheses. Figure 3.1 shows a schematic for the process of erosive wear. Particle attack is assumed to be the basis for wear which can cause mechanical stress and strain on the surface of the rubber. This may then lead to aging of the rubber, and within this aging, the rubber physical and viscoelastic properties as well as chemical changes to the rubber can occur. These form the basis for the hypotheses for this study.

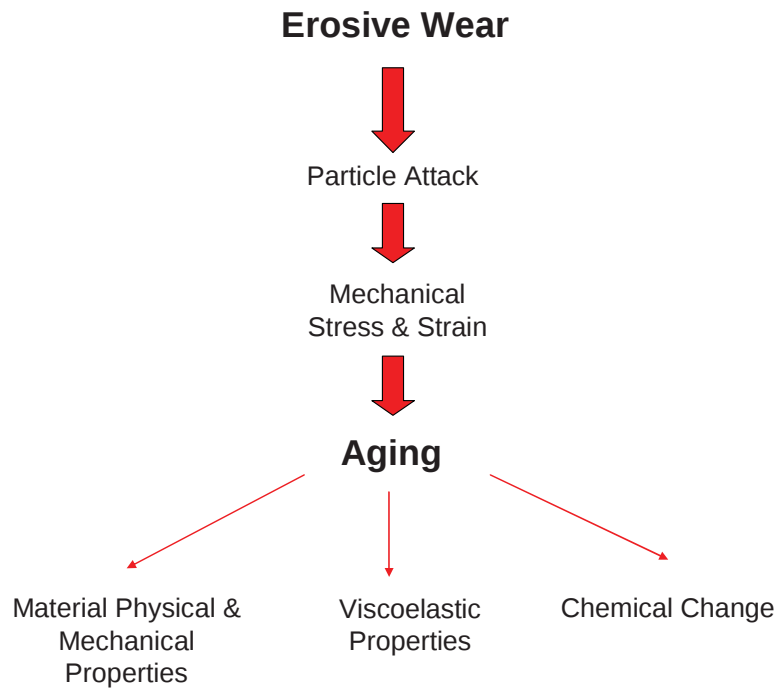


Figure 3.1 Basis for regarding hypotheses erosive wear in rubber pump lining materials outlining the effect of each and their interaction.

3.2 *Hypotheses*

Hypotheses for this project are outlined below and in Figure 3.2:

1. The physical and viscoelastic properties of the rubber will be influenced by the erosive wear process as a result of heat and time. Elevated temperature aging will result in material property degradation. Aging occurs in the erosive wear of rubber pump lining materials used in minerals processing which leads to a change in the physical and viscoelastic properties of the rubber.
2. Chemical change and chain scission of the polymer molecules occurs during the erosive wear process. The higher degree of chain scission will lead to an increase in

wear rate during the pump operation. In particular the C=C bond and the sulphur bonds will be of interest. Crosslink density relates to the amount of vulcanisation that occurs during the processing of the rubber. A higher degree of crosslinking will result in a higher wear rate during the erosive wear process.

3. Particle attack on the surface of the rubber will result in cutting and gouging that will lead to failure of the material. This particle attack will also lead to chemical change and aging on the surface of the rubber. This will result in a decrease in the material properties. By using particular methods of wear testing, this will simulate the erosive

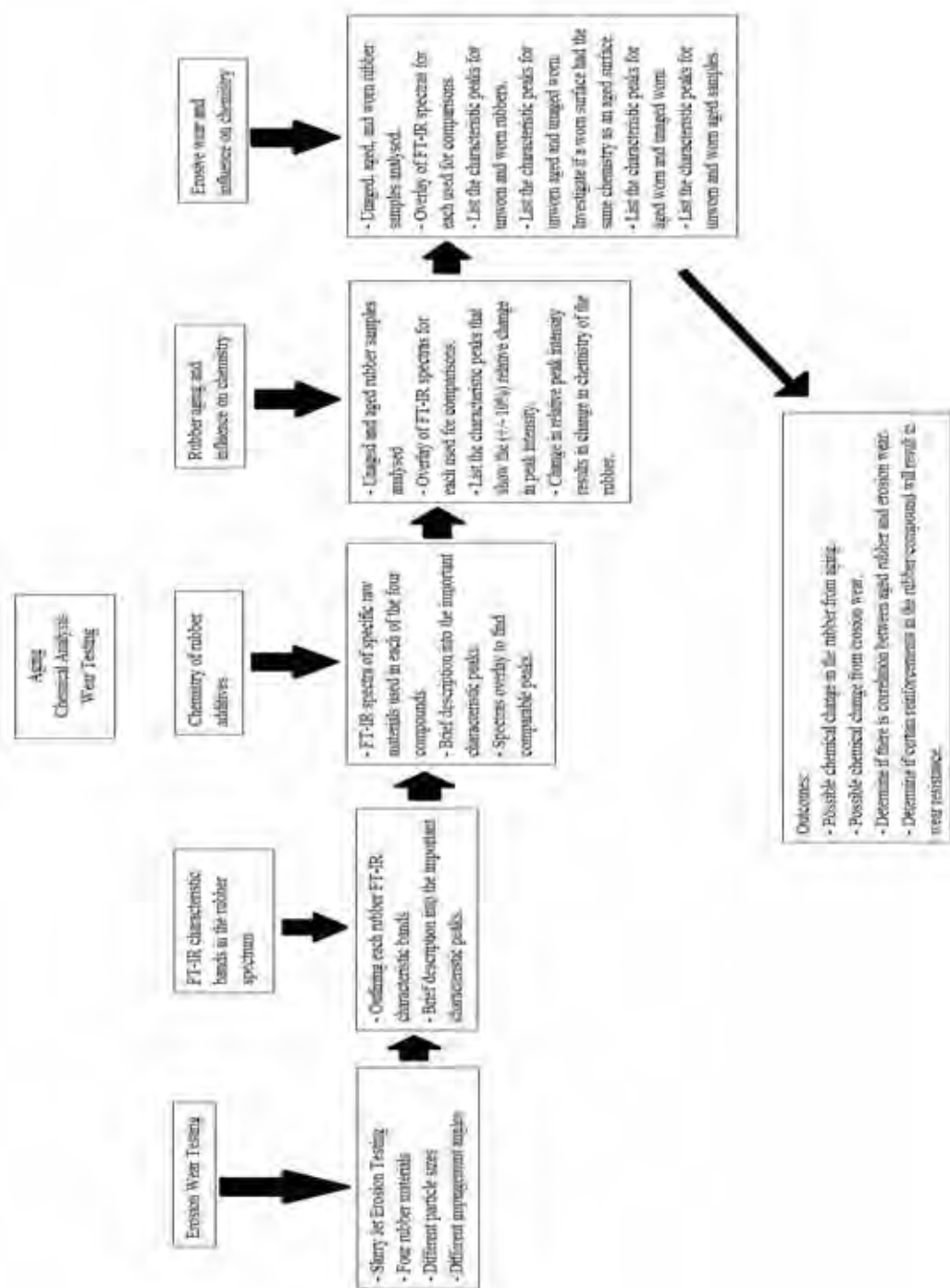


Figure 3.2 Project plan and approaches to address the hypotheses

3.3 *Approaches to Address the Hypotheses*

3.3.1 Aging

Aging of rubber will affect properties of the rubber as mentioned in the literature review. The wear life of the slurry pump may be anywhere from a week to a few years, therefore an understanding of the affects that aging will have on the rubber materials is of importance in predicting wear life. A theory to the wear life of a rubber material degrading over time is that if the temperature is increased, physical and viscoelastic properties will decrease in comparison to an unaged rubber. This decrease in properties is a result of oxidation and chemical bond scission that occur in the rubber macromolecules. The important point to consider in this subtopic of aging is the relationship between aging and erosive wear mechanisms. One must answer the question: if the rubber sample is aged at a particular time and temperature will this lead to a change in the wear rate of material? There are a number of methods that can be used to determine the aging affects on the rubber. Traditional testing such as wet and dry air aging can be used to obtain physical property relationships.

The viscoelastic properties are measured using a rotorless oscillating shear rheometer (RPA – Rubber process analyser). It is important to consider the viscoelastic properties after the optimum cure time as this best simulates the rubber in service. An area of interest during erosive wear process is the impacting affect of each individual particle that can lead to polymer degradation. This impact can be simulated by vibrational frequency sweeps using the RPA. The viscoelastic properties can then be measured from this and will change after aging for a specified time and temperature. The elastic modulus G' measured from this testing will decrease after aging as the rubber becomes over-cured and the viscous modulus G'' will increase as the rubber becomes more highly crosslinked and can absorb more of the impact energy from the attacking particles. In summary, polymer degradation under erosive wear conditions is a result of aging and thermal attack altering the viscoelastic and physical properties of the rubber.

Many studies have attempted to correlate wear with physical properties of the rubber. However, these have been completed with limited success as rubbers behave in a unique manner due to their viscoelastic structure. During the wear process, heat aging occurs as particles impact the surface of the rubber. Heat aging leads to weakening of the sulphur crosslink bonds between the elastomer chains leading to premature failure. It is of interest to correlate these results with the viscoelastic properties from the RPA aging tests and more importantly to determine whether the physical properties of the rubber relate to the erosive wear process during the operation of a slurry pump.

3.3.2 Wear Testing

Wear testing of rubber samples is of importance in the study of erosive wear of pump lining materials as this method best categorises and ranks each material according to the conditions. As mentioned in the literature, not one wear test can determine if the material is suitable for a particular application in the field. It is often a series of tests that rank each material according to resistance.

Directional impingement wear is experienced in particular locations of the slurry pump, in particular the impeller and various areas of the pump liner. Different particle sizes and angles of impingement can be catalogued and used to rank each material according to wear rate. Low angle sliding bed wear is also evident during the operation of a slurry pump. In this case, the pump lining and the throatbush are usually the areas where wear is most evident. Not only will this testing be useful in ranking the materials resistance to abrasive slurries, but it will also indicate the critical particle size and impingement angle of each material.

3.3.3 Chemical Change

The chemical change of the material is often a major factor when considering wear of rubber tyres. However, during the erosive wear of rubber in the slurry pump, it is not known for certain that a chemical change occurs. Previous studies have indicated that erosive wear of rubber is merely a mechanical process where a harder erodent material will remove the softer material. The backbone of natural rubber is the C=C double bond which gives rubber its physical strength. This double bond breaks during the erosive wear process as a result of sharp impinging particle impacting on the surface of the rubber. A theory for this double bond to break is that some chemical change occurs to the surface of the rubber as particles contact. This chemical change is the result of depolymerisation due to hysteresis resulting in a sticky, chewing gum like rubber.

When considering bond breaking in a vulcanised rubber, one must take into consideration the vulcanising agent. Rubber parts used in slurry pumps are usually formulated to contain sulphur as the vulcanising agent. The sulphur atoms react with the long chains of rubber molecules resulting in crosslinking. Crosslinking of the rubber molecules improves the tensile properties of the rubber due to greater flexibility and lability of polysulphidic crosslinks. However, rubbers with a high proportion of polysulphidic crosslinks are more susceptible to heat deterioration and chemical attack. As mentioned above, during heat ageing of the rubber the physical properties will change accordingly due to heat deterioration, over-curing effects and chemical attack. At this stage it is important to note that the C-C bond is more stable than the C-S bond. The dissociation energy for the C-C bond is slightly higher than the C-S bond, therefore, it is expected that the C-S bond would break before the C-C bond during the wear process.

It is also important to consider the crosslink density when considering the crosslinking of a rubber. Crosslink density is defined as the number of crosslinks per unit volume, which is inversely proportional to the average molecular weight of polymer chain between crosslinks. This concept is important when considering the chemical change and aging of

rubber during the wear process as properties will change. In particular, with increasing crosslink density the modulus and hardness of the rubber will increase, whereas the fatigue resistance, tear strength and toughness will increase initially to a peak then decrease as crosslinking increase to a point where it behaves more as a solid. With decreasing crosslink density, hysteresis, permanent set and creep formation will be influenced as a result of short chain segments between the crosslinkages and the distance which they can move on deformation decreases causing heat build up in the rubber.

4 Experimental Methods and Materials

The experimental plan of this project will be based on the simulation of erosive wear and analysis of worn test samples. In a previous study, it was found that the Eductor wear tester best fits the condition of directional wear experienced in a slurry pump [3]. This test involves a high pressure jet of water in which abrasive particles are added to simulate the directional wear. A number of variables can also be altered such as; angle of impingement ($15^\circ - 90^\circ$), particle size, jet velocity and test material. It was found that the critical impingement angle and particle size for severe wear to occur was 20° and $500\mu\text{m}$, respectively. This project will further develop the understanding in these critical variables as well as further testing impingement angles and abrasive particle sizes not tested before. Three rubber materials will be tested and analysed and their descriptions are as follows:

- A1 a natural rubber consisting of gum rubber and small amounts of reinforcing agents.
- A2 a natural rubber highly reinforced with precipitated silica.
- A3 a polymer blend of natural rubber and polybutadiene reinforced with granulated silica.
- A4 also a polymer blend of natural rubber and polybutadiene highly reinforced with carbon black.

The physical properties of the rubber will be tested including; Shore A° hardness, Lupke resilience, Shore resilience, density determination by liquid displacement, tensile strength, elongation at break and tensile tear. The results from this testing will be used to set up control standards. The viscoelastic properties are also of interest in this project. many of the physical properties correlate. In particular the elastic modulus G' , viscous modulus G'' and $\tan \delta$. Frequency and strain sweeps are run in the RPA to simulate the conditions rubber experiences during service. This data can then be used to determine the limiting factors in regards to material properties during the erosive wear process.

One outcome of this project is to develop a further understanding in the erosive wear mechanisms of rubber. The hypotheses of erosive wear are illustrated in Figure 3.1. Erosive wear could be a result of particle attack that causes mechanical stresses and strains resulting in aging. A number of methods can be used to test aging; these include wet aging, hot air aging and aging using the RPA. The wet and air aging tests are used to simulate the conditions rubber will undergo during storage, transport and application. The RPA aging is a test method developed in this study to better understand the changes to the viscoelastic properties during aging. The selected aging temperatures used in this study were to simulate the operational temperature in a slurry pump and at higher temperatures during the manufacturing of rubber slurry pump parts. Temperatures used in this study were 75°C, 100°C and 150°C. At higher temperatures reversion of the rubber crosslinks can occur resulting in a significant decrease in material properties.

Chemical degradation as a result of wear testing and aging can be analysed using the Fourier Transform Infrared Spectroscopy (FT-IR). Unfilled natural rubber will be used as a control since the vibrational $\nu_{C=C}$ bond is clearly observed from the literature at the characteristic peak of 1665cm^{-1} . The rubber based compounds will then be analysed and compared with this characteristic peak to observe any changes resulting in chemical bond breakage. The crosslink density is another property that will be investigated to calculate the amount of crosslinking that occurs after the rubber is vulcanised. This is also an important test in relation to degradation which will indicate if the chemistry of the rubber has been altered during wear testing. Another method of determining the extent of crosslinking is by the determination of free sulphur in the rubber. The amount of free sulphur is calculated using a titration method.

4.1 *Experimental Procedures*

4.1.1 Raw Materials

Rubber materials A2 and A3 used in testing are produced from Toyo Tyre and Rubber Australia located in Minto, N.S.W. Rubber materials A1 and A4 is produced from Nepean Rubber located in St Marys, N.S.W. The material descriptions are as follows; A1 is a natural rubber consisting of pure gum rubber. A3 is a polymer blend of natural rubber and poly-butadiene reinforced with granulated silica. While A2 is a natural rubber reinforced with precipitated silica. All rubbers are mixed using a Banbury Mixer in batches of approximately 100kg at Nepean Rubber and 250kg batches at Toyo Tyre and Rubber Australia. Samples of the final batch mix were used in sample preparation for the testing of physical properties, aging tests and wear testing.

4.1.2 Sample Preparation

Sample preparation of the green rubber was set out in accordance to AS 1683.19 – 1981 [91]. Green rubber was obtained and vulcanised rubber sheets produced by milling the green rubber then pressing into moulds at a specific temperature and pressure. It is important to run a “cure curve” test in the RPA before any sample preparation commences. This test determines the optimum cure time and temperature required for vulcanisation to take place. By curing the rubber at this optimum cure time and temperature the rubber samples will not be exposed to post curing affects during aging tests. Post curing will influence the physical properties of the rubber. For the current study, four rubber materials were used; A1, A2 A3 and A4 which all have different cure systems and require vulcanisation at different temperatures and cure times. The resulting rubber samples are cut to size using a guillotine or die cutter presses where they are then measured to dimensional tolerances and tested.

4.1.3 Physical Property Testing

4.1.3.1 Tensile and Tear Strength

Physical property testing was completed for each material (A1, A2, A3 and A4). Physical property testing includes tensile tests and tensile tear tests in accordance to ISO 4661/1 [92]. For tensile tests, three samples are measured in dimensions in accordance to ASTM D412_1993 [93] and tested. For tensile tear tests, three samples of tear B and tear C are measured in dimensions in accordance to AS1683.12_1990 [91] and tested.

The tensile strength was measured at room temperature using an Instron 5564 Tensile Tester in accordance to AS2193_1978 [94], Methods of Calibration and Grading of Force-Measuring Systems of testing machines, ASTM D412_1993 [93], Standard Test Methods for Rubber Properties in Tension and AS1683.11_1990 [91], Methods of Test for Elastomers – Tension testing of Vulcanised Rubber. Rubber dumbbell samples are cut from the vulcanised sheet rubber using die presses. The dumbbells have the dimensions of 6.2mm in width and the thickness must be between 1.3mm and 3mm thick. Tensile testing is required for all material evaluation as it is used to determine the tensile strength of the rubber.

Tear strength of nicked and un-nicked samples was measured at ambient temperatures using a 90° angle sample in accordance to AS2193_1978 [94], AS1683.12_1990 [91] and ASTM D412_1993 [93]. The rubber tear samples are cut from vulcanised sheet rubber using die presses. Tear B samples must be nicked or cut with a sharp blade directly in the centre of the test specimen. This nick or cut will ensure a point of failure within the test specimen. The Tear C sample are un-nicked and the failure point of tear initiation will depend on the rubber composition or quality of the rubber. Tensile tear testing is especially important in rubber property characterisation as it determines the tear strength that in theory can be correlated with erosive wear. Since the process of erosive wear involves sharp particles cutting and gouging the surface of the rubber, it is assumed that higher tear strength should result in a decrease in wear loss of material during erosion. However this

was not the case in a previous study [3]. An attempt to correlate the tearing energy of the rubber with wear loss of material contradicted the theory above.

4.1.3.2 Density Determination

A liquid displacement method was used to determine the density of the rubber materials at room temperature in accordance to ASTM D297/15 1989 [95]. Samples were cut to size 15mm x 15mm x 15mm $\pm$ 1.5mm ensuring a clean edged cut otherwise air or gas will be entrapped in rough areas of the specimen when immersed in the liquid giving an inaccurate result. The formula used for density calculation is as follows:

$$\rho_{solid} = \frac{W_{dry} \times \rho_{liq}}{W_{wet}}$$

The density determination test is primarily used to check the quality of the rubber. Inaccurate mixing or poor quality rubber will lead to a variation in the density calculations.

4.1.3.3 Shore Rebound Resilience

Resilience was determined by vertical rebound method in accordance to ASTM D2632-01 [97]. The Instron Shore Resiliometer was used to test the vertical rebound of the rubbers. Standard rubber test button samples of 30mm in diameter and 12.5mm thick were prepared for testing. The Resilience by vertical rebound method involves an identical rubber test button sample placed on a stage where the resilience is determined as a ratio of rebound height to drop height of a metal drop weight of prescribed mass and shape which is allowed to fall on the rubber sample [97].

Resilience is a function of both dynamic modulus and internal friction of the rubber [1, 3, 5, 6, 33, 37, 42, 67, 98]. This property can hence be related to the viscoelastic properties of

the rubber. In a previous study [3], the physical property of resilience was measured by using a different test method (ASTM D7121). Although this test method is different to the method used in this thesis, the physical property of the rubber is still measured as a percentage rebound. ASTM D7121 involves the material being initially deformed by a pendulum; energy is stored in the rubber during this 1st initial contact. Due to the elastic nature of the rubber, the metal drop weight rebounds to a point on the scales where this value is recorded. The elastic modulus G' can therefore be considered as the point of elastic rebound during the test and the viscous modulus G'' can also be considered as the amount of energy being stored in the rubber during the point of impact giving the relationship between resilience testing and $\tan \delta$. A low value of G' and a high value of G'' , this will result in a large $\tan \delta$ that will cause a low value of resilience and hence may affect wear loss during the erosion process [3].

4.1.3.4 Shore A° Hardness

The indentation hardness of the rubber material is measured using a Frank Shore A° Durometer in accordance to ASTM D2240-91 [99], and ASTM D1215-18 [100]. Standard test rubber blocks of 50mm x 50mm x 12.5mm were used. The indenter presses onto the rubber block, inducing a force on the surface. This force is dictated by the speed at which the indenter is forced onto the surface of the rubber. The indenter must be completely immersed into the surface of the rubber to ensure an accurate reading. 5 different positions on the specimen about 6mm apart were measured.

The hardness of the rubber is of most importance when considering the wear life of a pump liner as different hardness values may correlate with a variation in wear loss during the erosion process. High hardness rubbers tend to undergo fatigue and micro cracking as a result of the harder surface along with the lower value of resilience [3]. The hardness of the rubber can also be correlated with elastic modulus as stated in the literature [3, 33, 42]. In a previous study [3], it was observed that a rubber with a high value of hardness also had a high value of G' . This resulted in lower resistance to erosive wear particularly at low

impingement angles of $10^{\circ} - 30^{\circ}$. At these low angles the elastomer will suffer an increase in tearing and cutting wear mechanisms. An increase in hardness of the rubber can also be attributed to the amount of work imposed on the surface. This work will then in turn also increase the elastic modulus G' .

4.1.4 Erosive Wear Testing

Eductor wear tester was used to assess erosive wear of the rubber samples under different conditions. The test was carried out with slight variations to ASTM G73-04 [101] and ASTM G76-07 [102]. The variations being the jet stream which consists of abrasive particles and water. The eductor wear tester best simulates the directional wear behaviour of each material during the erosive wear process such that each test variable can be modified. Test variables considered are angle of impingement, jet velocity, particle kinetic energy and particle shape and size. During the operation of a slurry pump, abrasive particle impingements are randomly distributed. There is a need to characterise the angles of impingements to determine the effects of each and the extent of wear on the surface of the rubber. It is therefore important to identify each variable during the slurry pump operation as mentioned above.

The impingement angle refers to the angle at which the abrasive slurry strikes the test piece. However it is important to characterise each impingement angle in relation to particle size to construct a graph that reaches both a maximum and a minimum. The direction of the slurry jet to the sample was subjected to test angles of 20° , 45° , 60° and 90° .

Particle impact energy refers to the kinetic energy of the particle which is transferred to the rubber. It is influenced by the density, size, and hardness of the particles and the velocity of the jet stream. Due to the limitations of the Eductor wear tester, the impact velocity is set and calibrated at 20m/s. Brown and white fused alumina particles were used in the wear testing. The particle shape used was angular to sharp as this best represents the particle shape of the abrasive within a mining slurry. A scanning electron microscope (SEM) was

used to record high magnification micrographs. Figure 4.1 shows an SEM picture of abrasive particles used as wear media. The particle sizes for the Alumina particles were varied between 100 μm , 200 μm , 250 μm , 500 μm , 750 μm and 1000 μm . The hardness and density values for the Alumina used in wear testing can be seen in Table 4.1.

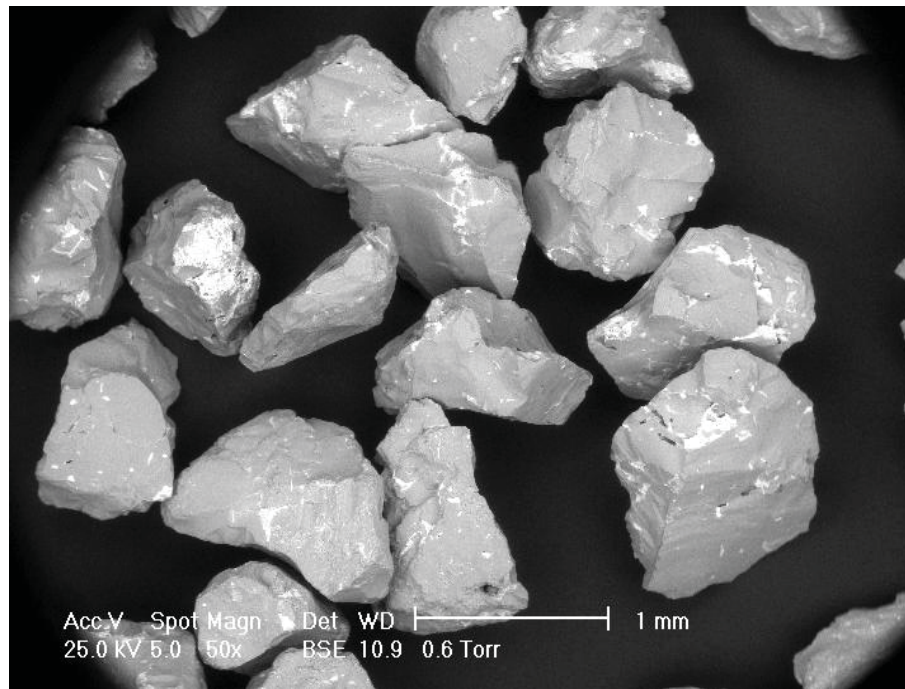


Figure 4.1 SEM picture of 1000 μm Al_2O_3 sharp abrasive particles at low magnification (50x).

Table 4.1 Density and hardness values for abrasive materials.

Property	Silica (SiO_2)	Alumina (Al_2O_3)	Silicon Carbide (SiC)
Density (g/cm^3)	2.5	3.9	3.2
Hardness Vickers (kg/mm^2)	500 - 800	2600	3000 - 3500

*Data obtained from CRC Materials Science Handbook 2nd edition.

4.1.5 Slurry Particle Concentration for Erosion Wear Testing

The wear test solids concentration was calculated per test set to determine the influence on the wear loss. Table 4.2 shows the different test times, slurry concentration by weight and slurry concentration by volume in relation to particle size. The total mass of water was per test was measured to calculate the total volume of water per test. The total mass of slurry per test was calculated by adding the total mass of the erodent into the total mass of water per test. The slurry concentration by weight (C_w) and the slurry concentration by volume (C_v) were calculated with the following:

$$\text{Slurry } C_w (\%) = \text{total mass of solids} / \text{total mass of slurry} \quad (4.1)$$

$$\text{Slurry } C_v (\%) = (1 / 1 - 3.9 + (3.9 / C_w)) \quad (4.2)$$

where 3.9 is the specific gravity of the abrasive material Al_2O_3 .

Both the slurry concentration by weight and volume do not significantly differ from each particle size. Therefore the slurry solids concentration can be considered as constant throughout the particle size range. Figure 4.2 – 4.4 illustrate graphical representations of the particle size against test time, slurry weight and volume concentrations.

The volume for each particle was calculated assuming that the shape of each particle was an octahedron.

$$\text{Volume of each particle } (V_o) = \left(\sqrt{\frac{2}{3}} \right) \times a^3 \quad (4.3)$$

The mass for each particle is then calculated by the following equation:

$$\text{Mass for each particle } (m_o) = \rho \times V_o \quad (4.4)$$

Finally, to calculate the number of particles per wear test is shown in the following equation:

$$\text{Total number of particles per wear test } (n_o) = \text{Total mass of particles per test} / m_o \quad (4.5)$$

Hence the wear loss per particle impingement is calculated by the following:

$$\text{Wear loss per particle impingement} = \text{Wear loss} / m_o \quad (4.6)$$

Figure 4.2 shows the influence of particle size on test time. This test was carried out using the Eductor wear tester mentioned in chapter 4.1.4. The particles are feed through a hopper with fixed diameter with the only variable as the particle size. Each particle size was timed using a stopwatch and it was observed that the larger particles took more time to feed into the slurry jet stream since the diameter of the feed hopper was constant. The experimental data is shown in Table 4.2.

Figures 4.3 and 4.4 show the influence of slurry concentration by weight (Cw) and volume (Cv) respectively. This data shows that as the particles increase in size, the slurry particle concentration will decrease, however, the total mass of slurry increases for the larger particle sizes.

Table 4.2 Slurry weight and volume concentration calculations in relation to particle size.

Particle Size (mm)	Ave test time (mins)	Total Volume of water per test (L)	Total Mass of Slurry per test (kg)	Slurry Cw (%)	Slurry Cv (%)	n_o
1000	3.98	74.98	75.98	1.32%	0.34%	530330
750	3.28	61.80	62.80	1.59%	0.41%	1257079
500	2.82	53.13	54.13	1.85%	0.48%	4242641
350	2.67	50.30	51.30	1.95%	0.51%	12369215
200	2.92	55.01	56.01	1.79%	0.46%	66291261

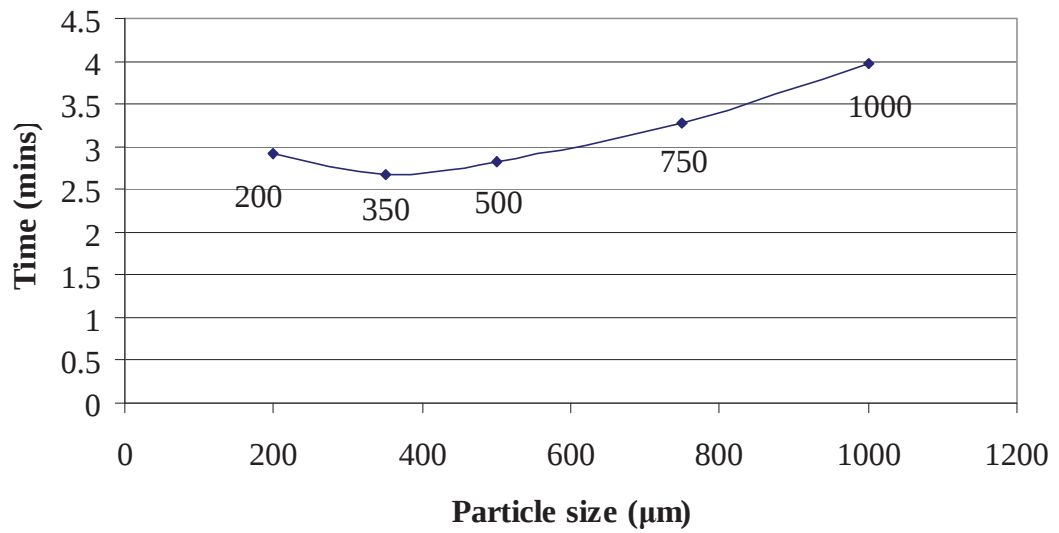


Figure 4.2 Particle size vs test time

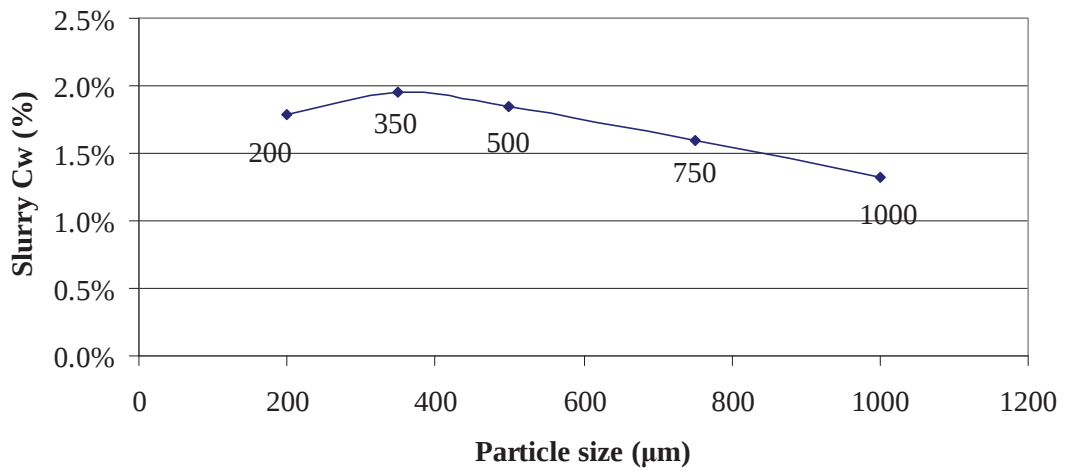


Figure 4.3 Particle size vs Slurry Cw

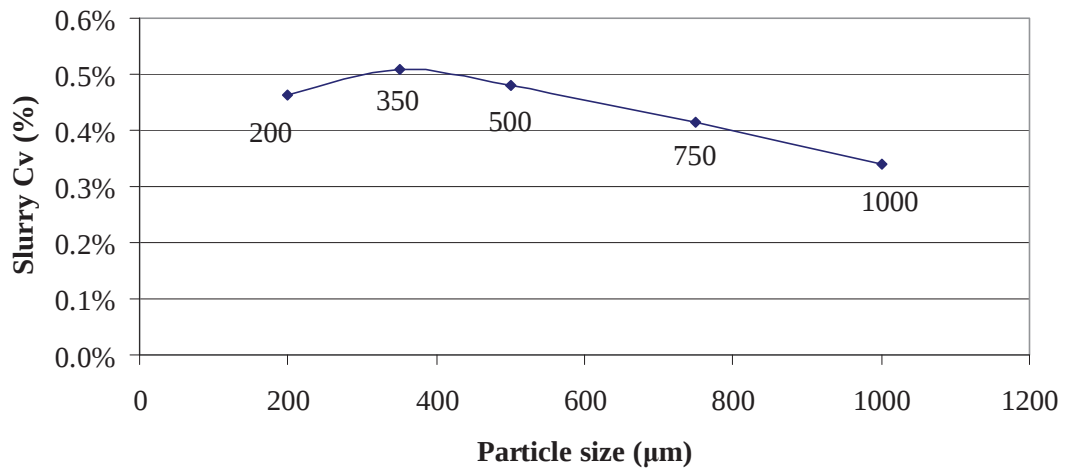


Figure 4.4 Particle size vs Slurry Cv

4.1.6 Chemical Analysis

4.1.6.1 Fourier Transform Infrared (FT-IR) – Attenuated Total Reflectance (ATR)

The samples used in this study were prepared according to Experimental Procedure 4.1. Chemical analysis was carried out in accordance to ASTM D3677 [103] to determine the chemical change to the surface of the rubber after wear testing. Control samples of rubber were analysed and their spectra were then compared with worn sample spectrums. Wear test samples were analysed in the FT-IR ATR no later than 24 hours after wear testing to ensure any chemical changes that occur to the surface of the wear scar were kept to a minimum. It is essential for the ATR to be clean from all dirt and contaminants before running the sample to ensure the spectrum collected is highly accurate. This was achieved by using ethanol to clean the surface of the diamond crystal before analysis.

The samples were examined on a Thermo Nicolet 380 FT-IR spectrometer with a Smart Orbit ATR attachment using a Diamond crystal. All spectra were collected at 16 scans at 8

cm^{-1} resolution and 3.857 cm^{-1} data spacing. Data analysis was evaluated using Thermo OMINC software.

The spectra of each condition were then used to compare visually by using the “overlay” and “stack” function from the software. The peak search tool is a more accurate method of evaluation as each peak wavenumber is identified within the spectrum. The wavenumber of each peak is unique to the chemical bond within the chemical compound being analysed.

4.1.6.2 FT-IR Data Analysis Method for Determining Relative Peak in rubber compounds

The raw data obtained from the FT-IR testing needed to be analysed further using a method outlined here in this section. The data from FT-IR can drift depending on the background noise of the initial FT-IR scan; hence by using the overlay software tool, the true spectra of each compound is skewed.

In this study, a relative peak search method was used to determine any chemical change in the rubber analysed using the FT-IR. This method involves taking one wavenumber in the spectra and calculating the relative intensities of every other point to this initial point. After this calculation is complete, the next wavenumber is selected and the relative intensities of every other point are calculated. This calculation is continued until the final wavenumber showing a peak in the spectra is completed.

The rubber compounds A1, A2, A3 and A4 were tested using this method. Each sample was analysed before and after wear testing. Figures 5.30 – 5.32 show the calculation table that is used for this relative peak search method. A 10% change increase or decrease in relative peak intensity was considered as a significant difference to result in a chemical change of the rubber compound.

4.1.7 Surface Analysis

4.1.7.1 Scanning Electron Microscope (SEM)

A Hitachi TM-1000 tabletop microscope was used for examination of rubber sample before and after wear testing. An important component in tribology is the study of wear mechanisms through analysis surface damage. By using high magnification microscopy, the surface damage, ever so minute can be viewed and examined to correlate with theory. The rubber samples were examined before and after wear testing at magnifications from 100x to 8000x. Wear test samples were analysed in the SEM no later than 24 hours after wear testing to ensure any chemical changes that occur to the surface of the wear scar were kept to a minimum.

4.1.7.2 Profilometer Analysis

A Taylor Hobson Talysurf CLI1000 was used to analyse the rubber samples after wear testing. The 300 μ m and 3mm Chromatic Length Aberration Gauge (CLA) was used to analyse the surface profile of each sample. Rubber samples after wear testing were analysed using the CLA 3mm gauge at a measurement speed of 30mm/s and data spacing of 60 μ m and 50 μ m in the X and Y directions. Samples that had low levels of wear were analysed using the CLA 300 μ m at a slower measurement speed of 1mm/s and smaller data spacing range. This was to ensure small step height measurements from those wear scars were accurately measured.

The Talymap software was then used to manipulate, analyse and visualise the data obtained from the data collection. Volume wear loss calculations were made using the Talymap software “Volume of a Peak/Hole” function. Volume wear loss values obtained can then be used to develop a wear loss rate for each material tested.

The Talymap software was also used to produce 3D images, profile extractions, and distance measurements of the wear scars. 3D images are useful in determining the shape of the wear scar at different angles of impingement. The shape of the wear scar can then be catalogued according to the given condition. Profile extractions are useful in visualising the profile at a particular point on the wear scar. These extractions are important in determining the maximum depth of the wear scar.

4.1.8 Viscoelastic Property Testing

4.1.8.1 Rubber Process Analyser (RPA)

The Alpha Technologies RPA 2000 rubber process analyser (RPA) was used to test the rubber samples for their elastic and viscous modulus behaviour and $\tan \delta$ under different conditions. Tests were carried out according to ASTM standards D5992 [104], D6204 [105] and D6601 [106].

The RPA was used to determine the optimum cure time of each rubber. The temperature was set at 140°C as this is the specification temperature for all the rubbers. Frequency and strain were set at 100cpm and 0.50 deg respectively. The data obtained from this cure test will indicate the 99% cure time (T99') which is critical to the optimum cure time for the rubber.

Simulation RPA aging tests were carried out for 12, 24 and 72 hours at 75°C, 100°C and 150°C. The RPA aging test is split into a series of 7 subtests to ensure that the rubber is treated to a specific condition so the data collected can be compared. The initial subtest involves curing the green rubber to optimum time and temperature before aging takes place. The temperature was then stabilised from 140°C to 60°C for 20 minutes before the frequency sweep and strain sweep. The frequency sweep test is designed to stress the rubber through vibrations of from 2 to 2000 cycles per minute (cpm). The temperature was set at a constant temperature of 60°C and the strain constant at 0.20 degrees. The strain sweep test similarly, strains the rubber from 0.1 to 3 degrees at a constant temperature of

60°C and constant frequency of 6cpm. The viscoelastic properties for each subtest are then calculated. The following subtest then involved retaining the sample at a specified time and temperature for aging to occur. The frequency and strain sweep tests are then repeated after the age test so that the viscoelastic properties before and after aging can be compared.

4.1.9 Aging Testing

Hot air and wet aging tests were carried out on rubber samples. Hot air aging was undertaken in accordance to ASTM D573 [107]. Rubber tensile samples, resilience test buttons and wear test blocks were made according to procedure 4.1. Samples were placed in a controlled temperature oven at 75°C, 100°C and 150°C for 12, 24 and 72 hours. The samples were then rested for 16 hours and tested against control samples for comparisons of physical properties and wear test performance. Wet aging was undertaken with slight variations to ASTM D471 [108]. Tensile and resilience samples were immersed in water at a constant temperature of 75°C and 100°C for 12, 24 and 72 hours. The samples were again rested for 16 hours before testing against control samples for comparisons of physical properties and wear test performance.

Aging is a topic that can be debated as to whether it occurs during the wear of a slurry pump or during the storage prior to use. During the operation of a slurry pump, elevated temperatures and liquid with the presence of solids will in theory, relate to heat degradation and aging of the material. It is therefore important to consider these aged properties when characterising the wear performance of a particular rubber.

5 Results and Analysis

5.1 Physical Properties

Table 5.1 Physical Properties of A1, A2, A3 and A4

Material	Tensile Strength (MPa)	Tear B Strength (kN/m)	Tear C Strength (kN/m)	Hardness Shore (A°)	Density (g/cm³)	Resilience (%)
A1	24.89	45.11	28.17	39	0.982	70
A2	31.06	122.24	76.85	58	1.075	63
A3	25.18	84.24	42.02	50	1.066	65
A4	21.17	128.08	94.74	61	1.114	40

The four rubber compounds were tested in accordance with the experimental test methods outlined in chapter 4.5. Table 5.1 shows a brief summary of the physical properties of A1, A2, A3 and A4. The hardness of A1 is low as a result of high weight percentage of natural rubber (NR) content in the compound formulation with minimal filler reinforcement. A4 has the highest hardness value due to its large percentage of carbon black filler reinforcement in the compound. The A4 material also has the highest density value of the four rubbers investigated. The tensile strength of the rubbers are all above 20 MPa with A2 being the highest and A4 the lowest. Tear B strength refers to the amount of energy required to break a rubber sample that has been initially cut. Tear C strength similarly refers to the amount of energy required to break a rubber sample that has been moulded with an initiation failure point. A4 has the highest tear B and C strength in contrast to the A1 which has the lowest tear B and C strength. It can be seen from these results in that the hardness of the rubber can be correlated to the tear strength. As the hardness of the rubber increases, so does the tear strength. A4 has the highest tear strength and high hardness whereas A1 has the lowest tear strength and hardness. A2 and A3 have a similar chemical composition in which they both use silica as a reinforcing agent and silane as a coupling agent, however

their physical properties differ. This occurrence will be discussed in a later chapter in this thesis.

The four rubber compounds investigated in this project are natural rubber based, devised from 1,4 *cis*-polyisoprene. The art of relating the properties of rubber materials to wear, in particular wear in a slurry pump applications is a challenging task. However, with better understanding of the mechanisms involved, the material behaviour at a molecular level and the physical and viscoelastic properties, a relationship is sought.

5.2 *Rubber Process Analyser (RPA) Cure Curves*

Cure curves are used for determining the optimum cure time for each rubber material. They are ascertained by measuring the Elastic Torque (S') over a certain period of time. The elastic torque relates to the rubber's elasticity. It is basically the torque response that is in-phase with the applied strain [57]. A fully cured rubber occurs at a point where the S' becomes constant with time. In this project, the RPA was used initially to determine the quality of the rubber before sample preparation. The test program "120-140 cure" was run as this represents the cure temperature of the rubbers at 140°C and cure time of 120 minutes. At T'99 the rubber is cured to 99% and the S' is near the maximum. Therefore, the T'99 time was used to determine the optimum cure time for each rubber. Figure 5.1 illustrates the S' vs. time graph for each of the rubbers investigated. It can be seen that the S' flattens out with time indicating that the vulcanisation process is complete. The cure time data was then used to cure the rubber samples for wear, tensile, resilience, hardness and density tests. This flattening out of the graph and cure time data will be discussed further in a later chapter.

Problems with the A2 and A3 materials arose during the testing of physical properties. The cure test program was altered to run at longer testing time ensuring the optimum cure time for A2 and A3 was achieved. The optimum cure time was used for each rubber determining

aging, physical, viscoelastic properties and the overall wear performance. The optimum cure time and temperature for the four materials are listed in Table 5.2.

Table 5.2 Cure time and temperature for A1, A2, A3 and A4

Conditions	A1	A2	A3	A4
Cure Temperature (°C)	140	140	140	150
Cure time (mins)	25	35	60	20

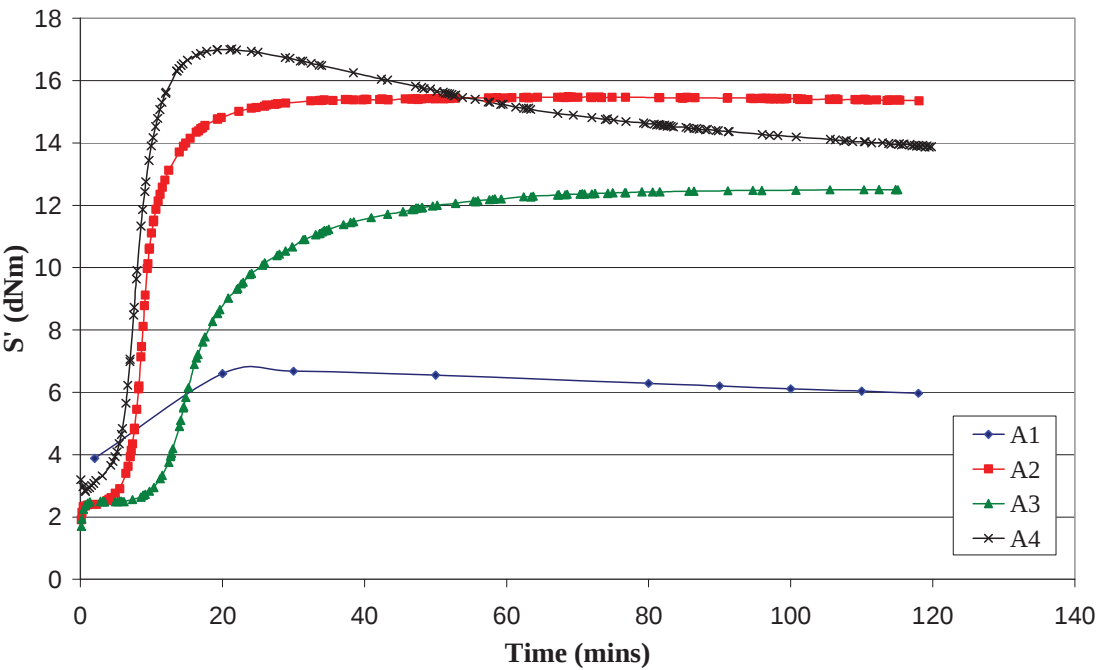


Figure 5.1 RPA cure curves for A1, A2, A3 and A4

5.3 Wear Behaviour

The wear behaviour of A1, A2, A3 and A4 was tested using the eductor wear tester. The eductor simulates the erosive wear that is commonly experienced by the slurry pump in service. The shape of the wear scars is dictated by the shape of the jet stream of the eductor wear tester. Since the shape of the jet stream is spherical, the wear scar is a reflection of this spherical shape depending on the angle of impingement. An optical micrograph of a worn sample tested at an impingement angle of 20° can be seen in Figure 5.2. The volume of this wear scar was then analysed using the Talysurf CLI1000 surface profilometer, see Figure 5.3. Impingement angles of 45° and 90° produced different wear scar shapes with 90° being the most representative of the jet stream shape. Figures 5.4a and 5.4b show optical photographs of wear scars attacked with abrasive particles at these angles.



Figure 5.2 A typical optical photograph of a wear scar with the angle of impingement at 20° . A2 material eroded with $300\mu\text{m}$ - $180\mu\text{m}$ Glass spherical particles at 20m/s [3]

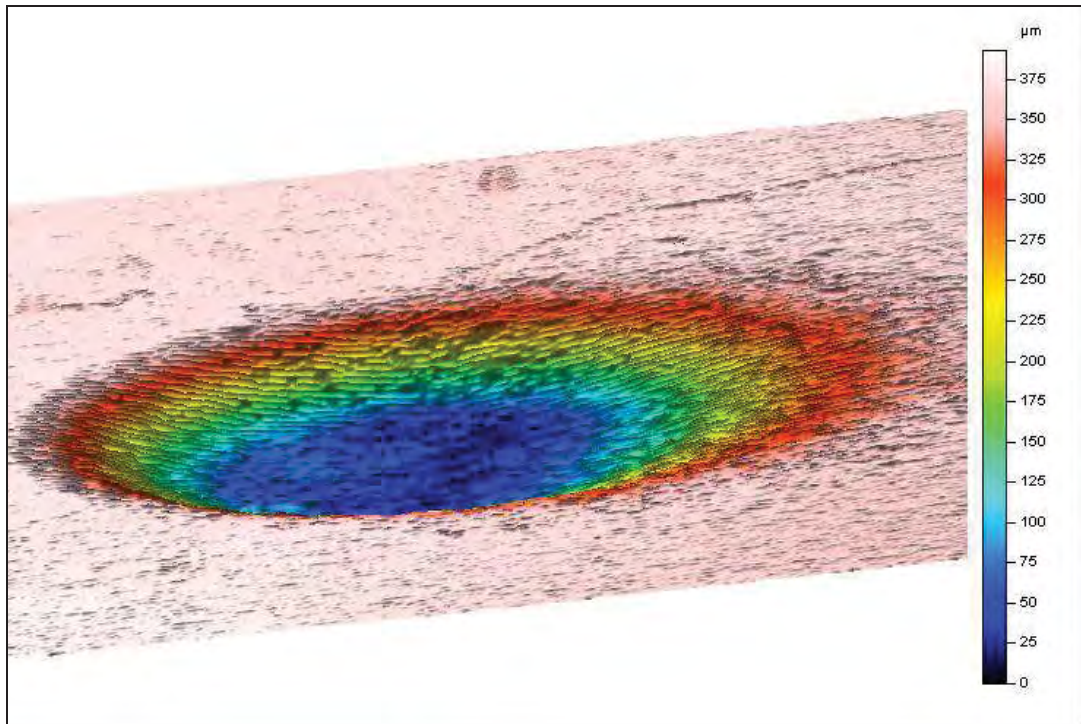


Figure 5.3 A typical 3D image of a wear scar with the angle of impingement at 20°



Figure 5.4a A typical optical photograph of a wear scar with the angle of impingement at 45° . A1 material eroded with $1000\mu\text{m}$ SiC particles at 45m/s [3]

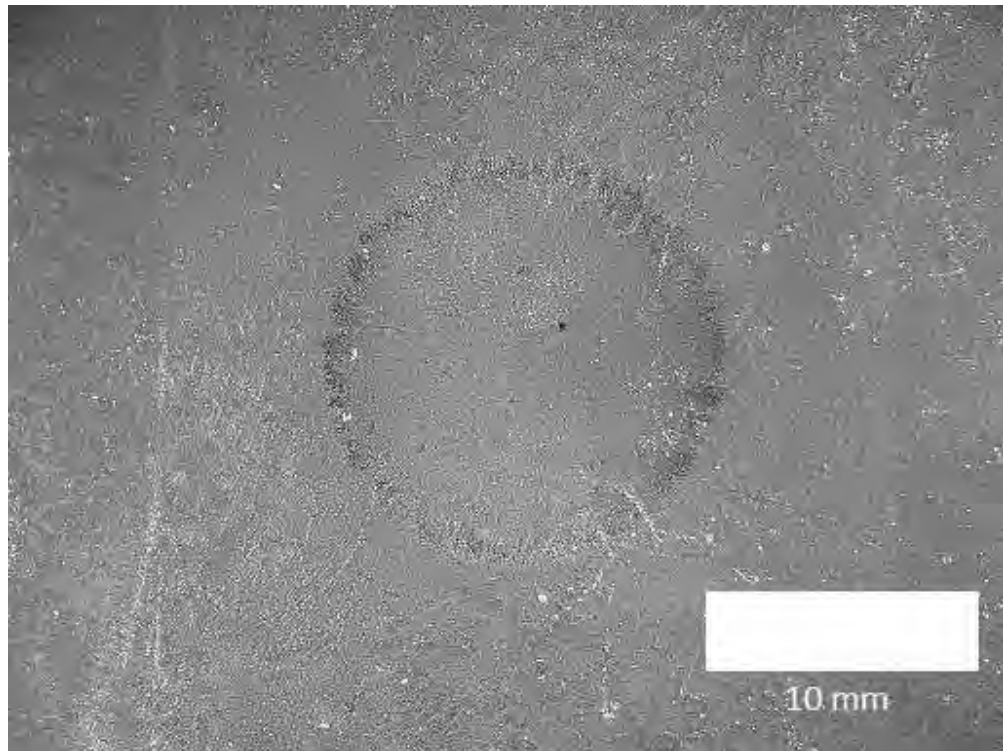


Figure 5.4b A typical optical photograph of a wear scar with the angle of impingement at 90° . A1 material eroded with $100\mu\text{m}$ Al_2O_3 particles at 20m/s [3]

5.3.1 Particle Size Effects

Figures 5.5 (a – d) shows the influence of particle size on volume wear loss per particle impingement. The calculation for the wear loss per particle impingement is shown in section 4.1.7.2. The graphs illustrate clearly the performance of each of these materials at different particle sizes. The general trend of the graphs shows that for smaller particles, wear resistance is similar for all materials. However, at larger particles there is a clear differentiation. In this case at impingement angles of 20° , 45° , 60° and 90° the A3 material is the most wear resistant material with A4 material the least wear resistant. Analysing Figure 5.5a it can be seen that particle sizes of $200\mu\text{m}$ and $350\mu\text{m}$, the differences between the four materials are minimal. This observation is also found in Figures 5.5(b – d), where contrasts between the four materials do not appear until after the particle size is above $500\mu\text{m}$. At this particle size, it is clearly shown that A3 has the lowest volume wear loss per

particle impingement. This trend continues as the particle size increases to the largest tested particle size of 1000 μm .

The trend of the graphs differs slightly between each wear test impingement angle. In Figure 5.5a at an impingement angle of 20°, A4, A2 and A1 have similar volume wear loss values up to 750 μm . At the largest particle size of 1000 μm , wear resistance is most differentiated. However, A1 and A2 perform similarly at 1000 μm with A3 the most wear resistant. Figures 5.5b and 5.5c show a different trend at 1000 μm where the wear loss data for A1, A2 and A3 cluster together. The impingement angles at 45° and 60° may not influence the wear behaviour of these materials in contrast to the 20° and 90° impingement angles. At the high impingement angle of 90° shown in Figure 5.5d, the wear resistance of each material is distinct from particle sizes above 500 μm to 1000 μm . A4 has the lowest wear resistance with A1, A2 and A3 to follow in ascending performance order.

The results from this testing supports the theory of particle size effect on the wear resistance of rubber materials. The wear loss of each tested material is increases with increasing particle size. This concept will be revisited later in this thesis.

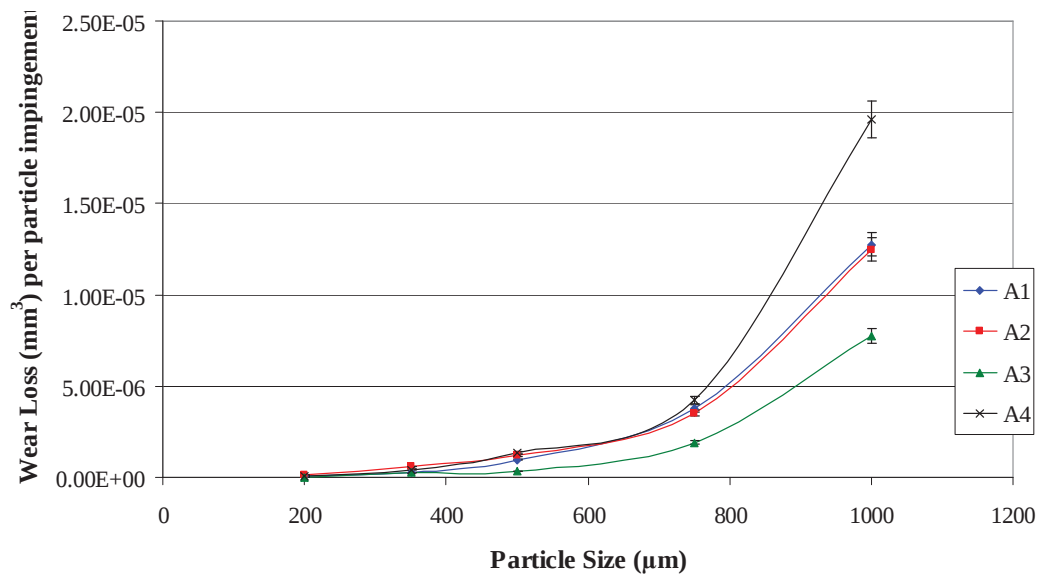


Figure 5.5a A1, A2, A3, A4 volume wear loss vs. particle size wear tested at impingement angle of 20°

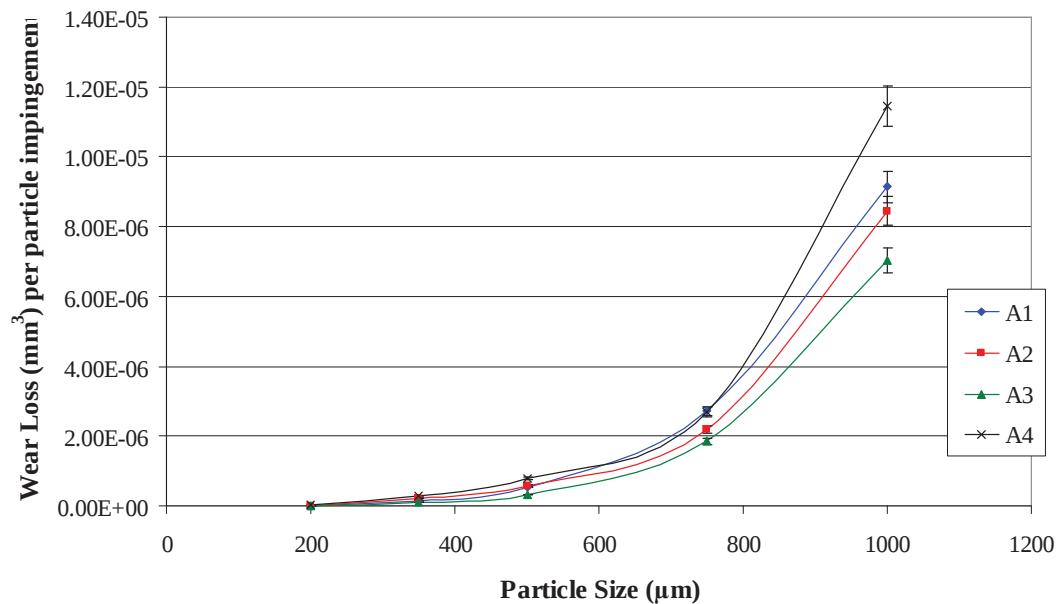


Figure 5.5b A1, A2, A3, A4 volume wear loss vs. particle size wear tested at impingement angle of 45°

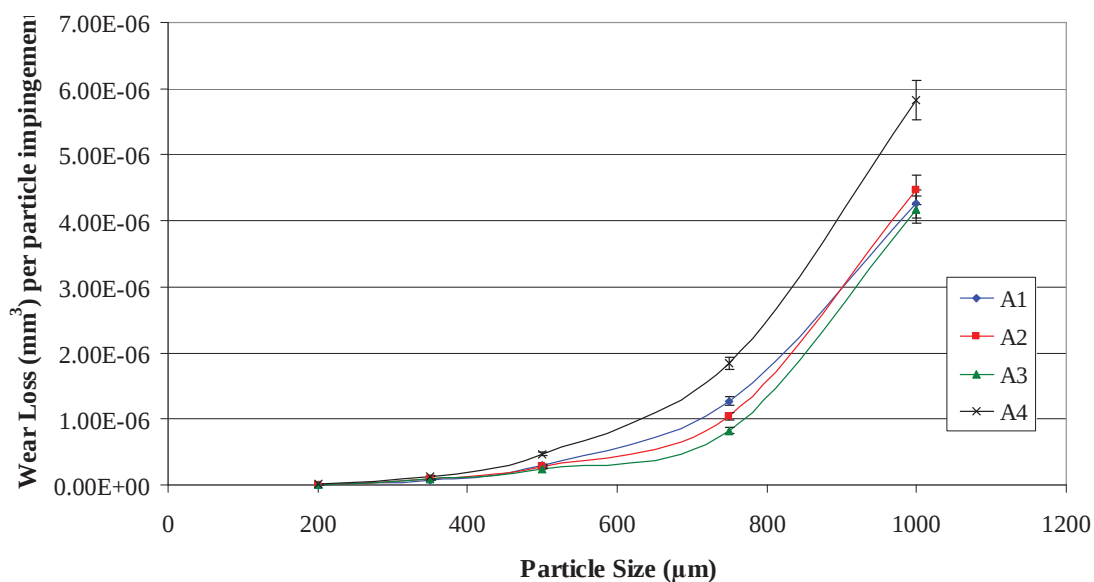


Figure 5.5c A1, A2, A3, A4 volume wear loss vs. particle size wear tested at impingement angle of 60°

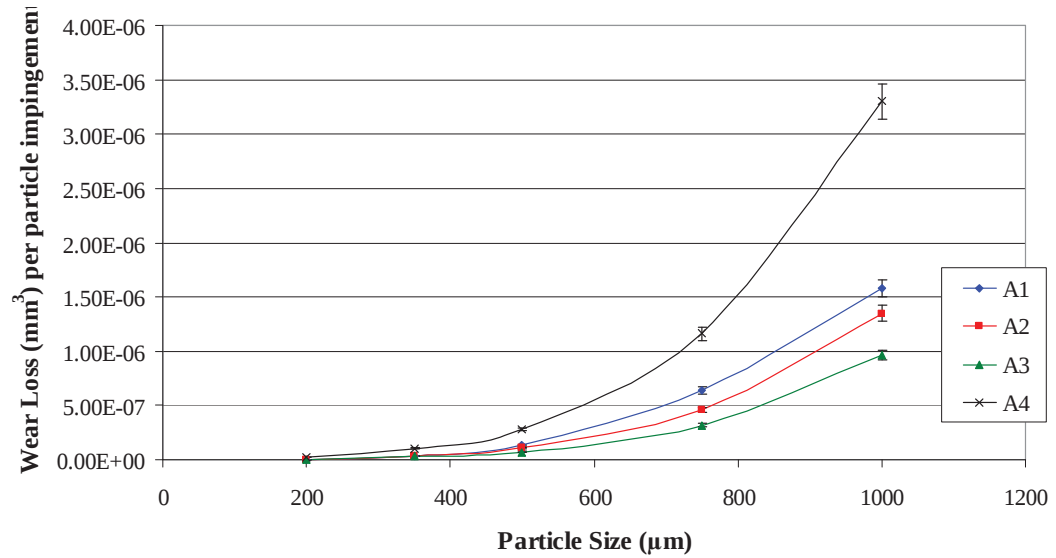


Figure 5.5d A1, A2, A3, A4 volume wear loss vs. particle size wear tested at impingement angle of 90°

5.3.2 Impingement Angle Effects

Figures 5.6 (a – e) show the data in Figures 5.5 (a – d) replotted to illustrate the influence of particle size on the wear behaviour of A1, A2, A3 and A4 at different impingement angles. The graphs show an inverse relationship between impingement angle and the wear loss per particle. The material performance however behaves differently from the variations on particle size. In Figure 5.6a the general trend for each material performance is clearly shown. A4 has the highest wear loss per particle impingement at all angles, A1 and A2 has similar wear losses at all impingement angles, while A3 has the lowest wear loss at impingement angles of 20° and 45°. A1, A2 and A3 tend to have comparable wear loss at higher impingement angles of 60° and 90°. These observations may be attributed to the wear mechanism and will be discussed later in this thesis. At the particle size of 750μm shown in Figure 5.6b, the trend of each material performance is similar to the 1000μm particle size test set. The difference is that the wear resistance of each material clearly shows A4 has the least wear resistance, followed by A1, A2 and A3 with the lowest wear loss per particle impingement at all tested angles.

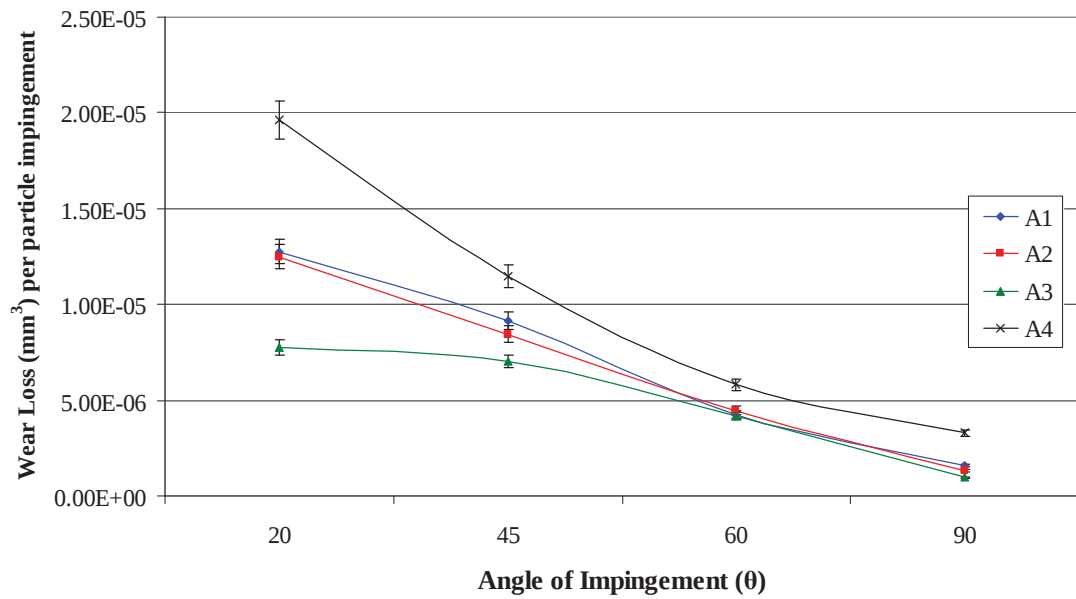


Figure 5.6a A1, A2, A3, A4 wear tested with Al_2O_3 particle size $1000\mu\text{m}$ at impingement angles of 20° , 45° , 60° and 90°

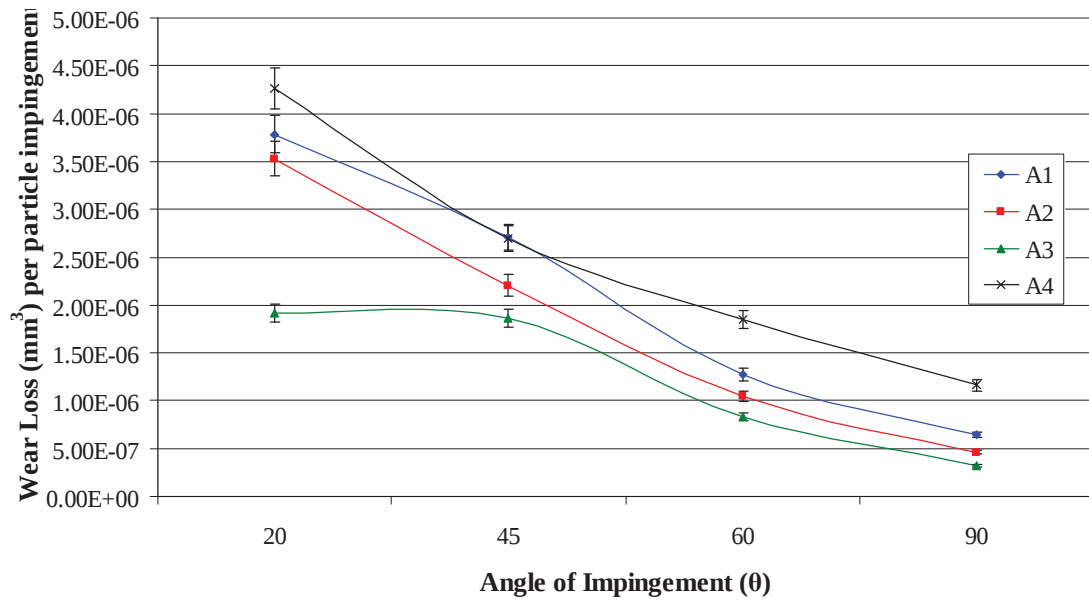


Figure 5.6b A1, A2, A3, A4 wear tested with Al_2O_3 particle size $750\mu\text{m}$ at impingement angles of 20° , 45° , 60° and 90°

Figure 5.6c shows similar trends of material performance with Figure 5.6a, where A4 has the highest wear loss and A1 and A2 have comparable wear loss per particle. However at the low impingement angle of 20°, A2 wear resistance is closer to A4 rather than equal to A1. This increase in wear loss per particle impingement in A2 is more evident in Figures 5.6d and 5.6e, where A2 develops into the worst performer. It is of interest to note that this trend only occurs at the impingement angle of 20°. As the impingement angles for wear testing are increased, the trend of the performance of A2 tends to match up with Figures 5.6a and 5.6c. The increase in wear loss per particle impingement could be related to the decrease in particle size from 500µm – 200µm. This variable could affect only A2 and not the other materials. The concept will be revisited and explained further in a later chapter of this thesis.

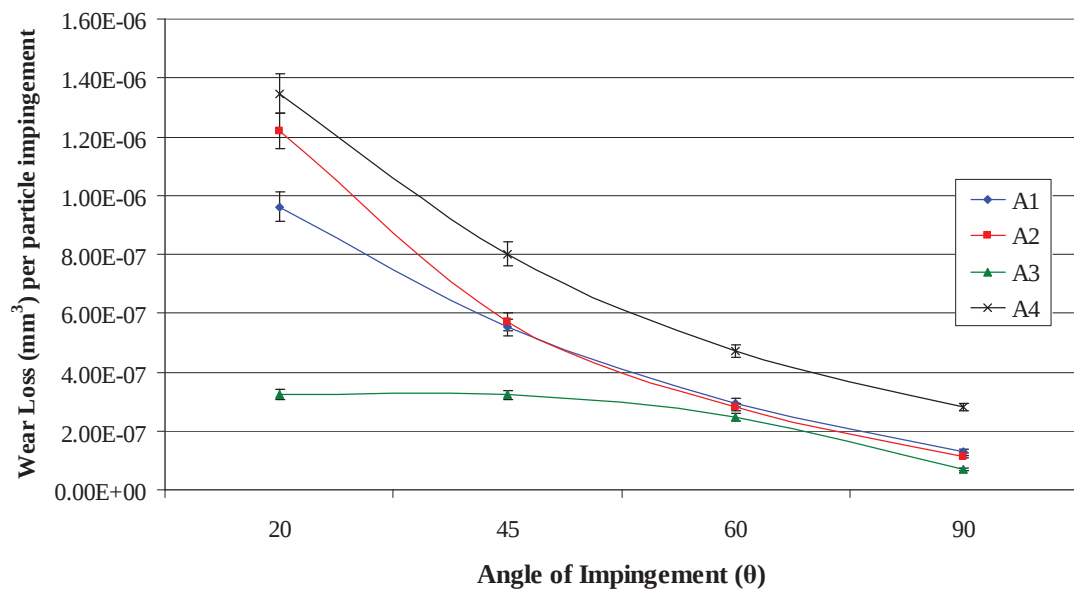


Figure 5.6c A1, A2, A3, A4 wear tested with Al₂O₃ particle size 500µm at impingement angles of 20°, 45°, 60° and 90°

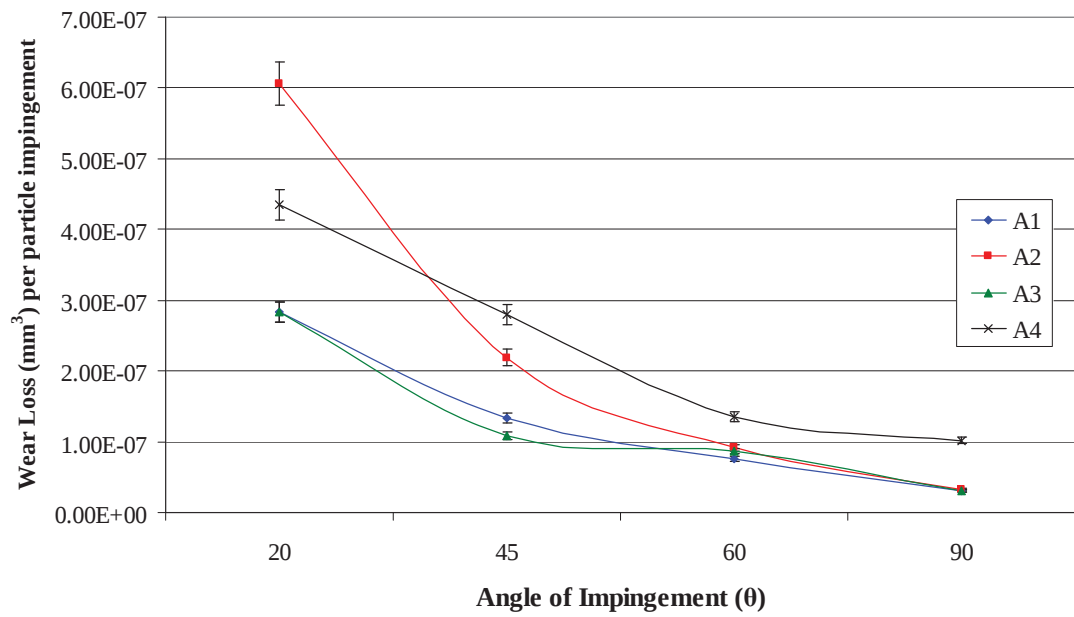


Figure 5.6d A1, A2, A3, A4 wear tested with Al₂O₃ particle size 350μm at impingement angles of 20°, 45°, 60° and 90°

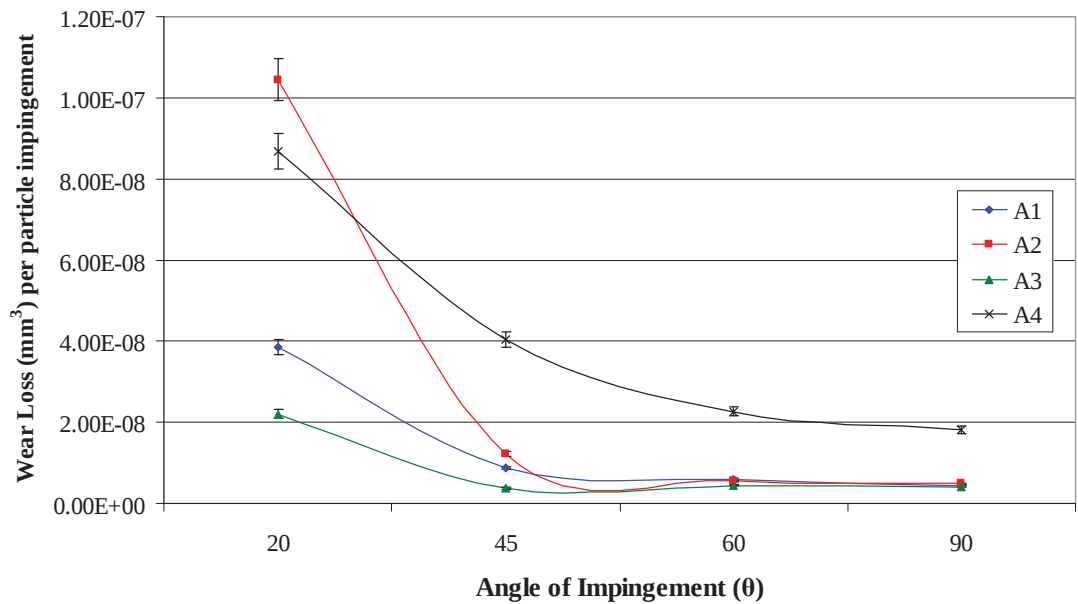


Figure 5.6e A1, A2, A3, A4 wear tested with Al₂O₃ particle size 200μm at impingement angles of 20°, 45°, 60° and 90°

5.3.3 Curing Effects

Erosive wear testing was carried out on rubber samples that have been air aged at 100°C and 75°C for 72 hours. Figure 5.7 shows the volume wear loss of A1, A2 and A3 after hot air aging at impingement angles of 20°, 45° and 90° with 750µm Al₂O₃ particles. It can be seen from the graph that A2 and A3 are more curing resistant than A1. This result is expected due to the heat resistant additives that make up A2 and A3. A1 is basically a natural rubber, not heavy reinforced nor filled with heat resistant additives. It can be seen from the graph that A1 aged for 100°C has a higher volume wear loss after wear testing than the A1 aged for 75°C. Therefore, the volume wear loss is expected to rise with an increase in aging temperature and time.

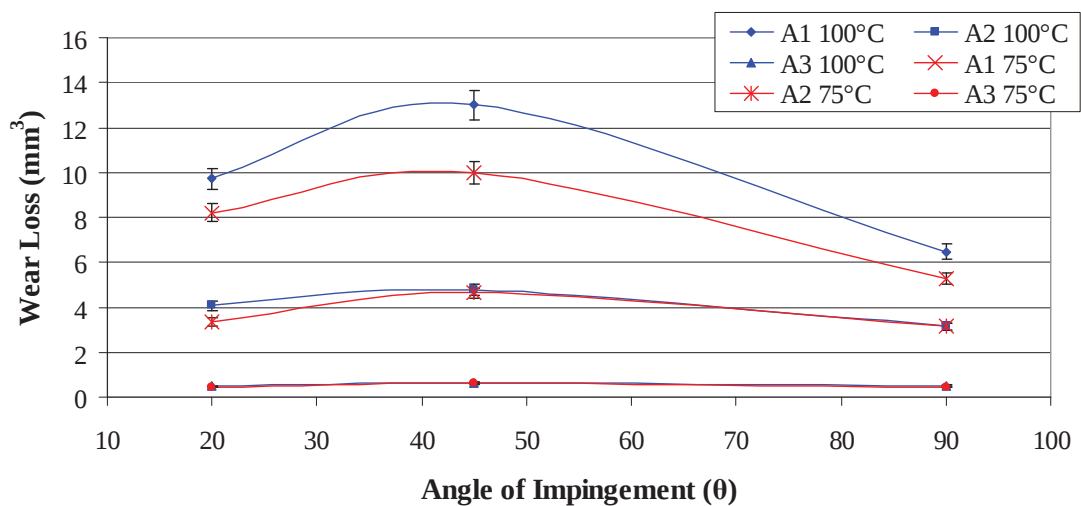


Figure 5.7 A1, A2, A3 samples air aged at 75°C and 100°C for 72 hrs then wear tested with Al₂O₃ particle size 750µm at impingement angles of 20°, 45° and 90°

Figure 5.8a shows the wear loss of the rubber samples after hot air aging at 75°C and 100°C for one month as a function of wear loss. At the hot air aging temperature of 100°C, the wear loss is increased significantly in comparison to the control samples and the 75°C aging temperature. A3 and A4 do not decrease in wear resistance drastically at the aging temperature of 75°C. However, at 100°C the wear loss is increased significantly with A4 resulting in three times higher wear loss than the control sample. Interesting to note that for

A1 and A2, when aged at 75°C, the wear loss decreases in comparison to the control samples. Figure 5.8b illustrates the wet aging influence on the rubber samples as a function of wear loss. The wet aging test reproduces the process conditions that a slurry pump would undergo in the field. The results indicate that each rubber will degrade between 30 to 50 percent more than the control sample following the wet aging process. A4 again has the highest wear loss before and after aging.

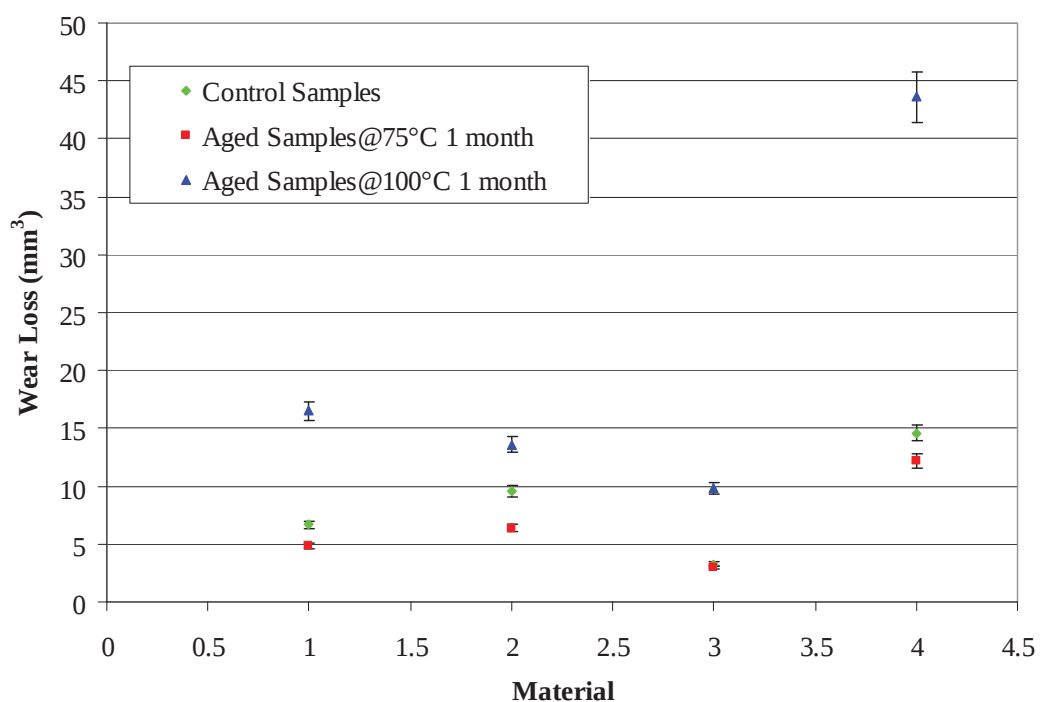


Figure 5.8a A1, A2, A3, A4 samples air aged at 75°C and 100°C for 1 month vs. control samples unaged.

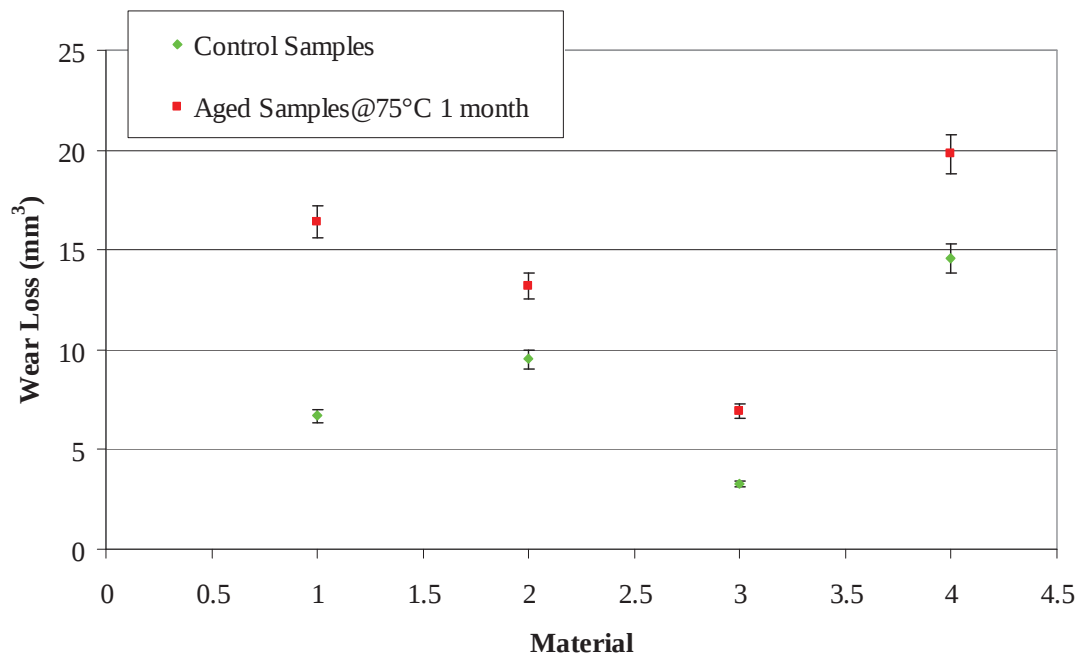


Figure 5.8b A1, A2, A3, A4 samples wet aged at 75°C for 1 month vs. control samples unaged.

5.3.4 Particle Size – Impingement Angle Relationship

The preceding sections have been analysing the wear test data from a chemical formulation view point. We must now consider the intrinsic particle size and impingement angle influence on the wear resistance of each of the materials. Figures 5.9 (a – d) shows the volume wear loss per particle impingement as a function of particle size for the tested rubber materials. It can be seen that A1, A2 and A4 follow the general trend that is with increasing particle size there is also an increase in wear loss. A decrease in impingement angle will also increase the wear loss as shown in Figure 5.9 (a – d). Lower angles of impingement tend to cause cutting and tearing of the rubber due to the sharp nature of the abrasive particles as opposed to indentation of the particles at higher angles of 90° where the rubber resilience shields the rubber from damage. This concept will be discussed further in a later chapter of this thesis.

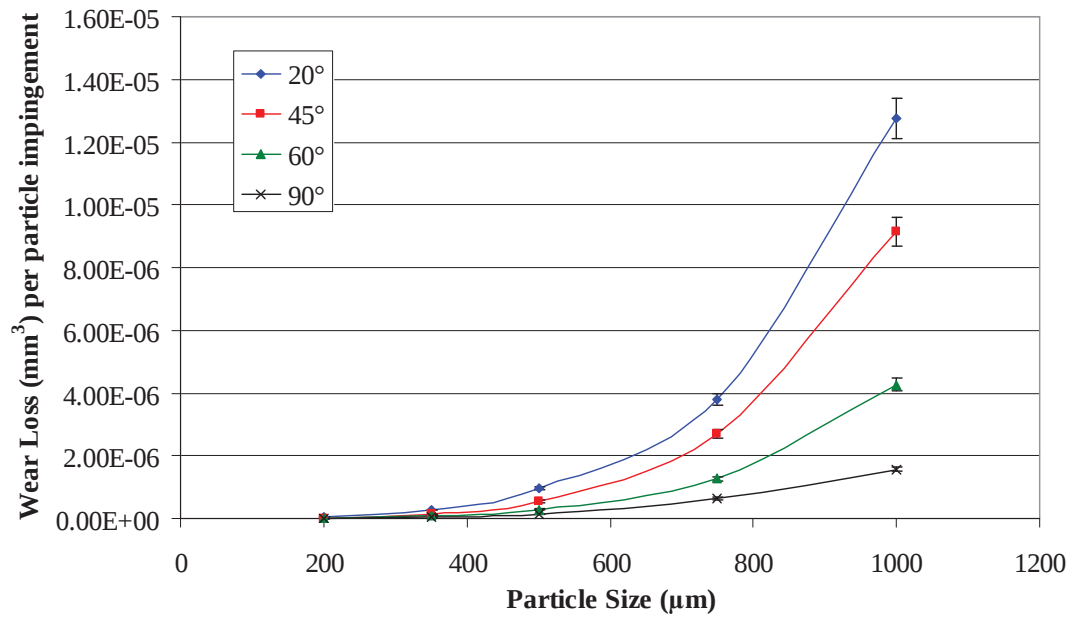


Figure 5.9a A1 volume wear loss vs. impingement angles of 20°, 45°, 60° and 90°

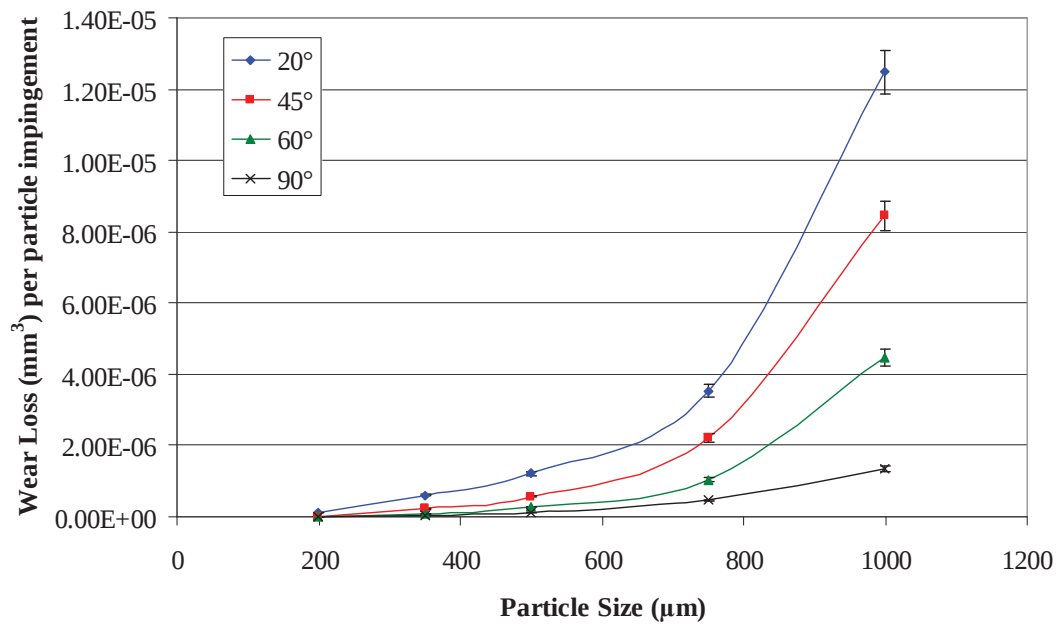


Figure 5.9b A2 volume wear loss vs. impingement angles of 20°, 45°, 60° and 90°

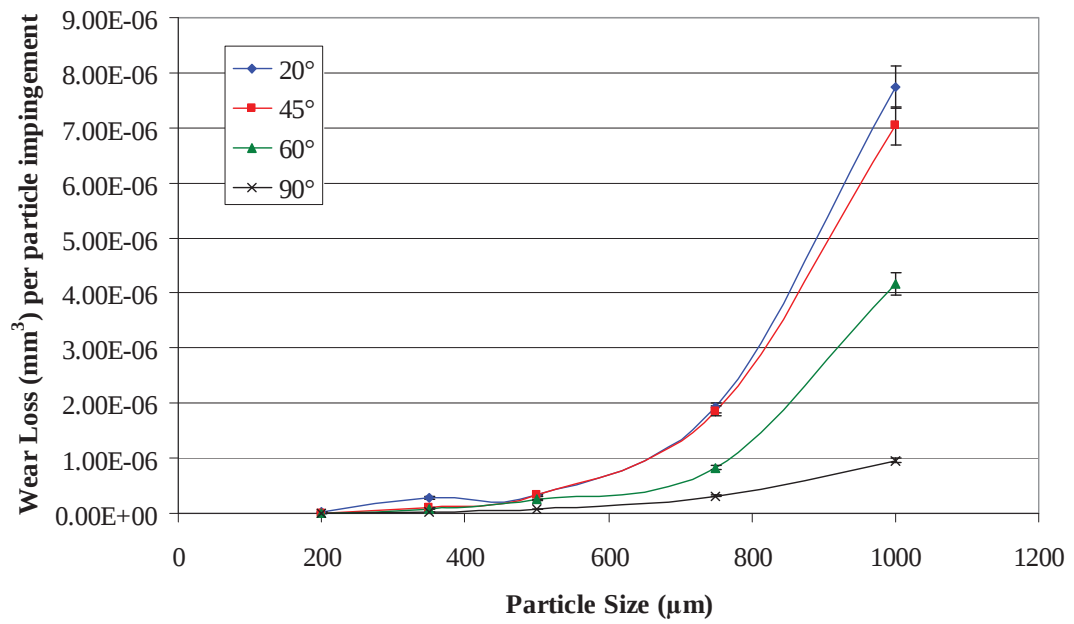


Figure 5.9c A3 volume wear loss vs. impingement angles of 20°, 45°, 60° and 90°

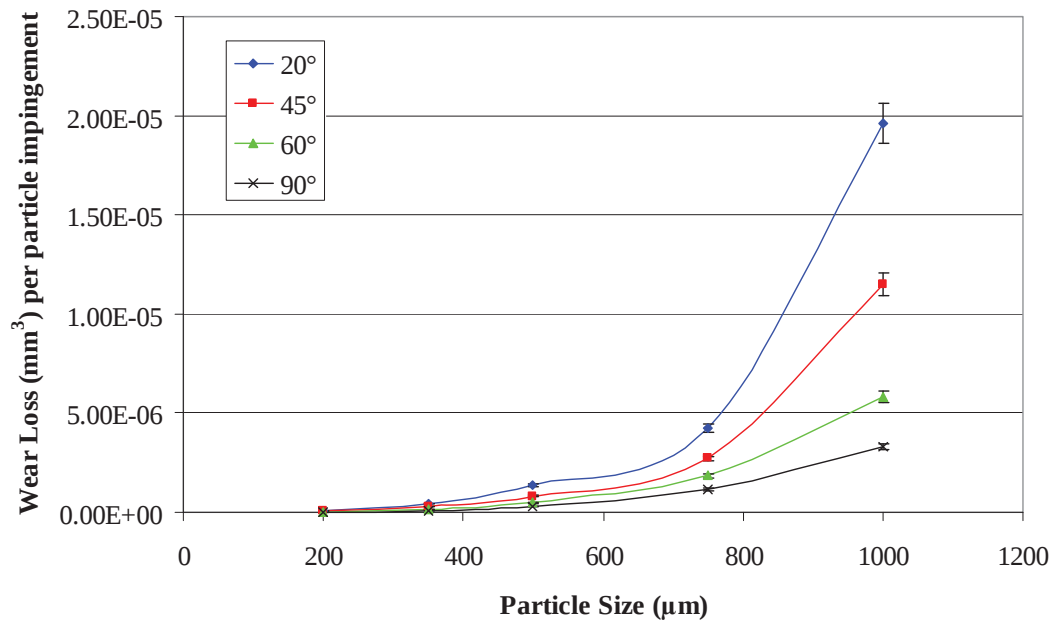


Figure 5.9d A4 volume wear loss vs. impingement angles of 20°, 45°, 60° and 90°

The accumulated wear loss for each material was evaluated against their relative physical properties outlined in section 5.1. Figures 5.10 – 5.14 shows the total wear loss of each material under all variables as a function of physical properties. The wear loss as a function of hardness is shown in Figure 5.10. The accumulated wear loss for A3 was the lowest whereas A4 had the highest. It is interesting to note that the total wear loss graphical trend did not match the graphical trend of the rubber material hardness. The data suggests there may be a wear resistance threshold at hardness range of 50 A° since at 60 A° the wear loss is significantly higher. However, the low hardness of the A1 material and 2nd least amount of wear does contradict this observation. One must consider the chemistry composition of the rubber in order to come to a rational conclusion.

Resilience as mentioned in literature [1, 3, 5, 6, 18] is a key physical property for rubber performance. Figure 5.11 shows the accumulated wear loss for each material as a function of resilience. The general trend of the data confirms the importance of a high resilient rubber in pump lining applications. A4 has the lowest resilience hence the highest accumulated wear loss whereas A1, A2 and A3 all have high resilience resulting in significantly lower accumulated wear loss. Within this group A2 has the lowest resilience leading to the highest accumulated wear loss however the same trend is not seen in A1 where it has the highest resilience in comparison yet the second best wear resistance in the group. Again more explanation is required as with the material hardness property to further understand why A1, A2 and A3 which all have relative resilience but all have different wear resistance.

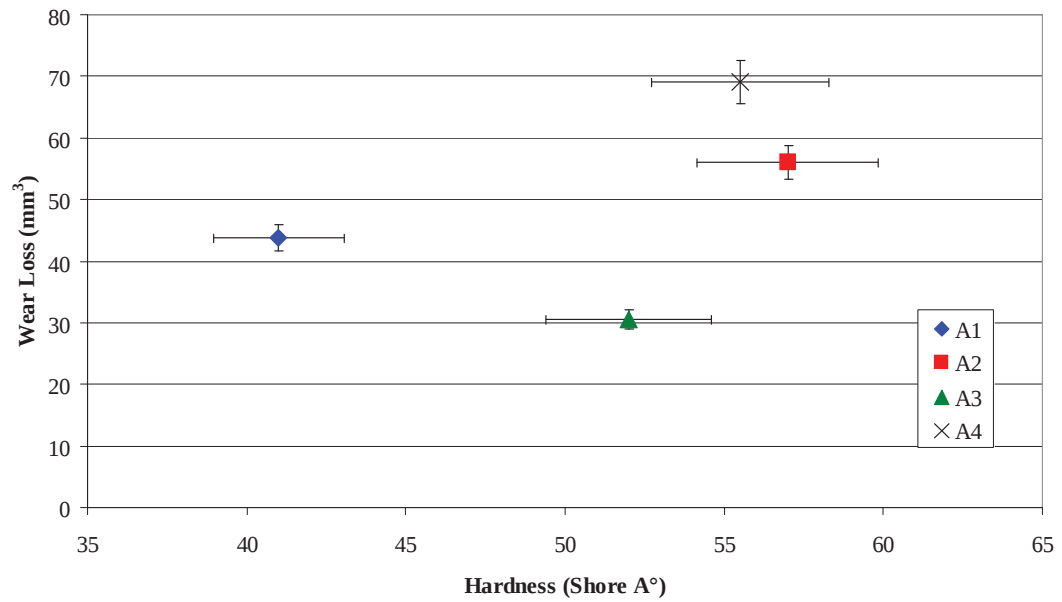


Figure 5.10 Accumulated wear loss of each material A1, A2, A3, A4 represented as a function of hardness

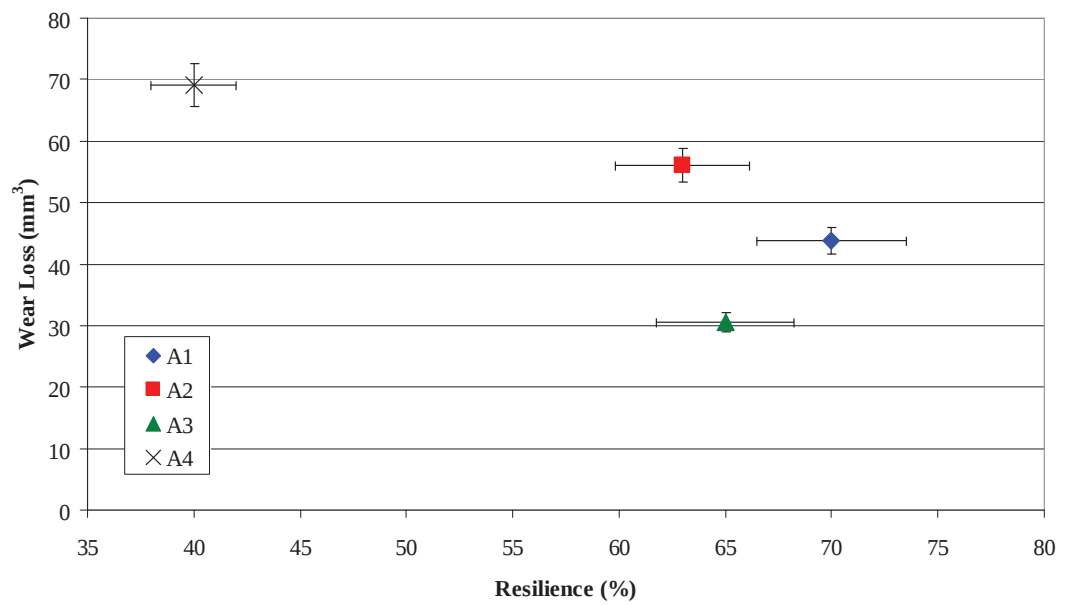


Figure 5.11 Accumulated wear loss of each material A1, A2, A3, A4 represented as a function of resilience

The tensile strength as a function of rubber material accumulated wear loss is shown in Figure 5.12. It was difficult to observe any correlation between tensile strength and the accumulated wear loss. Figures 5.13 and 5.14 show the tensile tear B & C test results as a function of accumulated wear loss. Tensile tear B test is often referred to as the tear propagation test where the sample is nicked or cut before testing. The tensile tear C test is often referred to as the tear initiation test where the sample is pressed and moulded with a 90° triangular point that is directional towards the centre of the sample causing the material to fail at that particular point. It can be seen from Figures 5.13 and 5.14 that high tear strength results in high wear loss.

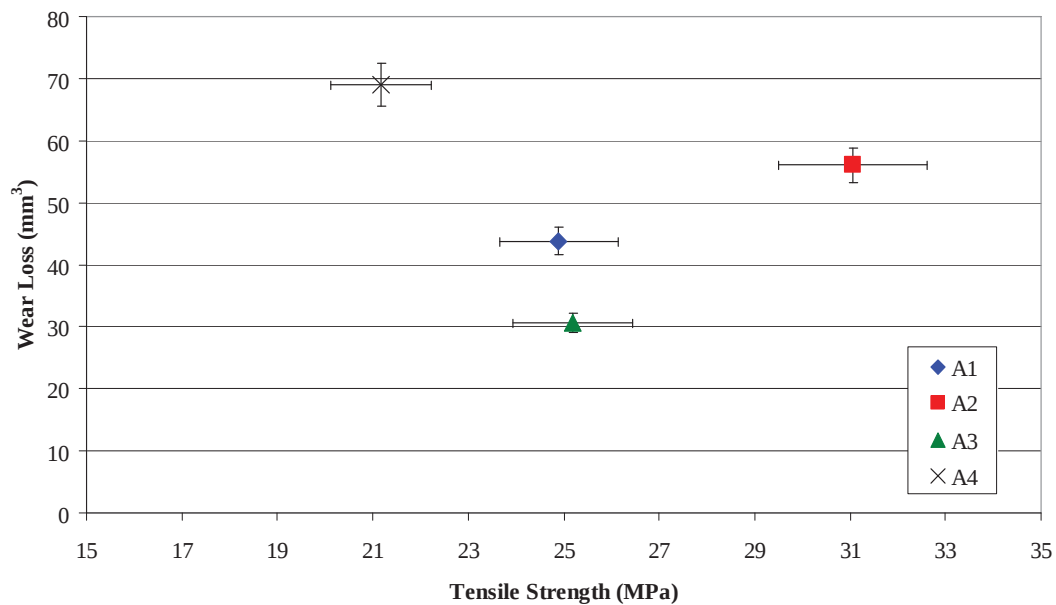


Figure 5.12 Accumulated wear loss of each material A1, A2, A3, A4 represented as a function of tensile strength

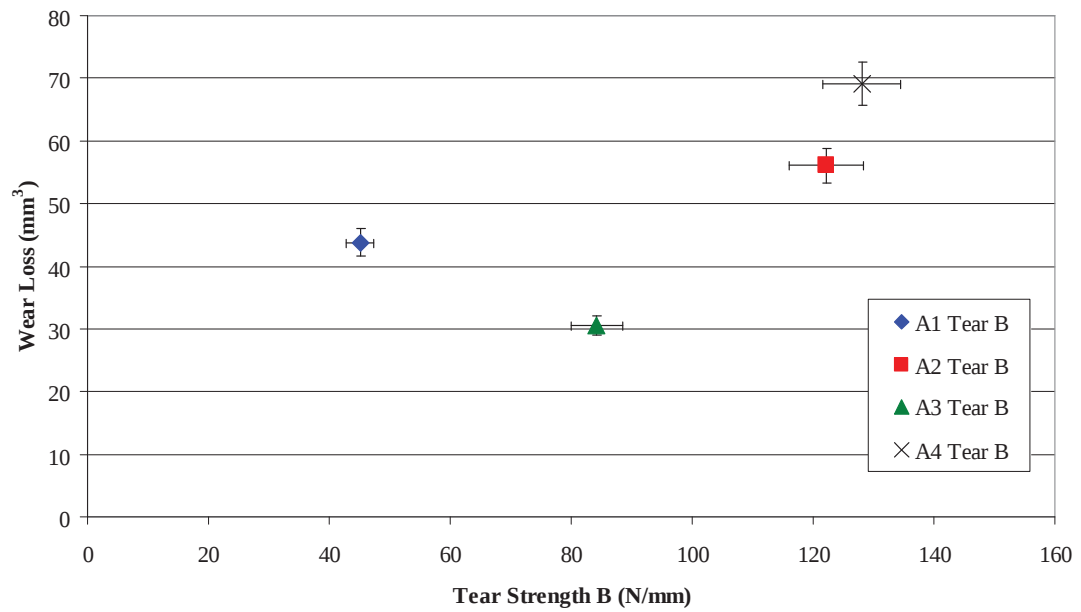


Figure 5.13 Accumulated wear loss of each material A1, A2, A3, A4 represented as a function of tear strength B

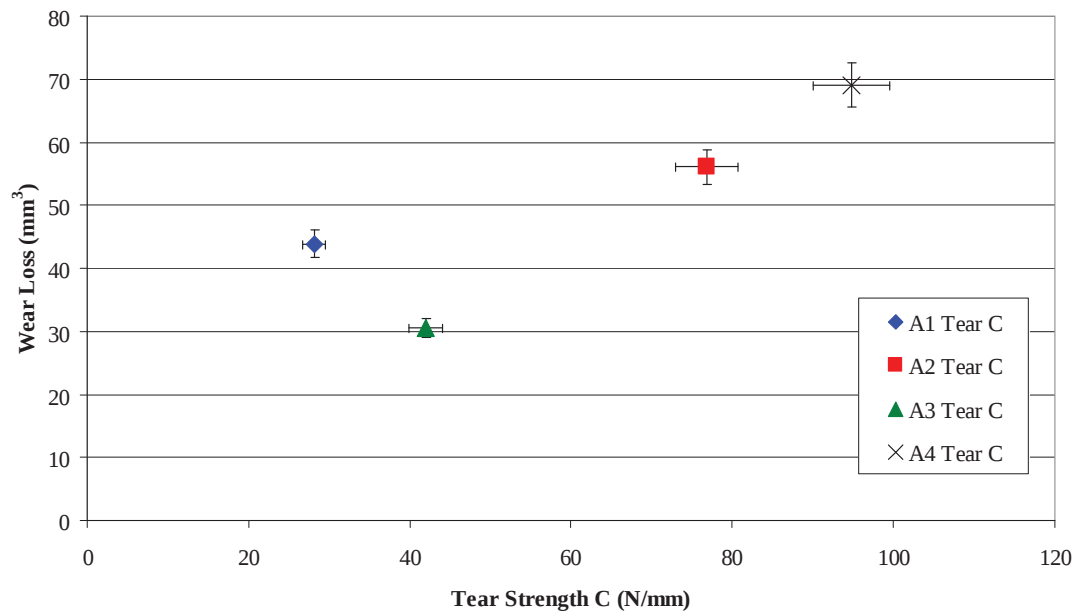


Figure 5.14 Accumulated wear loss of each material A1, A2, A3, A4 represented as a function of tear strength C

5.4 Aging of Rubber

Aging tests were carried out using the Rubber Process Analyser (RPA) on A1, A2, A3 and A4 at different temperatures and test times. The purpose of this testing is to determine the differences in the viscoelastic properties of the rubbers before and after aging in regards to their elastic shear modulus (G'), viscous shear modulus (G'') and tan delta ($\tan \delta$). Figure 5.15a shows the elastic shear modulus G' of each of the rubbers tested in this study. A4 has the highest G' due to its high level of reinforcement filler, carbon black, while A1 has the lowest G' due to its relatively low level of reinforcing agents.

The G'' of the rubbers can be seen in Figure 5.15b. The effect of carbon black as a filler is seen more clearly in this graph as A4's G'' is much higher than the others. Carbon black is known from the literature to absorb and retain heat when exposed to elevated temperatures. It is, therefore, expected that A4 will have the highest value of G'' . A1 has the lowest value of G'' and is represented in the graph. The $\tan \delta$ of each rubber is shown in Figure 5.15c. This ratio of G''/G' is often used to relate to the processability of rubber in the uncured state, the heat build up of the rubber and inversely proportional to the resilience of the rubber in the cured state. These results and findings will be discussed and explained further in a later chapter of this thesis.

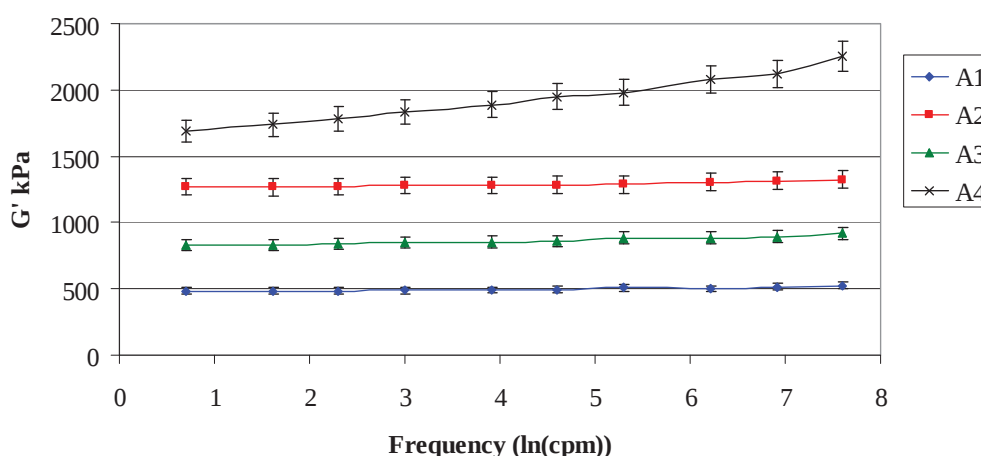


Figure 5.15a G' of A1, A2, A3 and A4 control samples using the RPA

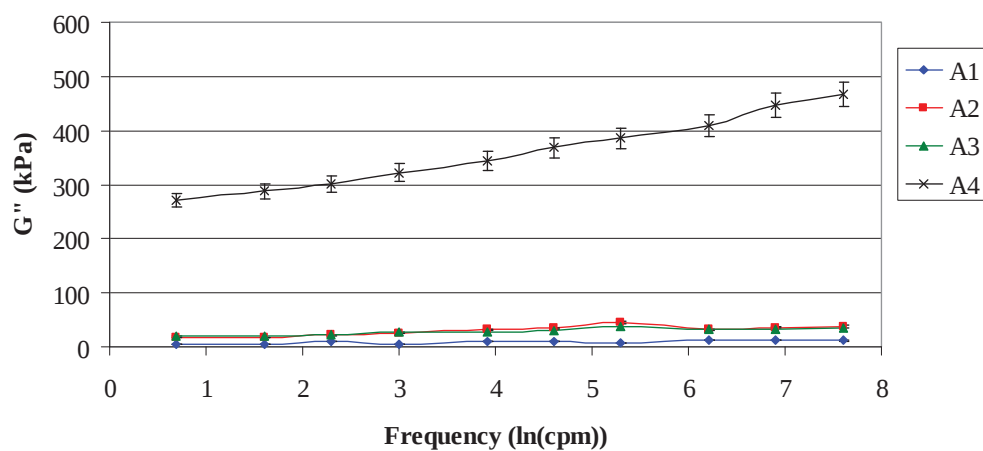


Figure 5.15b G'' of A1, A2, A3 and A4 control samples using the RPA

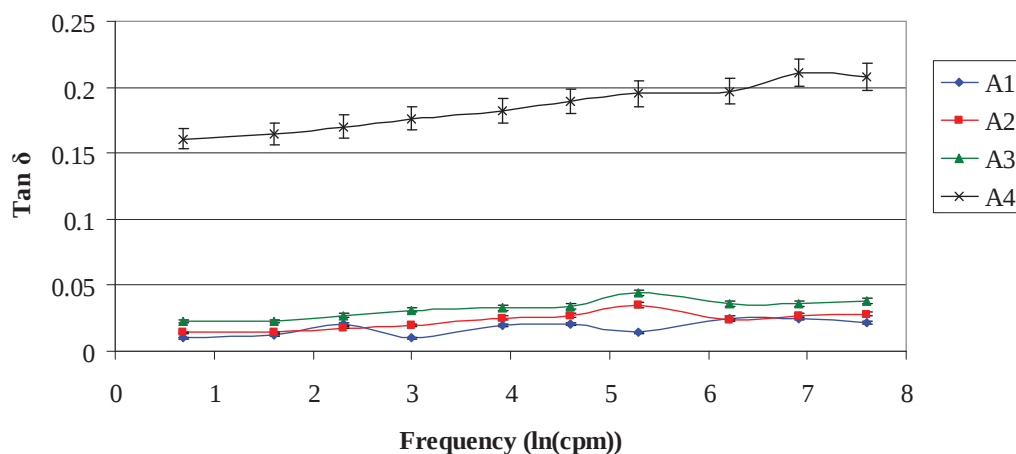


Figure 5.15c Tan Delta of A1, A2, A3 and A4 control samples using RPA

5.4.1 Effect of Curing Time and Temperature of Complex Modulus

G' was tested for A1, A2, A3 and A4 following different aging times (24 hours and 72 hours) and temperatures (75°C, 100°C and 150°C). The results can be seen in Figures 5.16 (a – d). At aging temperatures of below 150°C, the G' does not vary significantly in comparison to the control sample. This result is due to the temperature not being high enough to cause degradation of the viscoelastic properties. Figure 5.16a shows a significant

drop of A1's G' at 150°C for 24 hours. This is expected as A1 does not have heat resistant additives in its chemical compound formulation. The G' for A2, A3 and A4 at 150°C does not drop as severely as for A1. This resistance to high temperature is accredited to the heat resistant additives.

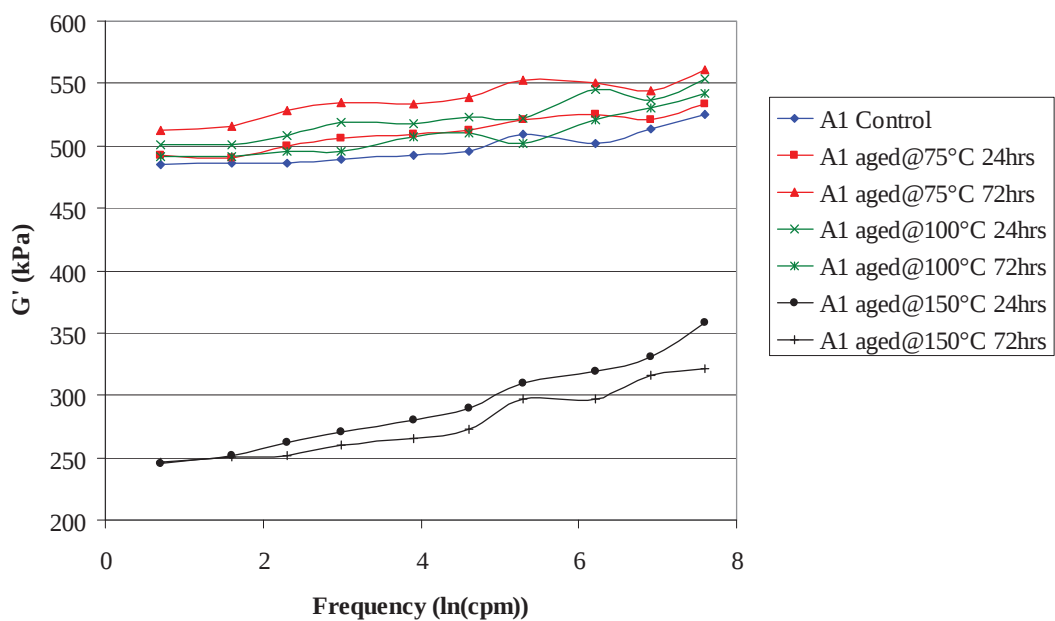


Figure 5.16a G' of A1 before and after aging at 75°C, 100°C and 150°C for 24 and 72 hours using the RPA

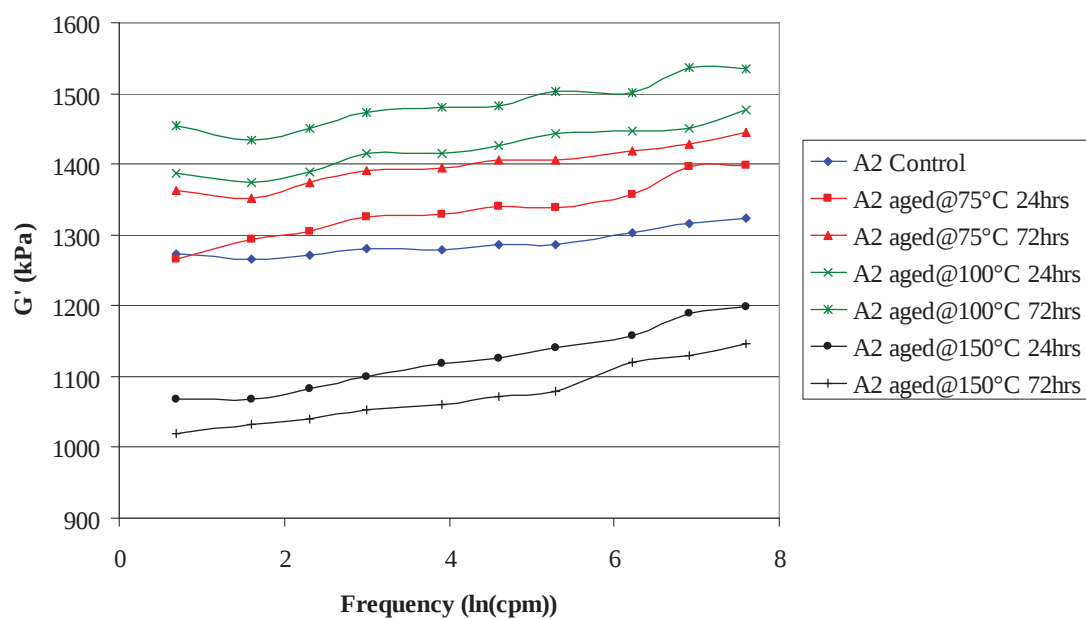


Figure 5.16b G' of A2 before and after aging at 75°C, 100°C and 150°C for 24 and 72 hours using the RPA

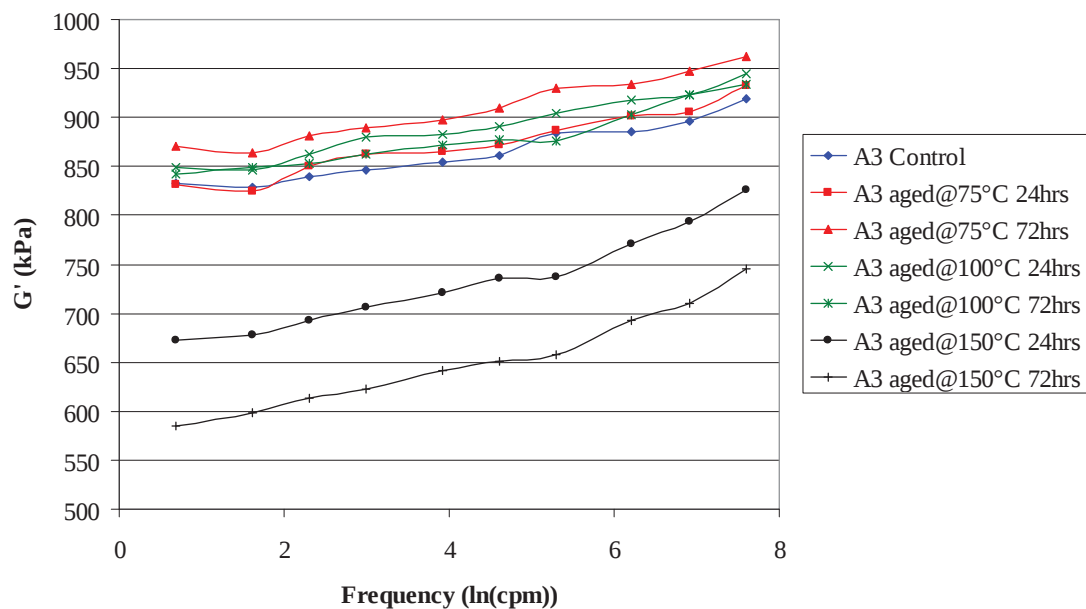


Figure 5.16c G' of A3 before and after aging at 75°C, 100°C and 150°C for 24 and 72 hours using the RPA

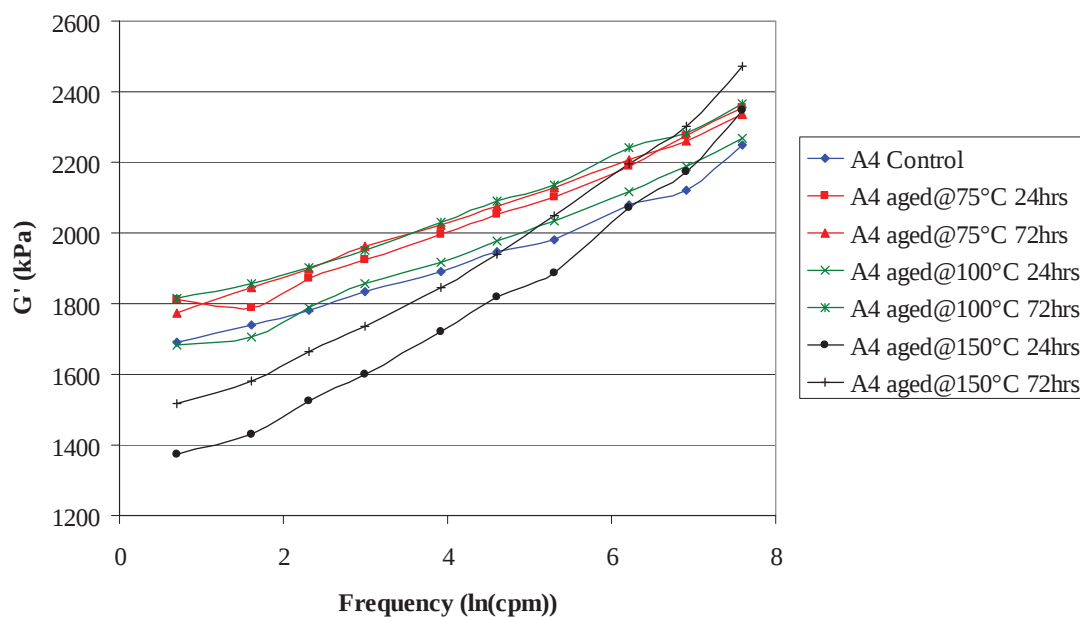


Figure 5.16d G' of A4 before and after aging at 75°C, 100°C and 150°C for 24 and 72 hours using the RPA

Figures 5.17 (a – d) shows the G'' of A1, A2, A3 and A4 aged at 75°C, 100°C and 150°C for 24 hours and 72 hours. Similar to the results for G' at high temperature, the G'' for all rubbers even at 150°C is somewhat higher than the control sample. However, the G'' of A1 does tend to increase significantly at high frequencies. Higher frequencies and stresses may cause the rubber to break down causing more heat dissipation through the rubber resulting in a higher G'' . This concept will be discussed further in a later chapter in this thesis.

The inconsistencies in the G'' data is attributed to the test method reaching the limitations of the RPA instrument. Although some single points of data fluctuate as the frequency is increased, the influence of aging temperature on each material and its viscoelastic property can be seen.

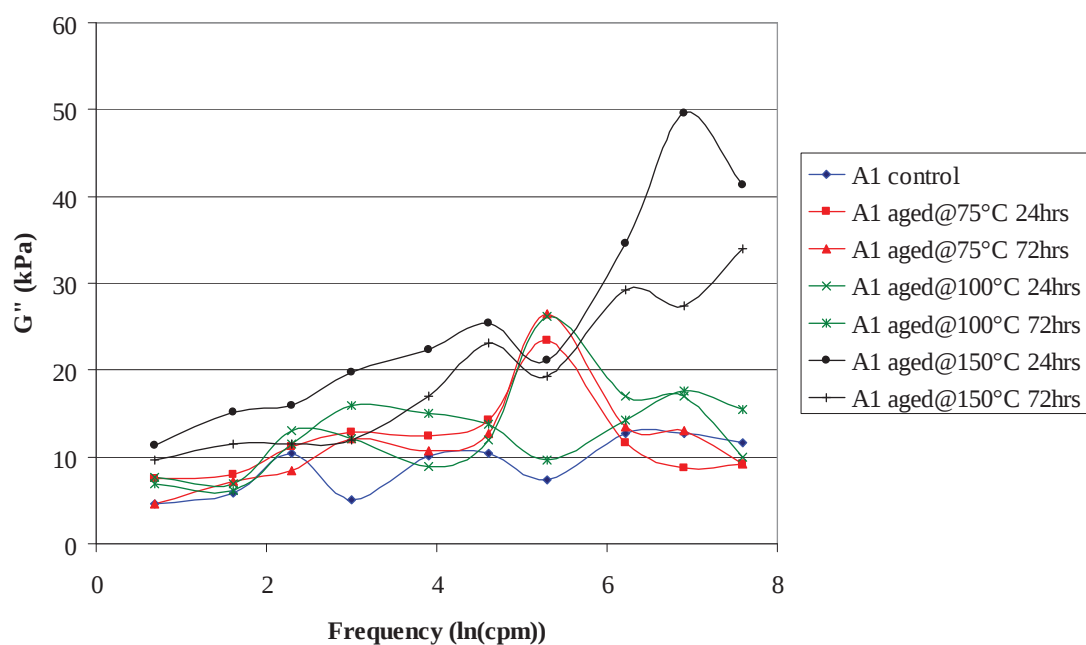


Figure 5.17a G'' of A1 before and after aging at 75°C, 100°C and 150°C for 24 and 72 hours using the RPA

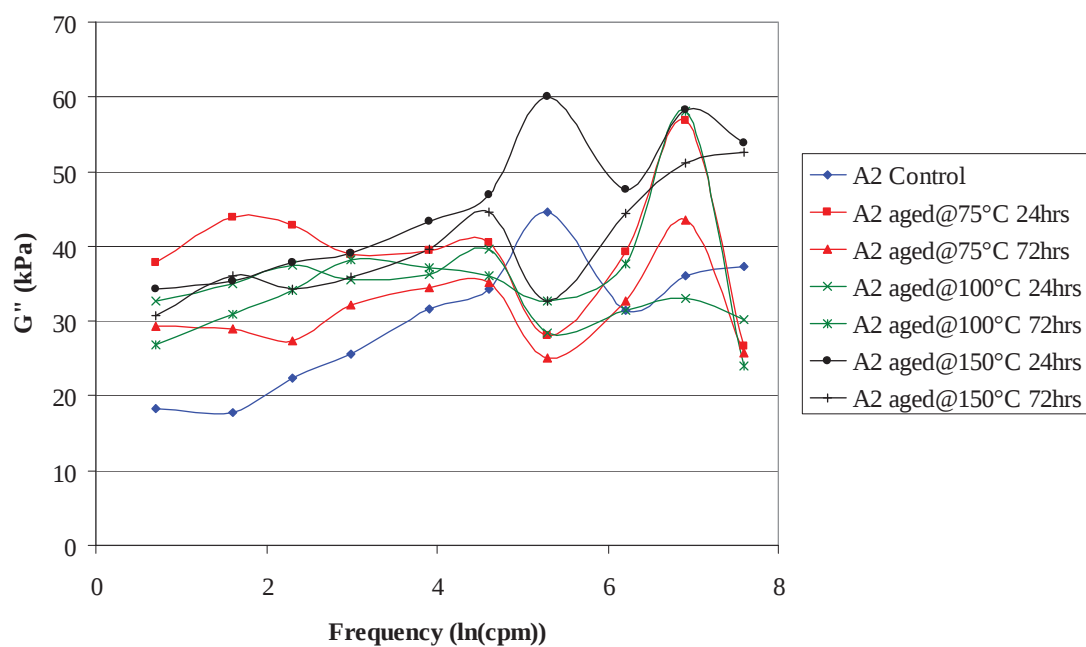


Figure 5.17b G'' of A2 before and after aging at 75°C, 100°C and 150°C for 24 and 72 hours using the RPA

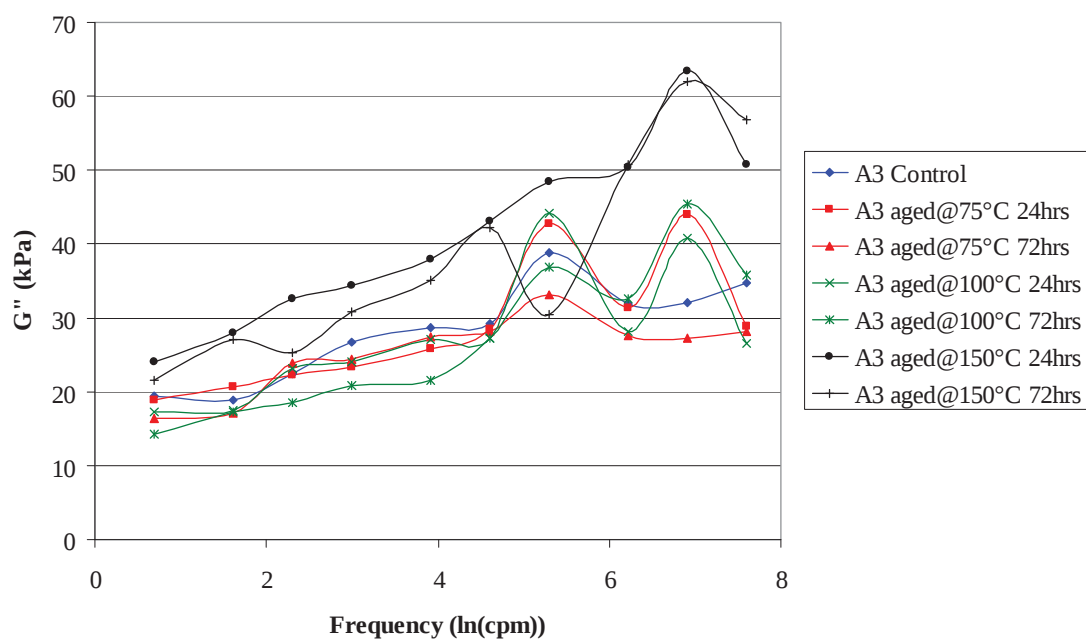


Figure 5.17c G'' of A3 before and after aging at 75°C, 100°C and 150°C for 24 and 72 hours using the RPA

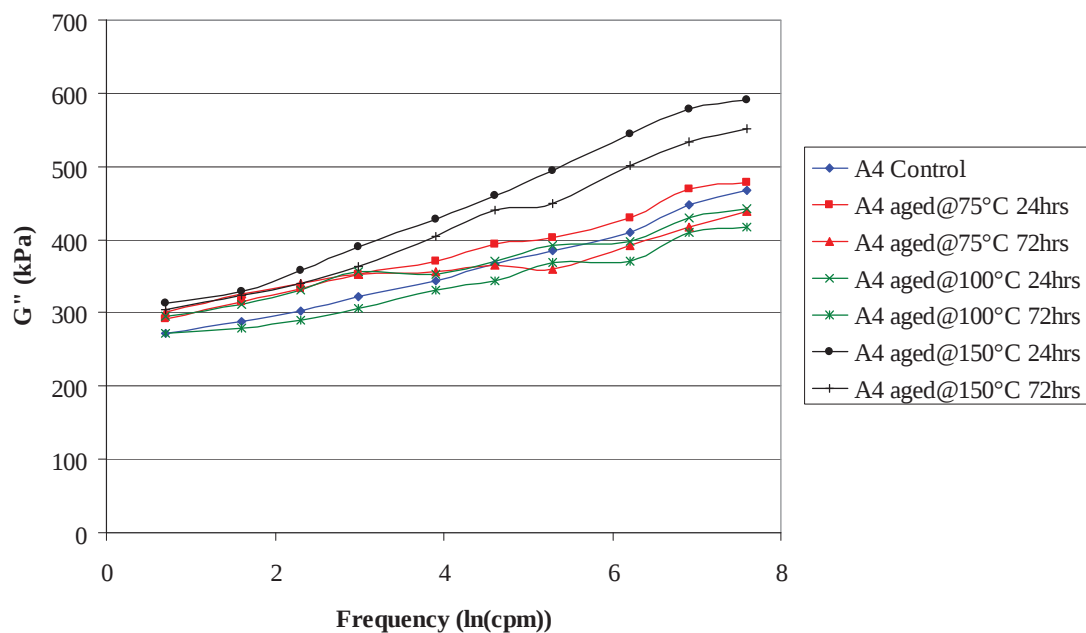


Figure 5.17d G'' of A4 before and after aging at 75°C, 100°C and 150°C for 24 and 72 hours using the RPA

The results from RPA aging tests for $\tan \delta$ are shown in Figures 5.18 (a – d). $\tan \delta$ is a ratio of G''/G' which can be related to the heat build up of the rubber and also the inverse behaviour of resilience. At high temperature aging, the rubber will lose its resilience as it becomes over cured and the rubber degrades. Therefore it will not be able to rebound to the same degree as if it has not been aged. Figure 5.18a exemplifies this resilience declination for the A1 sample aged at 150°C for 24 hours which has a steep jump in $\tan \delta$. This result is also apparent in A2, A3 and A4 samples as shown in Figures 5.18 (a – c), respectively.

The variability in the $\tan \delta$ results is caused by the inconsistencies in the G'' . $\tan \delta$ is calculated from the ratio of G''/G' , an inconsistent G'' will adversely affect the $\tan \delta$ result.

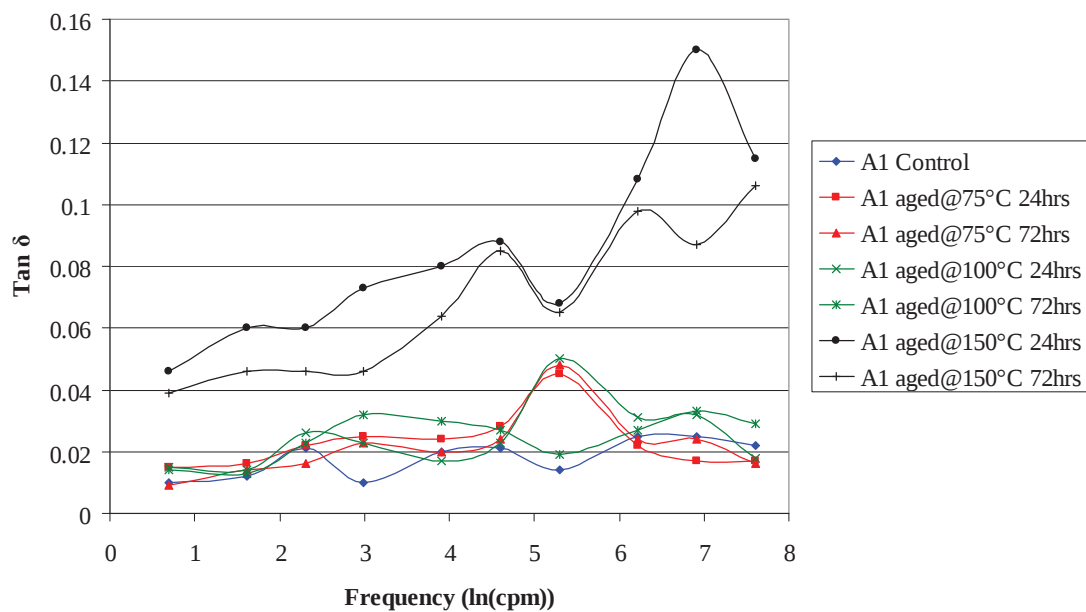


Figure 5.18a Tan Delta of A1 before and after aging at 75°C, 100°C and 150°C for 24 and 72 hours using the RPA

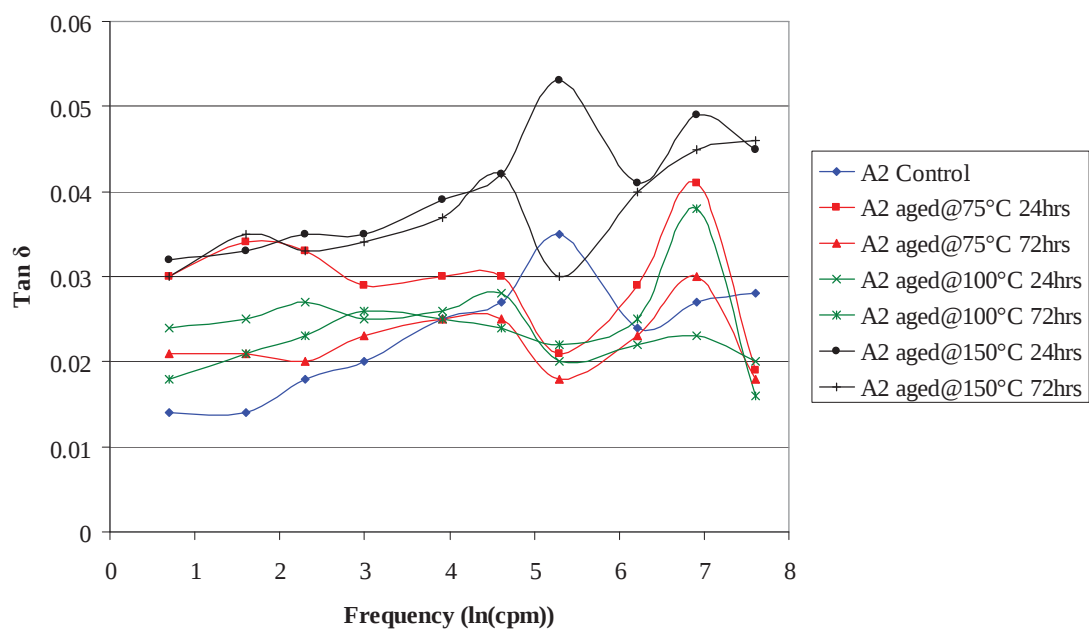


Figure 5.18b Tan Delta of A2 before and after aging at 75°C, 100°C and 150°C for 24 and 72 hours using the RPA

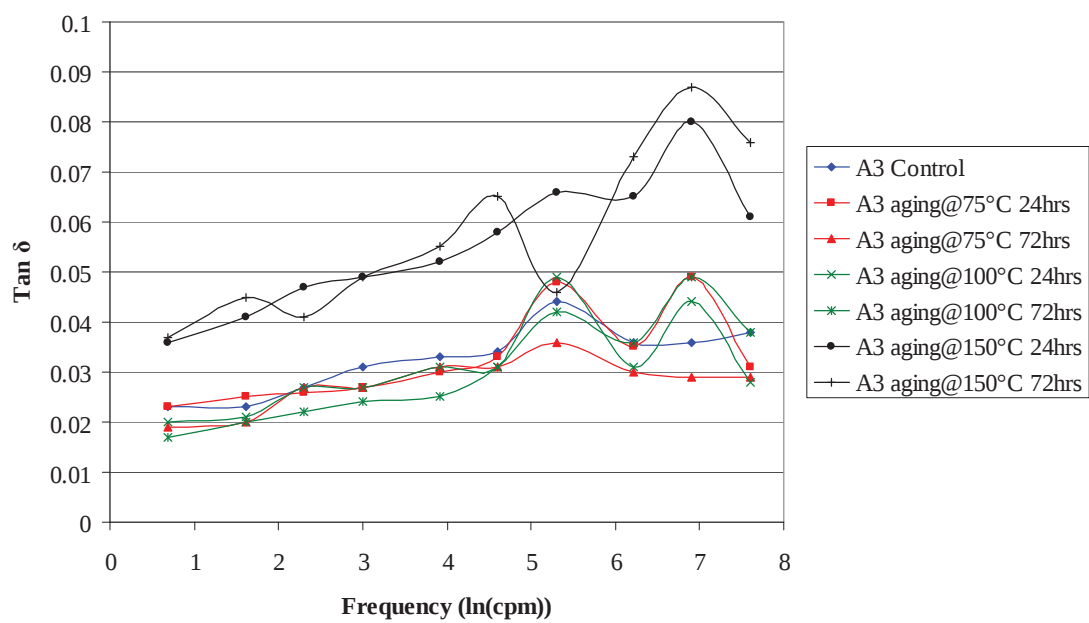


Figure 5.18c Tan Delta of A3 before and after aging at 75°C, 100°C and 150°C for 24 and 72 hours using the RPA

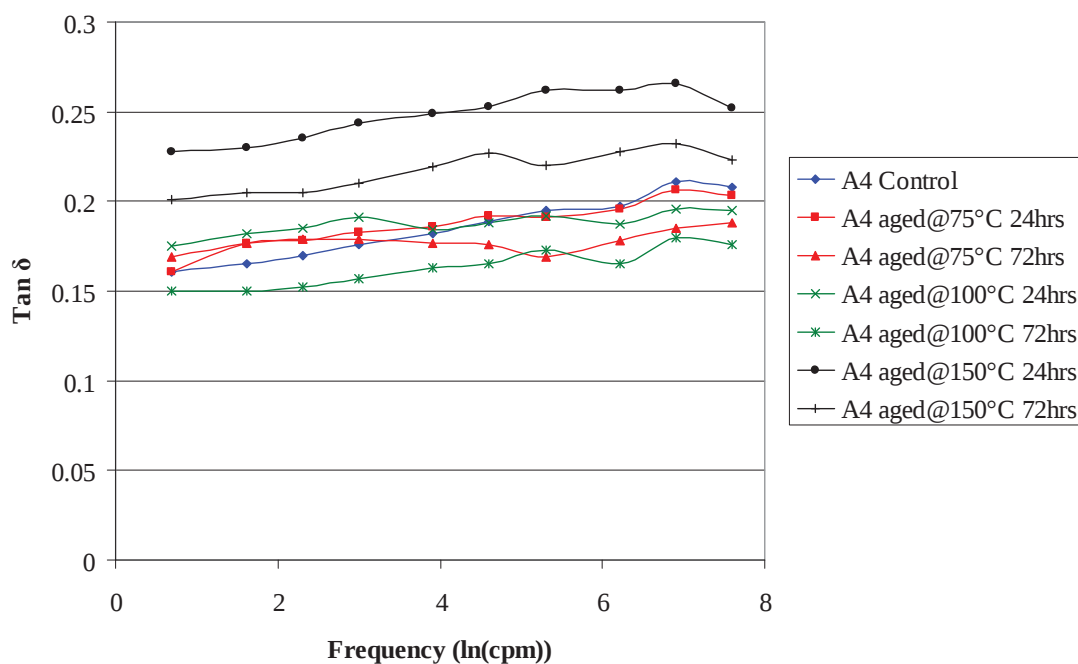


Figure 5.18d Tan Delta of A4 before and after aging at 75°C, 100°C and 150°C for 24 and 72 hours using the RPA

5.5 FT-IR Spectroscopy

The chemistry of A1, A2, A3 and raw materials were analysed using Fourier Transform Infrared Spectroscopy (FT-IR). Due to the complex nature of the rubber compounds, the FT-IR spectrums are extremely detailed. However upon analysis of the spectrum, characteristic vibrations can be identified through literature and library searches. Samples of each rubber were prepared as normal and erosion tested with 750 μ m Al₂O₃ abrasive particles at 20° angle of impingement. The worn sample was then compared with the unworn sample using the FT-IR spectral analysis. It is noted in the literature that carbon black affects the infrared or laser beam. Therefore a sample of each rubber was mixed and prepared without carbon black to observe the differences in the spectra.

Before analysis is done on the rubber compounds, the key raw materials were analysed in the FT-IR. Figure 5.19 shows the spectra of natural gum rubber raw material (SMR10).

Distinct peaks can be seen at 3030cm^{-1} ($=\text{C-H}$), 2959cm^{-1} (CH_3 asymmetric stretching), 2914cm^{-1} (CH_3 symmetric stretching) and 1663cm^{-1} ($\text{C}=\text{C}$ stretching). A complete summary of the vibrational bands of raw material standard Malaysian rubber grade 10 (SMR10) and rubber compounds analysed in this study can be seen in Table 5.3. Figures 5.20 – 5.22 show the FT-IR spectrums of Neodene 40, precipitated silica and sulphur, respectively. Neodene 40 is the trade name for polybutadiene which is used together with SMR10 for the polymer blend of A3. Precipitated silica is used as a filler and reinforcement for the A2 and A3 rubber compounds. The characteristic peak of SMR10 can be seen at 1089cm^{-1} , this peak will be used to compare the rubber compounds before and after testing to observe any degradation. Sulphur is used as the vulcanising agent for the rubber compounds and its characteristic peak is situated at the wavelength of 2359cm^{-1} . A4 is yet to be analysed as well as samples that have been aged to observe changes in the characteristic peaks which may indicate degradation is occurring.

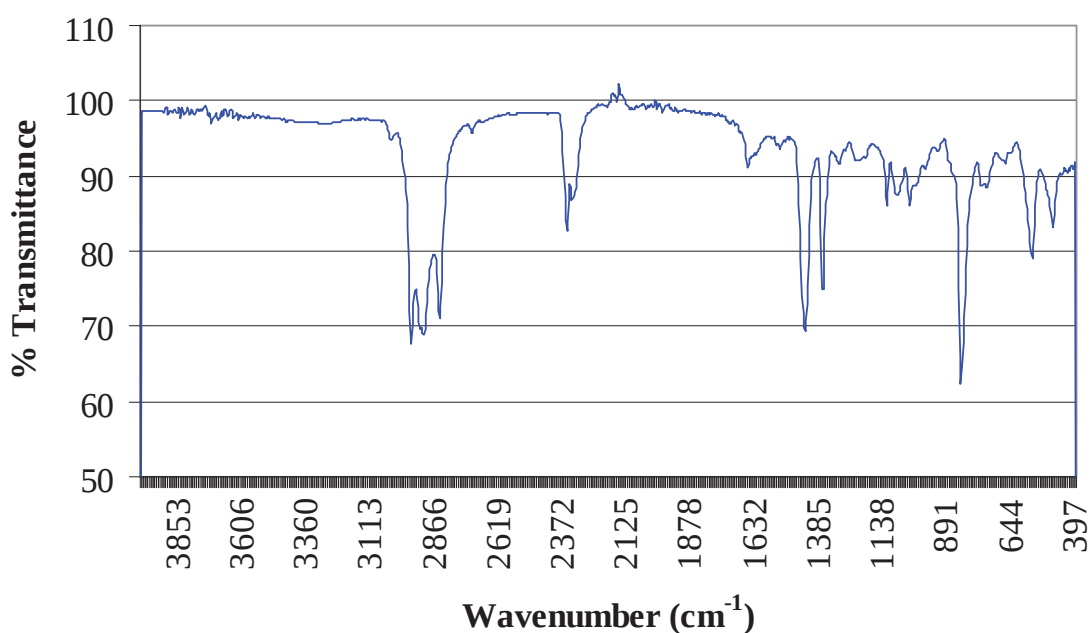


Figure 5.19 FT-IR analysis on SMR10

Table 5.3 Literature, SMR10, A1, A2, A3 and A4 wavenumbers (cm⁻¹) and assignment bands observed in FT-IR and Raman spectrum analysis [15, 74]

Literature [15, 74]	SMR10	A1	A2	A3	A4	Assignment
3032						=C-H stretching
2962	2959	2956	2958	2957		CH ₃ asymmetric stretching
2931						CH ₂ asymmetric stretching
2912	2914	2916	2916	2916		CH ₃ symmetric stretching
2885						
2854	2852	2849	2849	2849		CH ₂ symmetric stretching
2727						
		1735				
1666	1663	1661	1662	1661		C=C stretching
			1539	1538		
1452		1453	1447	1446		CH ₃ asymmetric stretching
1440	1445					CH ₂ deformation
		1397				
1375	1375	1374	1375	1374		
1363						CH ₂ deformation
1325						=C-H in-plane deformation
1311	1309	1308		1308		CH ₂ twisting
1287						CH bending
1243	1240					CH ₂ twisting
1208						=C-H in-plane bending
1143						C-H out-of-plane of <i>cis</i> -C(CH ₃)=CH wagging
1131	1127					CH ₂ wagging
	1084	1097	1080	1089		
1040	1037					CH ₃ rocking
1000						C-CH ₂ stretching
983						C-CH ₃ stretching
840	834	837		830		=CH out-of-plane bending
820			827			CH wagging
788						CH ₂ rocking
759						CH ₂ rocking
724	741	722		739		
596						C-C in plane bending
572	570	573	571	570		
492	491	468	461	464		=CC ₂ rocking and scissoring

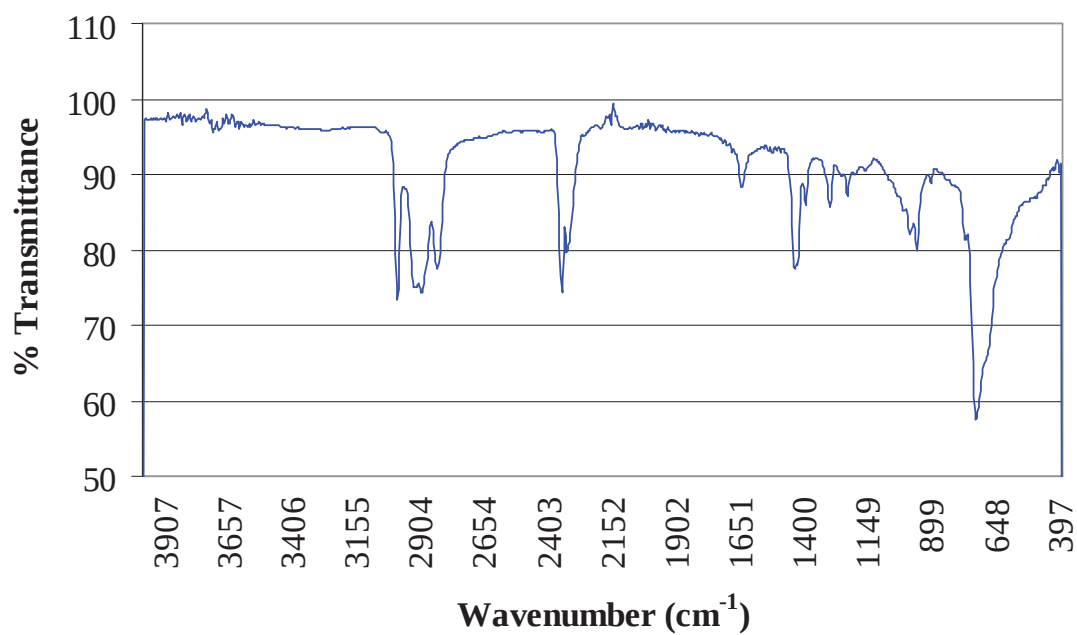


Figure 5.20 FT-IR analysis on Neodene 40

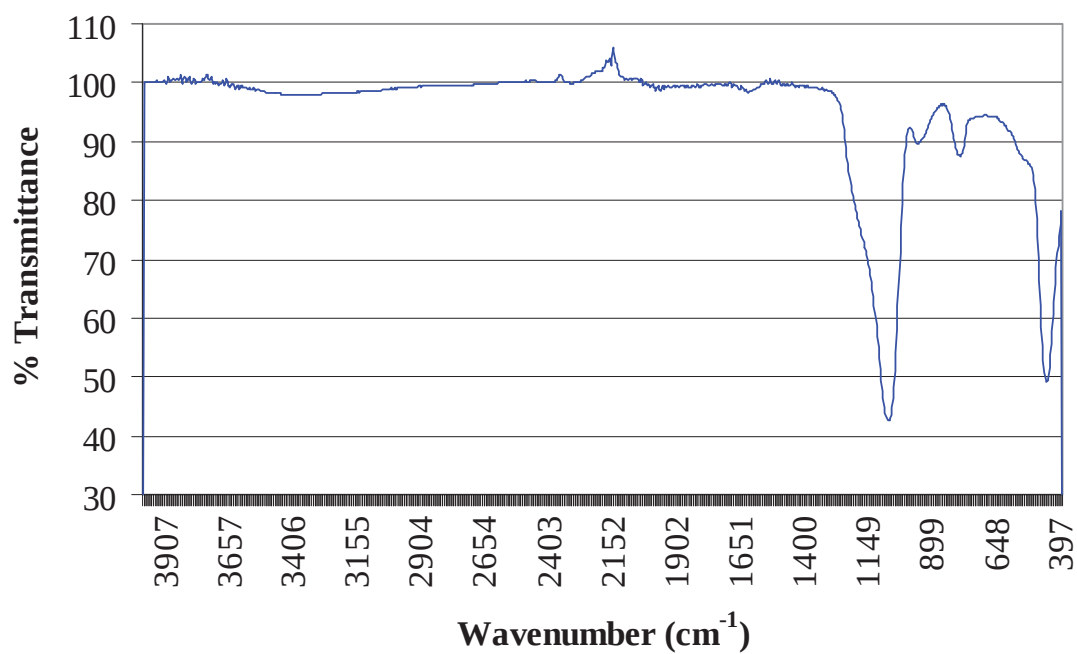


Figure 5.21 FT-IR analysis on Hi-Sil 190G (silica)

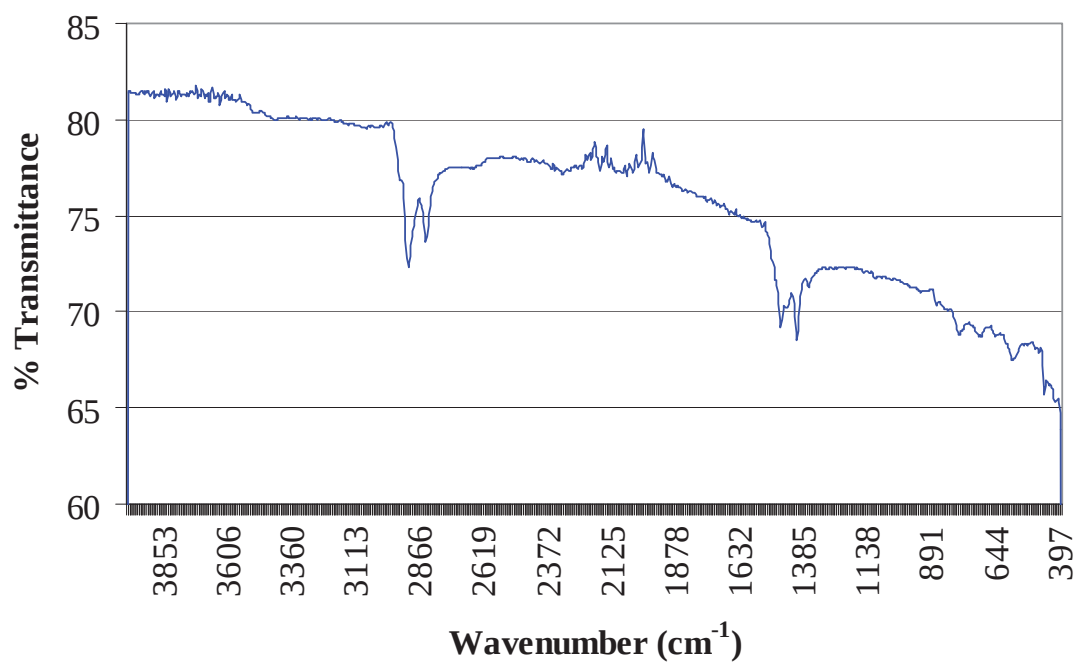


Figure 5.22 FT-IR analysis on Sulphur

The characteristic peaks of A1 before and after wear testing is shown in Figure 5.24. Figure 5.23 shows the FT-IR spectrum of a A1 mix without the addition of carbon black. The characteristic peaks are more clearly defined but there is very little variation to Figure 5.24. Similarly to this, the comparison of an unworn as opposed to a worn sample of A1 shows very little difference. This is expected as A1 does not contain a large amount of fillers, therefore the worn surface will have a similar spectrum to the unworn surface.

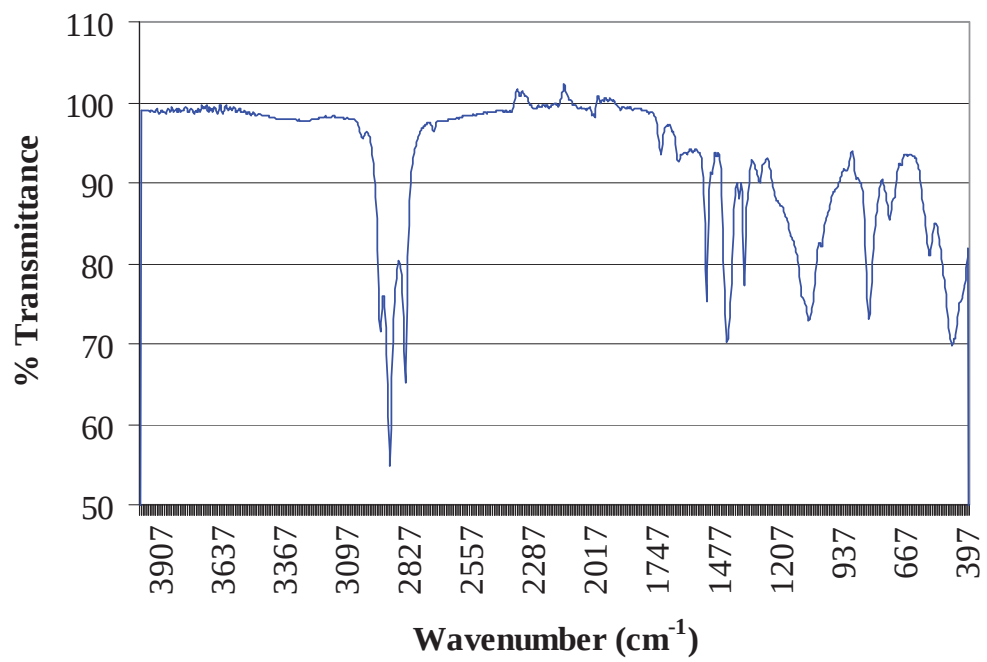


Figure 5.23 FT-IR analysis of “White” A1

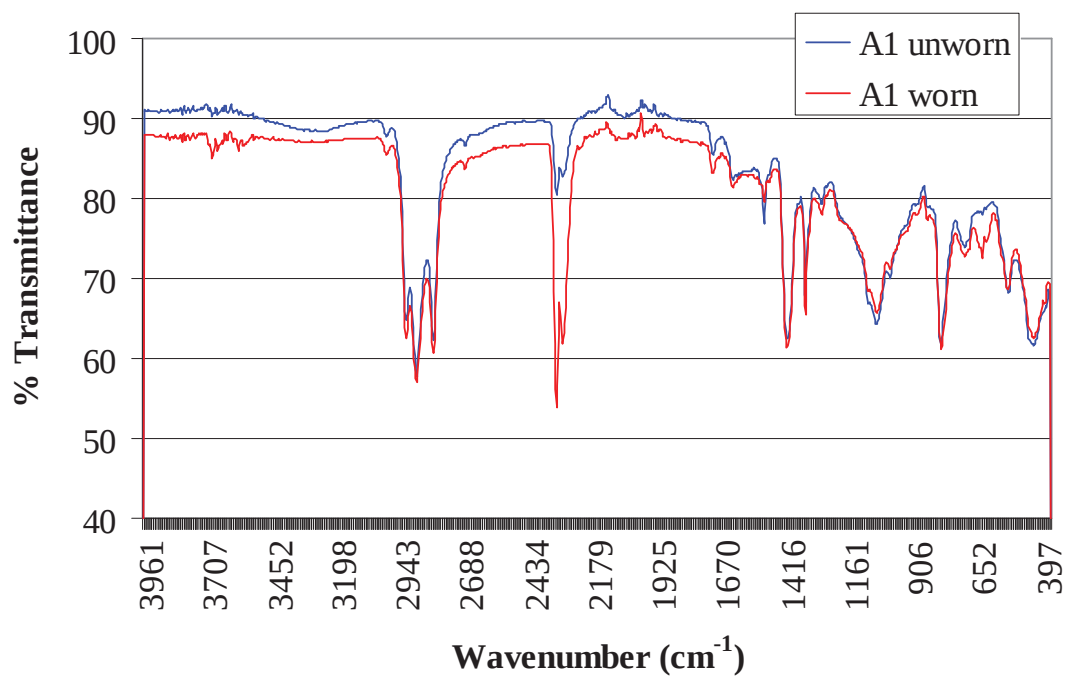


Figure 5.24 FT-IR analysis of A1 after wear testing at 20° impingement angle with 750 μ m Al₂O₃ abrasive particles

Figure 5.26 show the FT-IR spectra of A2 before and after wear testing. It can be seen that one of the characteristic peaks is at 1080cm^{-1} . This peak is comparable to the characteristic peak for silica at 1089cm^{-1} , shown in Figure 5.21. These characteristic peaks do not match up exactly as a result of the instrument limitations. They can be considered as comparable based on the results from literature, where similar discrepancies are shown [15, 74]. This result is expected as A2 contains a considerable percentage of silica. In the examination of A2 after wear testing shown in Figure 5.26, comparisons of the material before and after testing is made integration below the graph or peak that is of interest to calculate the area. A decrease in area relative to other peaks will indicate from the unworn sample that the fraction of a particular assignment (chemical bond) has decreased. This decrease may be a result of degradation from the wear process. Silica acts as a reinforcing agent and is critical in providing A2 with beneficial physical and viscoelastic properties.

The A2 spectrum of a sample that has been aged and heated to reversion still needs to be analysed to compare with the standard spectrum. Other characteristic peaks also need to be studied further to determine the full extent of degradation during the erosive wear process.

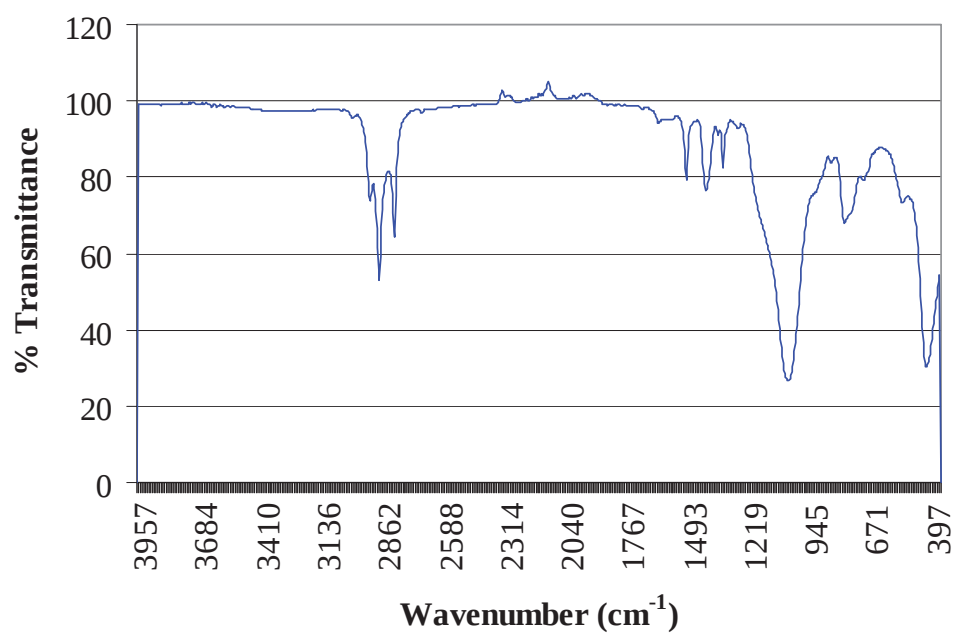


Figure 5.25 FT-IR analysis of “white” A2 before wear testing

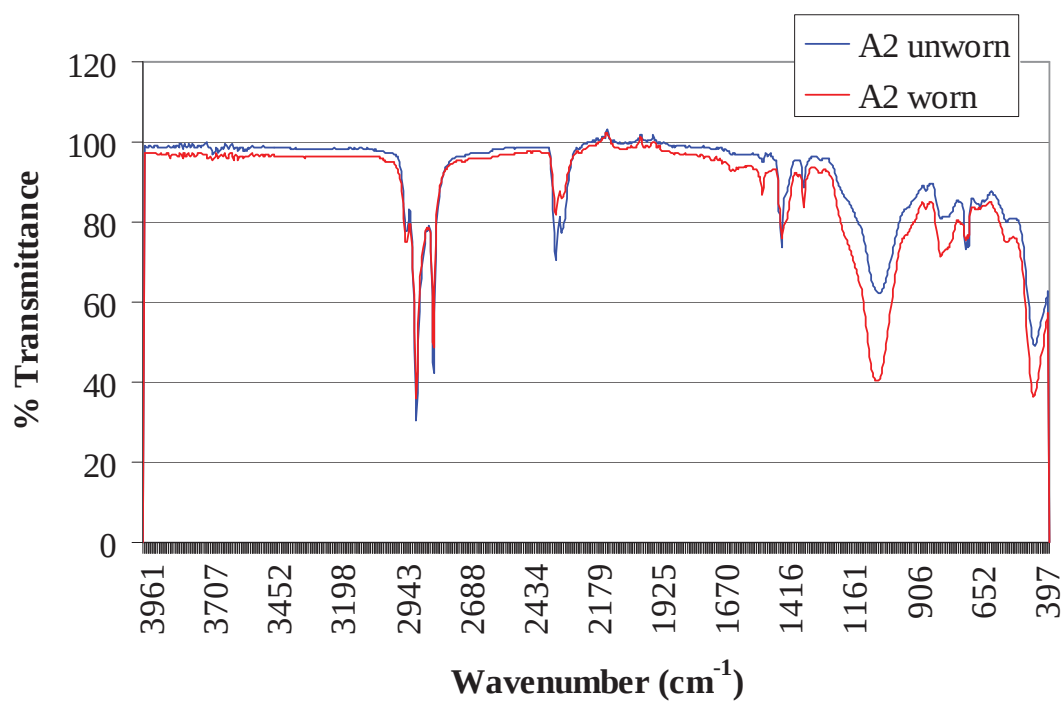


Figure 5.26 FT-IR analysis of A2 after wear testing at 20° impingement angle with 750 μ m Al₂O₃ abrasive particles

Similarly with A3, the silica signal strength for silica decreases significantly after wear testing. Figures 5.27 – 5.28 show the spectrums of A3 before testing, after testing and a sample without carbon black. It can be seen from Figure 5.27 that one of the characteristic peaks is at 1089cm^{-1} . This characteristic peak is identical to the characteristic peak of silica shown in Figure 5.21.

The A3 spectrum of a sample that has been aged and heated to reversion still needs to be analysed to compare with the standard spectrum. Other characteristic peaks also need to be studied further to determine the full extent of degradation during the erosive wear process.

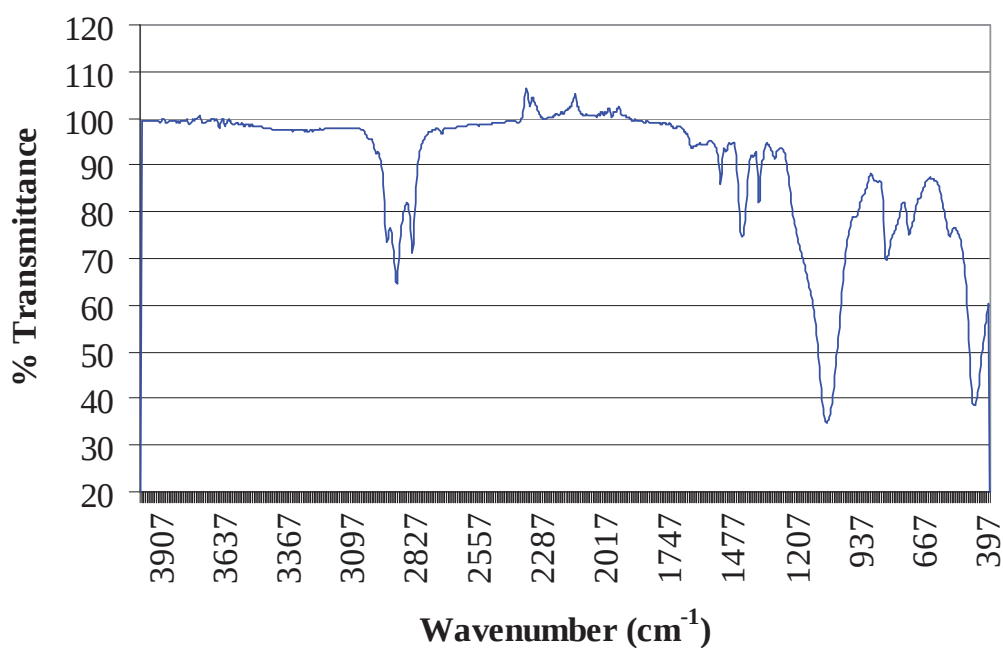


Figure 5.27 FT-IR analysis of “white” A3 before wear testing

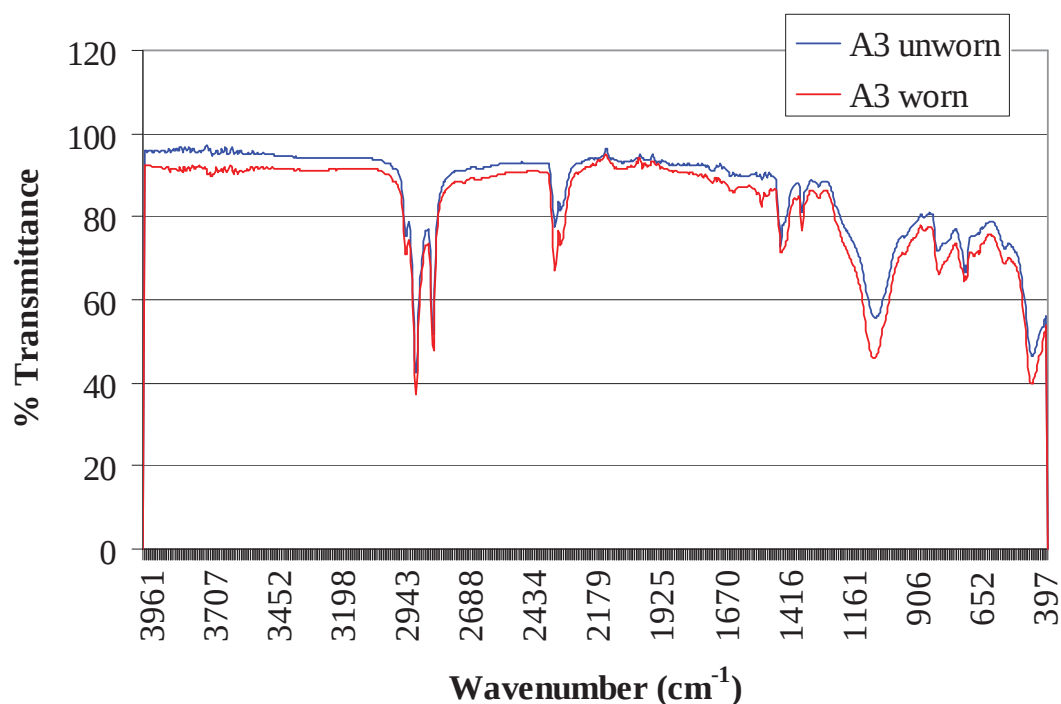


Figure 5.28 FT-IR analysis of A3 after wear testing at 20° impingement angle with 750 μ m Al₂O₃ abrasive particles

Each rubber has the same chemical backbone clearly shown in each of the spectra shown above, the only limiting factor which distinguishes one from the other is the polymer chemistry. A4 is highly filled with carbon black which will decrease the amount of reflectance of the IR beam significantly. Figure 5.29 show the FTIR spectra of the unworn and worn surfaces of A4. It can be seen that A4 is difficult to correlate with the other rubbers due to this reflectance issue with the FTIR. Due to this is inaccurate data the relative peak study was not investigated for A4.

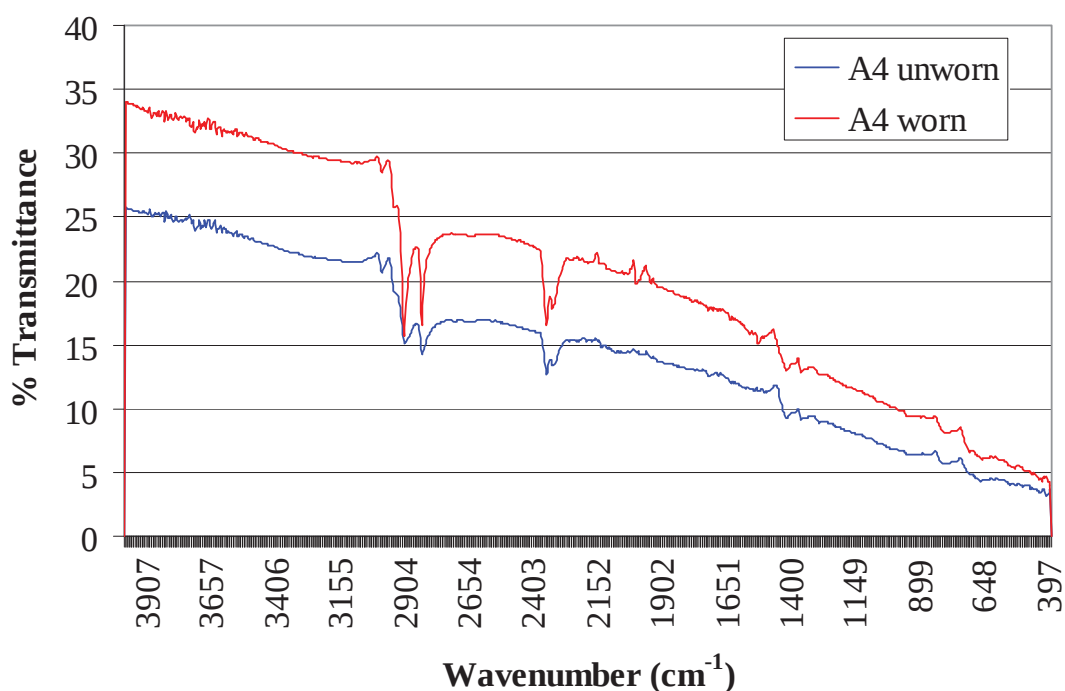


Figure 5.29 FT-IR analysis of A4 after wear testing at 20° impingement angle with 750 μ m Al₂O₃ abrasive particles

There is a concern with FT-IR spectra data that occurs. The baseline drift could possibly be the result of the environment, humidity, equipment calibration, etc. Therefore the spectra for each material before and after wear testing needs to be compared with a relative data point for each wavenumber and transmittance data point. By using this method of analysis, there is a direct relative comparison for the spectrum before and after wear testing. Figures 5.30 – 5.32 (Appendix 1) shows the relative peak data for A1, A2 and A3 respectively. The method for the calculation of this relative peak data is outlined in the experimental procedures chapter, section 4.1.6.2.

The relative data point that was greater than 10% over the unworn sample was highlighted in red and considered as a point of significant chemical change in the rubber. It can be seen from Figure 5.30 for A1 that the only occasion the relative peak data is greater than 5% is at the wavenumber 2360 cm^{-1} . This wavenumber is a characteristic peak for CO₂ present in the spectra analysis. Erosion tested A1 samples did not show a significant chemical change

in structure after testing. This statement/theory will be revisited in a later chapter of this thesis.

The relative peak data for A2 before and after wear testing is shown in Figure 5.31. It can be seen immediately from the number of red highlighted data points that this material behaves differently to A1 during wear testing. Again, the relative data points that were greater than 10% over the unworn sample were highlighted in red. The wavenumber characteristic peaks of interest from this analysis are 466.7cm^{-1} , 1095.4cm^{-1} , 2846.6cm^{-1} and 2916cm^{-1} . The wavenumber at 466.7cm^{-1} is not defined in literature; as a result further investigation is required to define this finding. At 1095.4cm^{-1} it is known in literature [15, 74] to be aromatic C-H plane bend characteristic bond. The characteristic wavenumbers of 2846.6cm^{-1} and 2916cm^{-1} are defined in literature [15, 74] as the methylene C-H symmetric and asymmetric functional group and assignment, respectively. From this data it can be stated that chemical change does occur to A2 after wear testing, particularly in the CH_2 bonds. This theory will be discussed further in a later chapter of this thesis.

Figure 5.32 shows the relative peak data for A3 before and after wear testing. The numbers of red highlighted data points are not as frequent as for the A2 material. The wavenumber characteristic peaks of interest from this analysis are 462.9cm^{-1} , 1099.3cm^{-1} and 2916cm^{-1} . The wavenumber at 462.9cm^{-1} is similar to the wavenumber of 466.7cm^{-1} from the A2 spectra. Again this wavenumber is not defined in literature as a result further investigation is required to define this finding. At 1099.3cm^{-1} , similar to A2 this wavenumber characteristic peak is defined in literature as an aromatic C-H plane bend characteristic bond. The characteristic wavenumber of 2916cm^{-1} is the same as in A2 and is defined in literature as the methylene C-H symmetric functional group and assignment respectively. It can be stated again that chemical change does occur in A3 during wear testing and will be discussed further in a later chapter of this thesis.

5.6 Rubber Chemistry Characterisation

The physical property correlation with wear loss is extremely difficult in this project as four very different rubber compositions are used in the study. There is a need to eliminate the variables in chemistry of each material to determine the root cause of wear during the slurry pump application. Polybutadiene (BR) is used in both A3 and A4 as a polymer blend with natural rubber to produce favourable wear properties. This experiment was set up to determine the influence of BR on the material wear performance. Figure 5.33 shows the different levels of BR in the rubber mix from 0% to 100% BR. The result was interesting, in the fact that at 0% BR (that is 100% natural rubber (NR)) the material performs the best and at levels of 50 – 100% BR content the material performs poorly. This poor performance is attributed to the physical properties of the rubber which can be seen in Figures 5.34 – 5.37. Figure 5.34 illustrates the dependence of NR content to increase the resilience of the rubber. There is a clear decreasing trend in resilience as polybutadiene levels increase. Conversely with the hardness shown in Figure 5.35, where the hardness increases as BR increases in the rubber chemistry. The tensile strength and the tensile tear strengths behaviour in a similar manner, decreasing with increasing BR levels.

Further testing and experimentation is required to develop this concept not in this project as it is out of the project scope. The materials of interest in this study only include existing commercial materials such as A1, A2, A3 and A4.

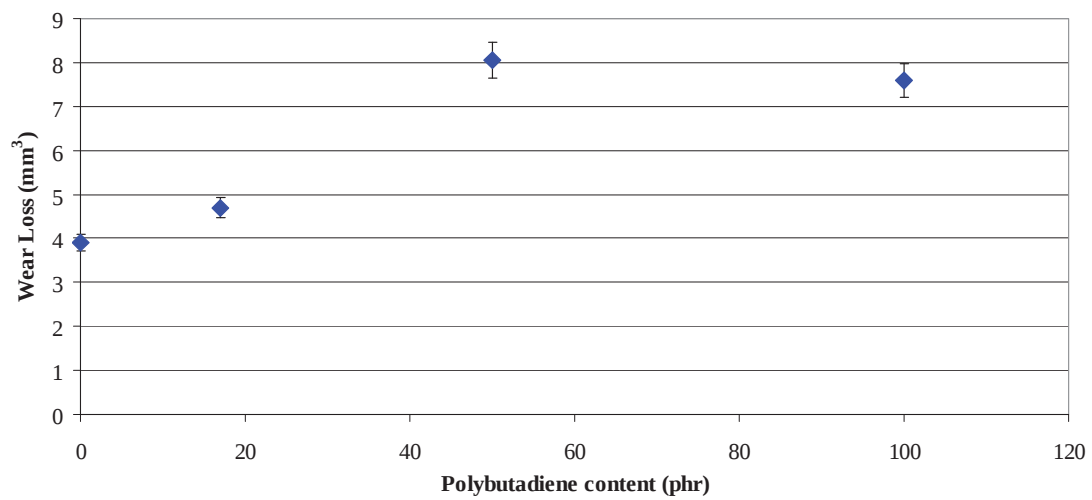


Figure 5.33 Effect of BR on wear loss.

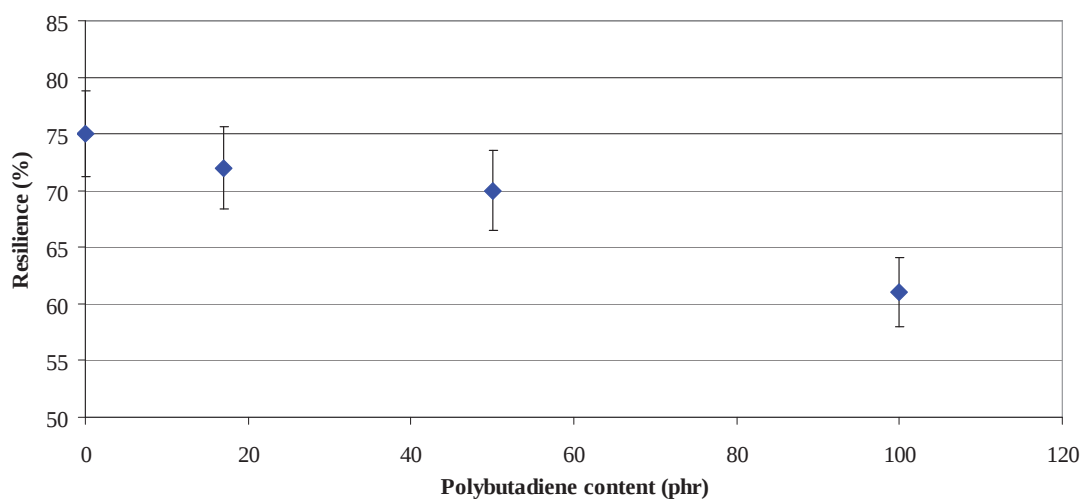


Figure 5.34 Effect of BR on resilience.

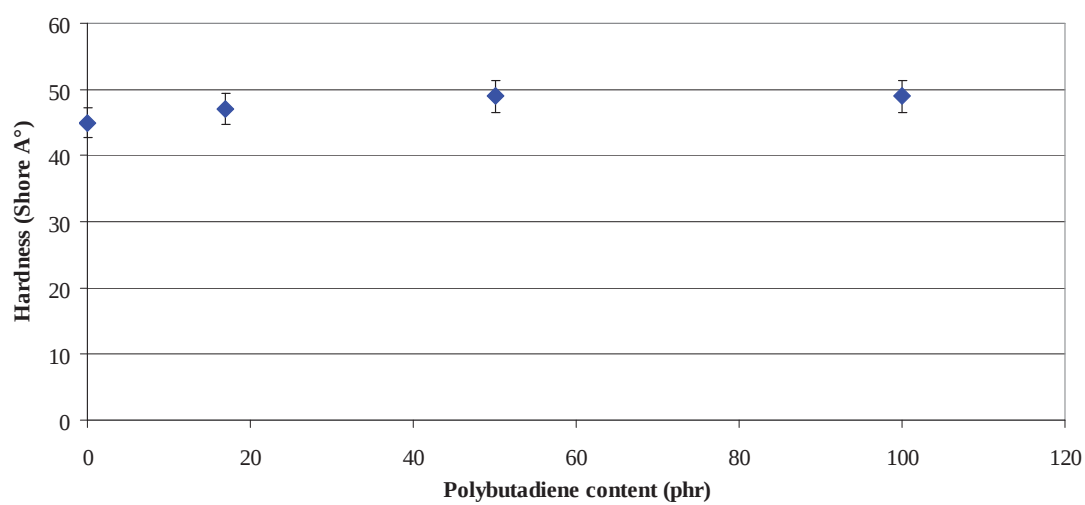


Figure 5.35 Effect of BR on hardness.

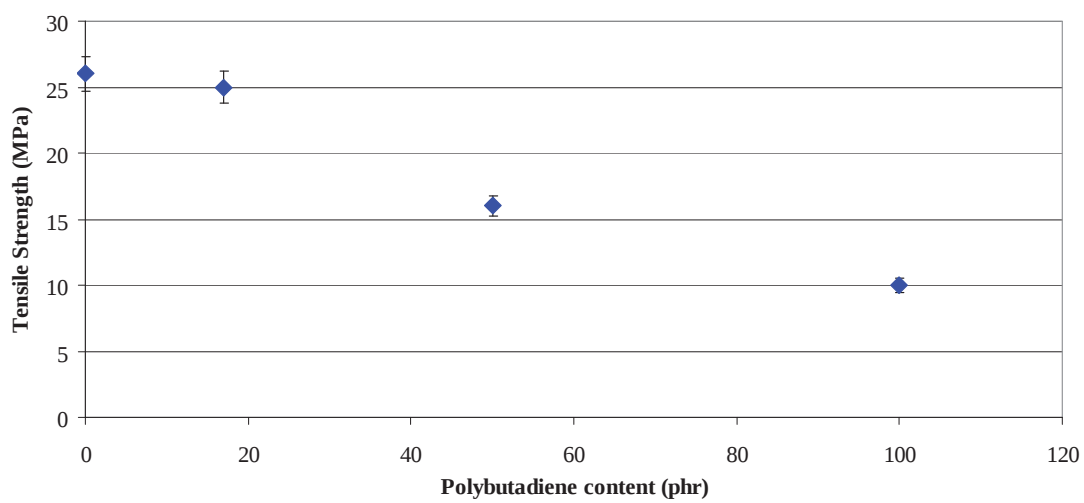


Figure 5.36 Effect of BR on tensile strength.

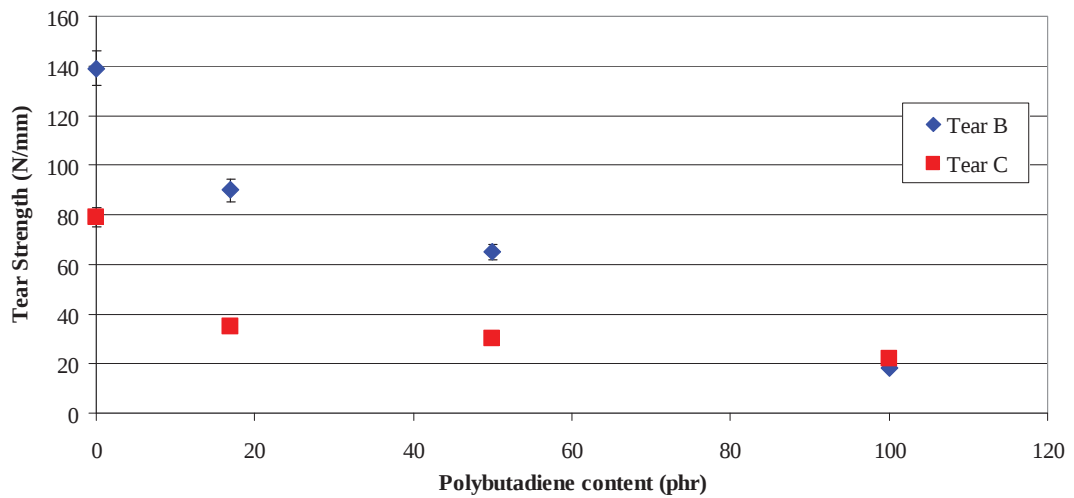


Figure 5.37 Effect of BR on tear B and C strength.

5.7 Summary

The testing and analysis of the four rubber compounds show differences in physical, viscoelastic, chemical and erosive wear properties. Key areas to highlight include the following: increase in G'' and $\tan \delta$ from heat aging, the erosive wear resistance of highly filled carbon black compound to the lower filled silica compounds, the influence of resilience and $\tan \delta$ on the erosive wear resistance, the observation of chemical change to the surface of the rubber using FT-IR before, after aging and after erosive wear testing, the relationship of tensile and tear strength to erosive wear, and the influence of particle size and angles of impingements of abrasive particles to the surface of the rubber during erosive wear. These key areas will provide the foundation to discuss the wear mechanisms established from erosive wear in rubber pump lining applications and their correlations with the physical, viscoelastic properties and chemistry of the rubbers.

6 Discussion

The chemistry of the rubber compounds analysed in this study can be divided into four subcategories:

1. FT-IR characteristic bands in the rubber spectra.
2. Chemistry of rubber additives.
3. Rubber aging and influence on rubber chemistry.
4. Erosive wear and influence on rubber chemistry.

The characteristic bands in each of the rubbers spectra were identified using Fourier Transform Infrared Spectroscopy (FT-IR). These characteristic bands were fundamental to describe the chemistry of A1, A2, A3 and A4 rubber compounds. A description of each important characteristic band is outlined in this subcategory. These will form the primary cause of chemical degradation in rubber compounds used as lining systems for minerals processing.

The chemistry of the rubber additives used in each of the rubbers is discussed in the next section. The spectra of the significant raw materials used in each rubber compound was analysed using FT-IR and their characteristic bands outlined. This raw material spectra data can be used to determine the influence of aging on the chemistry of the rubber compounds. A brief description of the important characteristic bands is outlined in this section. The raw materials and rubber compounds spectra are overlayed to find comparable characteristic bands.

Aged rubber compound samples were analysed using FT-IR. Using the data obtained from the rubber compounds and rubber additives, the characteristic bands were examined on samples that were aged. The relative change in characteristic peak intensity resulted in a change in chemistry of the rubber. The method to calculate this relative change is outlined

in Chapter 4.1.6. This subcategory brings together the previous sections to show the aging effects on the chemistry of the rubber compounds.

Finally, worn samples through the erosive wear test were analysed using FT-IR and correlations were established with the aged and control samples. This section outlines the relationship between erosive wear, rubber chemistry and aged samples of the rubber compounds analysed in this study.

6.1 Chemical Analysis

The basic concepts of infrared spectroscopy and the impact of the rubber molecular species and chemical functionality on the spectra have been outlined in Chapter 2.10. However these basic concepts do not consider the change in chemistry of the rubber that is subjected to aging and erosive wear commonly found in application. Consequently, there is a need to identify the chemical functional groups formed as a result of this chemical change on the surface of the rubber compound.

A chemical analysis of the aging of rubber is undertaken in this study. Aging of rubber is not usually associated with erosive wear, but generally linked to thermal degradation during application. Many other studies have shown that aging influences the performance of the rubber in reference to a reduction of physical properties. The aging of rubber and its influence on the rubbers chemistry as a result of slurry erosion is not researched extensively in the literature. This chapter will reflect on the chemical makeup of the rubber and how the chemical constituents are influenced by the environment the rubber is exposed to during erosive wear.

6.1.1 FT-IR characteristic bands in the rubber spectrum

The study of the FT-IR characteristic bands in the rubber spectrum was undertaken considering the different chemical constituents that make up the A1, A2, A3 and A4

formulations. The results from this study are presented in Chapter 5.5. The fillers, chemical peptisers, accelerators, and process aids which make up the rubber influence the FT-IR instrument and consequently the spectra result. A complete summary of the vibrational bands of raw material SMR10 and rubber compounds analysed in this study can be seen in Table 5.3.

The base rubber raw material SMR10 was analysed using the FT-IR as a control or standard spectrum to compare the four rubbers. A number of the wavenumbers from the analysis correlate with the literature values for natural rubber. The assignment band of 1666 cm^{-1} (C=C stretching) is clearly indentified in the FT-IR spectrum. The C=C bond is a key bond in the rubber polymer chain, resulting in many of the rubbers unique physical and elastic properties. Other assignment bands of interest include the following: $2800 - 2962\text{ cm}^{-1}$ (CH_3 asymmetric/symmetric stretching), 1300 cm^{-1} (CH_2 twisting) and $830 - 840\text{ cm}^{-1}$ (CH out of phase bending). The C=C double bond along with other assignment bands were examined before and after wear testing to ascertain the possible chemical changes caused by the erosion wear testing. These chemical changes will be discussed in section 3 of this chapter.

6.1.2 Chemistry of rubber additives

The rubbers investigated in this study consist of up to 10 different raw materials and chemicals including inert fillers, reinforcing fillers, accelerators, vulcanizing agents, anti-oxidants, processing aids and oils. The key raw materials of interest and their characteristic peaks were presented earlier in the results chapter. These included the Standard Malaysian Rubber 10 (SMR10), polybutadiene rubber, precipitated silica and sulphur. Figure 5.19 shows the spectra of SMR10. Characteristic peaks can be seen at 3030 cm^{-1} (=C-H), 2959 cm^{-1} (CH_3 asymmetric stretching), 2914 cm^{-1} (CH_3 symmetric stretching) and 1663 cm^{-1} (C=C stretching). Other characteristic peaks highlighted in the Table 5.3 illustrate common peaks for the SMR10 and the rubbers analysed in this study. However, there are a several peaks that disappear in the A1, A2, and A3 spectrum. These include 1040 cm^{-1} (CH_3

rocking), 1131cm^{-1} (CH_2 wagging), 1243cm^{-1} (CH_2 twisting) 1440cm^{-1} (CH_2 deformation) 2931cm^{-1} (CH_2 asymmetric stretching) 3032cm^{-1} ($=\text{C-H}$ stretching). The disappearance of these characteristic peaks is attributed to the chemical and physical reactions the rubber undergoes during the mixing process. The FT-IR spectra of SMR10 and rubbers analysed in this study are shown in Figures 6.1 – 6.3. The influence of the different chemistry is shown in these figures, in particular the intensities of the characteristic peaks. A decrease in intensity is attributed to the carbon black content in the finished rubber compound. It is well documented in the literature [87, 88, 89, 90] and seen in this study that carbon black obstructs the infrared light from penetrating the surface of the material, therefore giving a lower intensity in the measurements.

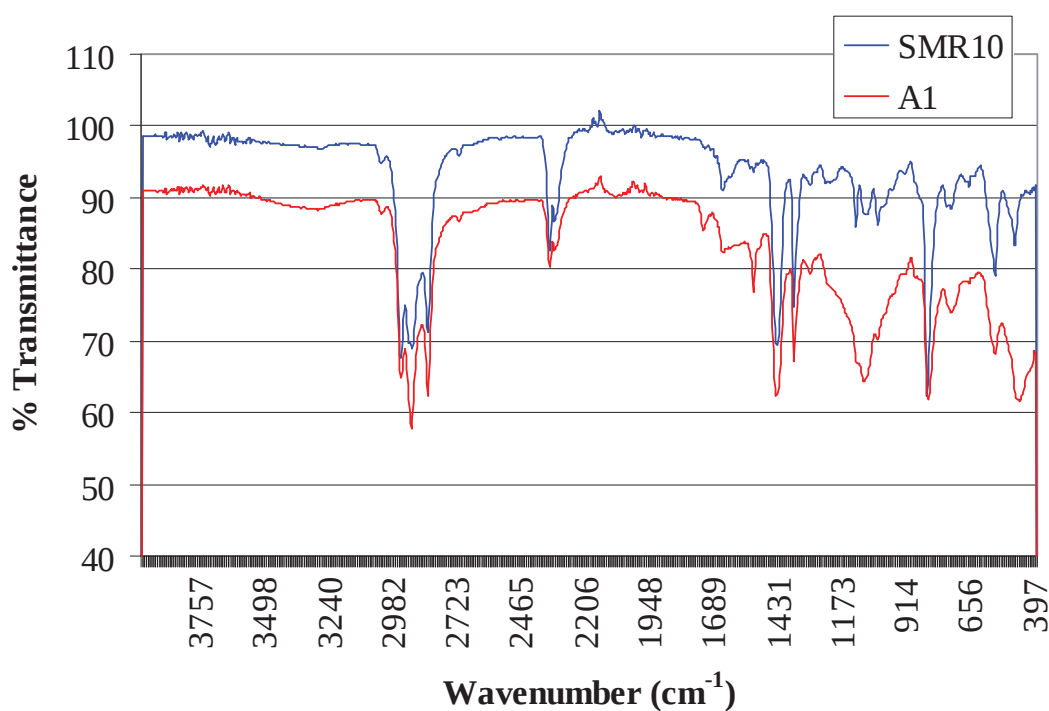


Figure 6.1 FT-IR spectroscopy of SMR10 vs. A1

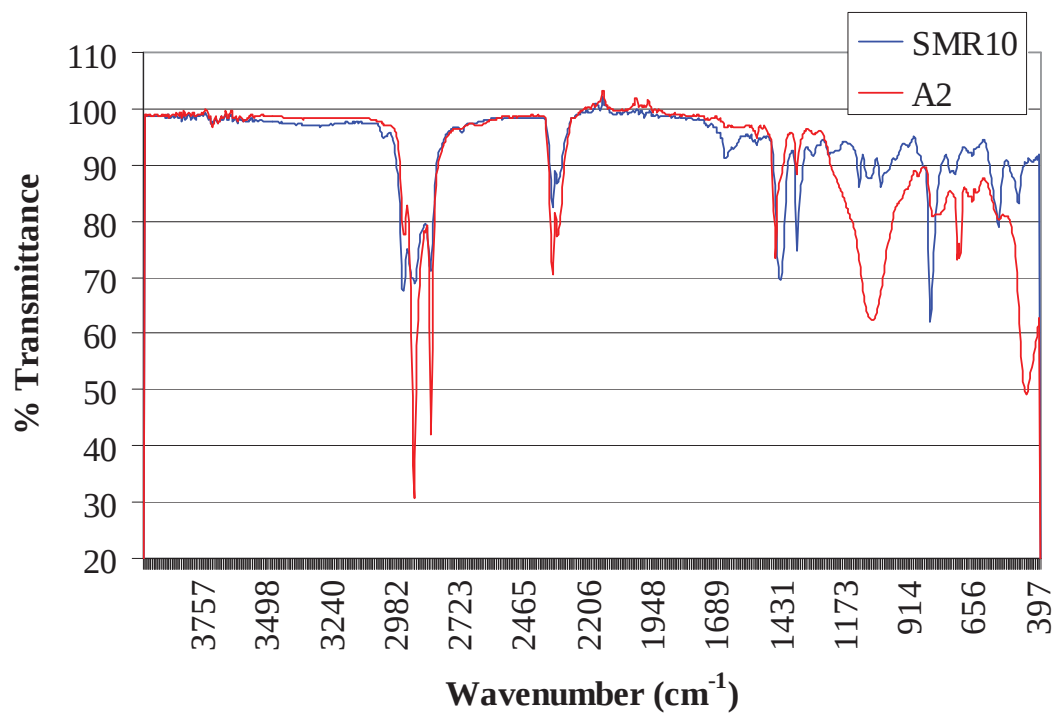


Figure 6.2 FT-IR spectroscopy of SMR10 vs. A2

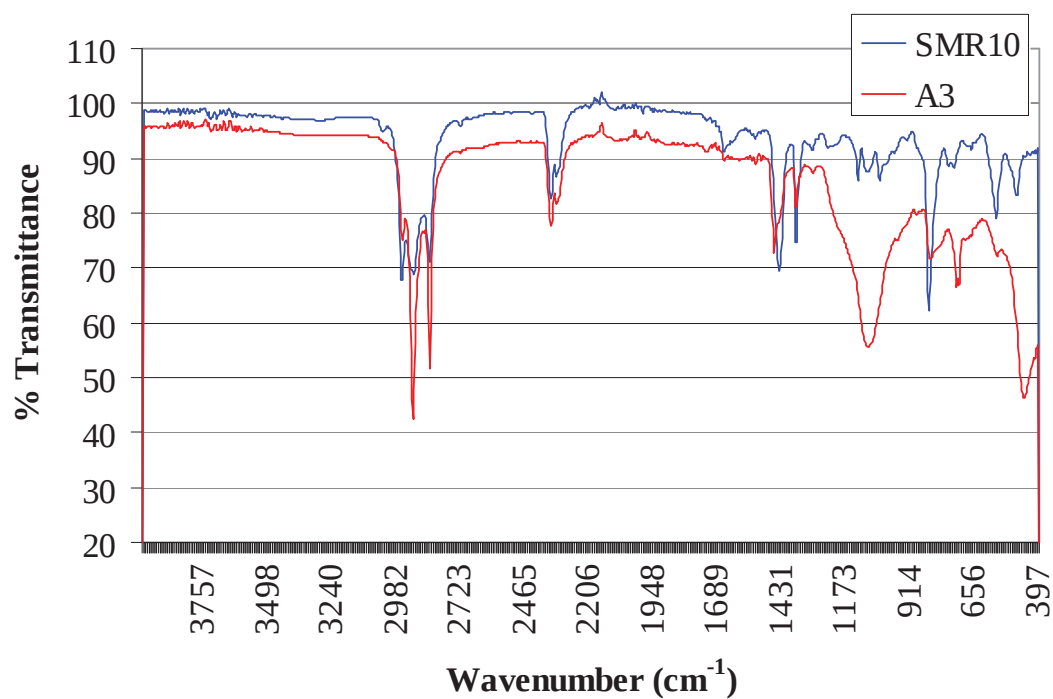


Figure 6.3 FT-IR spectroscopy of SMR10 vs. A3

The polybutadiene is the next predominant raw material in the rubber compounds, excluding A1 and A2 which do not contain polybutadiene. The polybutadiene used in A3 and A4 is known by the trade name Neodene 40. Neodene 40 is a white to honey brown ultra high cis-polybutadiene rubber with a cis content greater than 97.0% and is manufactured by solution polymerisation using a neodymium based catalyst in an aliphatic solvent. The Neodene 40 spectrum is shown in Figure 5.20. Similarly to the natural rubber spectrum, the Neodene 40 spectrum has characteristic peaks at 2914cm^{-1} (CH_3 symmetric stretching) and 1663cm^{-1} ($\text{C}=\text{C}$ stretching). Other characteristic peaks are highlighted in Table 6.1. The common peaks shared between Neodene 40 and A3 are shown in this table. The characteristic peaks for Neodene 40 at 1242cm^{-1} (CH_2 twisting) and 968cm^{-1} ($\text{C}-\text{CH}_3$ twisting) disappear in the A3 spectrum. As discussed in the previous section, the relative intensities of characteristic peaks increase and decrease after the mixing process as a result of chemical and physical changes of the rubber. Figure 6.4 shows the FT-IR spectrum of A3 and Neodene 40.

Table 6.1 Literature, Neodene 40, A3 wavenumbers (cm⁻¹) and assignment bands observed in FT-IR and Raman spectrum analysis

Literature	Neodene 40	A3	Assignment
3032	3005		=C-H stretching
2962		2957	CH ₃ asymmetric stretching
2912	2916	2916	CH ₃ symmetric stretching
2854	2850	2849	CH ₂ symmetric stretching
	2360		
1666	1659	1661	C=C stretching
		1538	
1452	1450	1446	CH ₃ asymmetric stretching
1375		1374	
1311	1311	1308	CH ₂ twisting
1243	1242		CH ₂ twisting
		1089	
983	968		C-CH ₃ stretching
840		830	=CH out-of-plane bending
724	740	739	?
572		570	
492		464	=CC ₂ rocking and scissoring

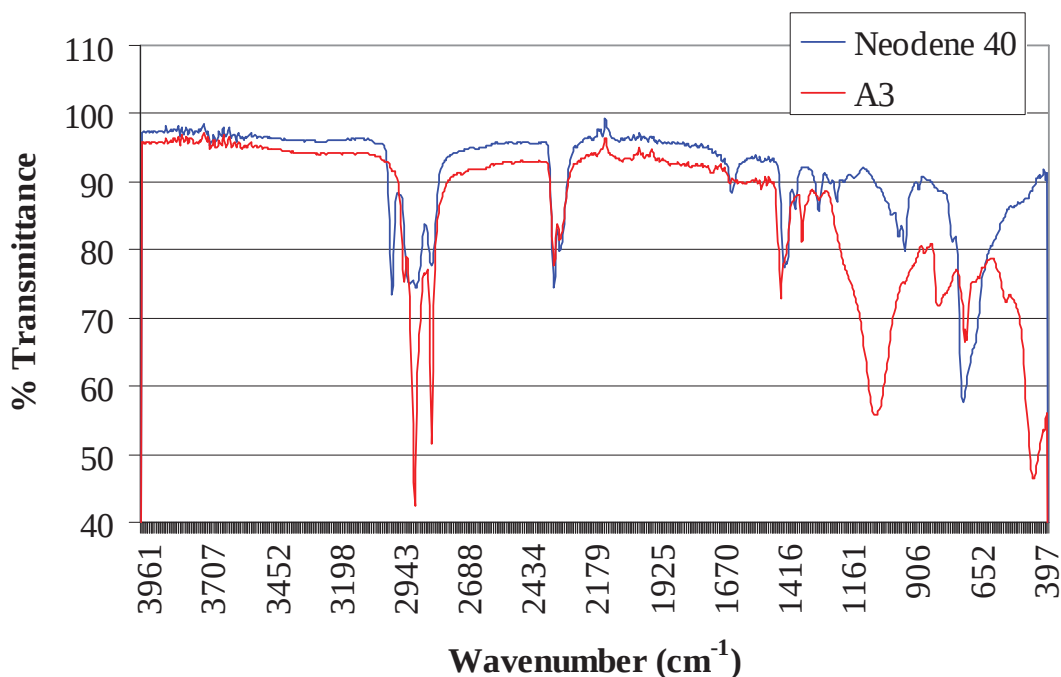


Figure 6.4 FT-IR spectroscopy of Neodene 40 vs. A3

Precipitated silica is used as a filler and reinforcement for the A2 and A3 rubber compounds. The characteristic peak can be seen at 1089cm^{-1} in Figure 5.21, this peak will be used to compare the rubber compounds before and after testing to observe any degradation. The broad characteristic peak for silica is at 1089cm^{-1} and this peak is clearly evident in the A2 and A3 spectra. However, this peak is also shown in the SMR10 and A1 spectra although at lower intensities. This data suggests at the characteristic peak of 1089cm^{-1} , the identification of silica reinforcement is dependant on the intensity of the peak. The A2 and A3 both have clear characteristic peaks at 1089cm^{-1} , therefore the silica in these compounds can be identified from the spectra.

Sulphur is used as the vulcanising agent for the rubber compounds and its characteristic peak is situated at the wavelength of 2359cm^{-1} , see Figure 5.22. This characteristic peak does not appear in the spectra of the rubbers tested as a result of the vulcanization process resulting in C-S bonds. The C-S bond does not appear in the rubber spectra and in this case

there is no left over sulphur that had not reacted in the system. This is expected since each compound was optimally cured before testing.

6.1.3 Rubber aging and its influence on rubber chemistry

The aging of rubber during erosive wear applications is possible as a result of their duration and temperature conditions. Not only is the application temperature a factor in aging, one must also consider the aging of the rubber due to the erosive wear process. A systematic approach was taken in this study where each rubber sample was aged at 75°C and 100°C for one month. Each sample was then wear tested and correlated with samples that had not been aged. Figure 6.5 – 6.12 show the FT-IR spectra of A1, A2, A3 and A4 aged and not aged surfaces of each rubber. The characteristic peaks do not disappear after aging, however some do fluctuate in intensity. Outlined in Chapter 4.1.6.2, a reference point was used for each spectra and a relative value was calculated for each data point. This reference point was defined as the peak intensity relative to the other key peaks. Any relative variation of more than 10% was considered as a change in the chemistry of the rubber during the aging process. The characteristic peaks of interest from this study are shown in Table 6.2, enlarged table located in Appendix 10.2.

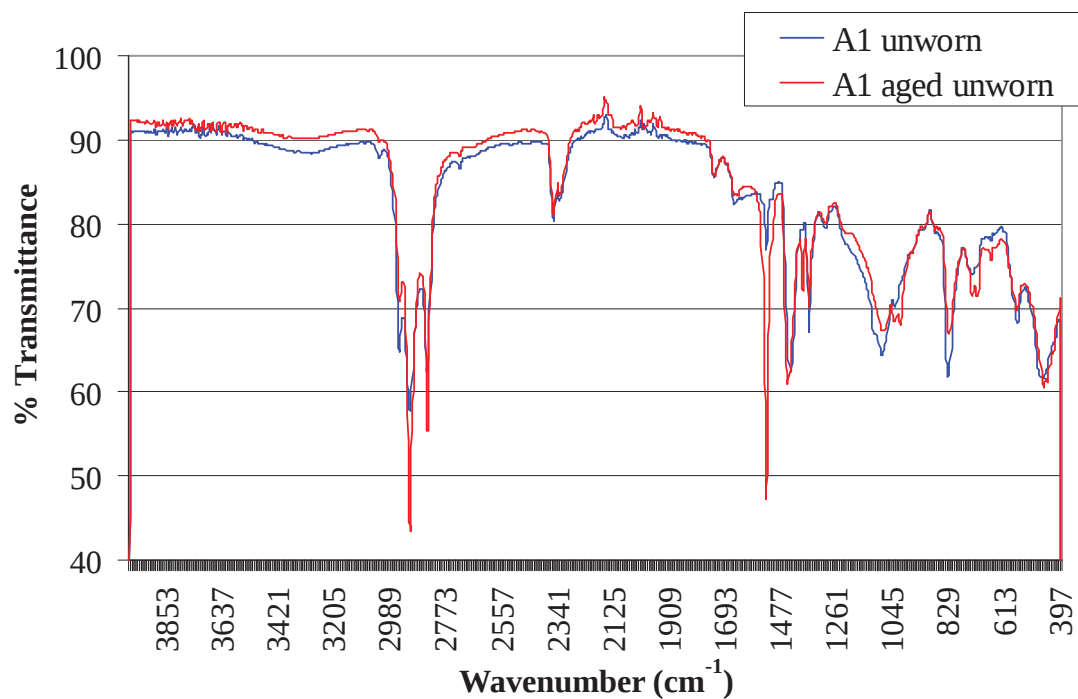


Figure 6.5 A1 spectra of unworn surface unaged and aged at 75°C for 1 month.

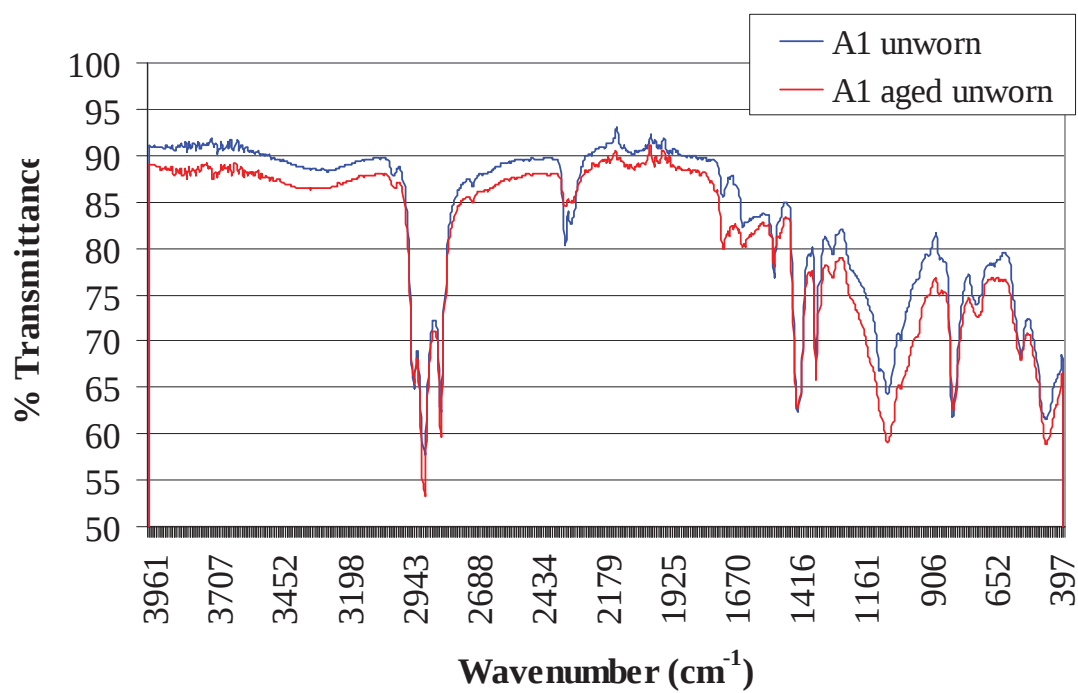


Figure 6.6 A1 spectra of unworn surface unaged and aged at 100°C for 1 month.

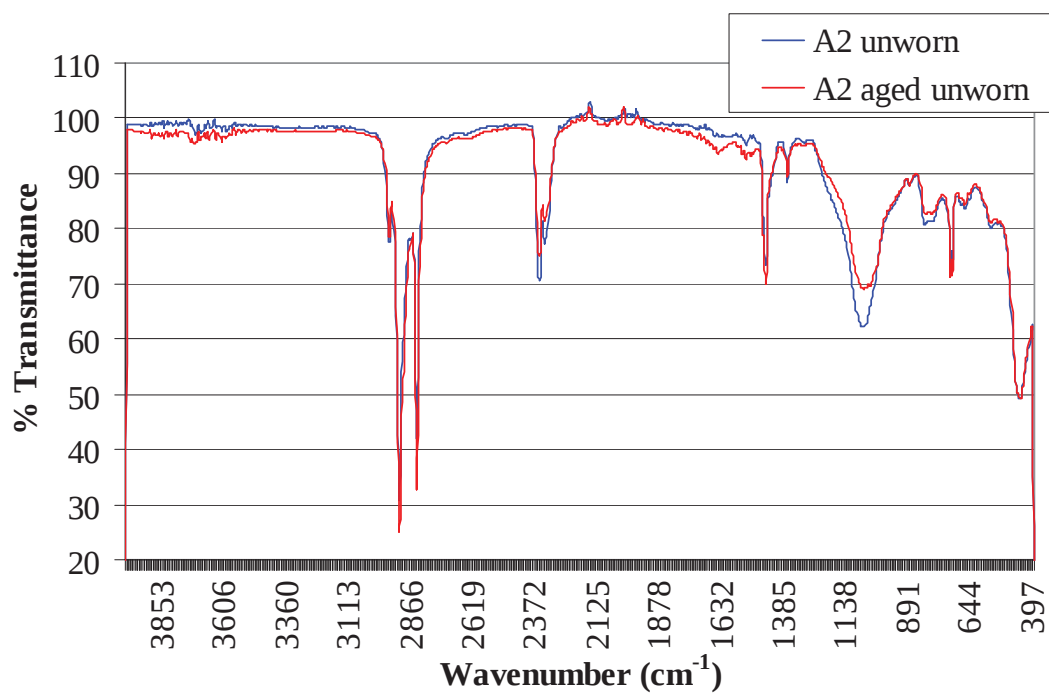


Figure 6.7 A2 spectra of unworn surface unaged and aged at 75°C for 1 month.

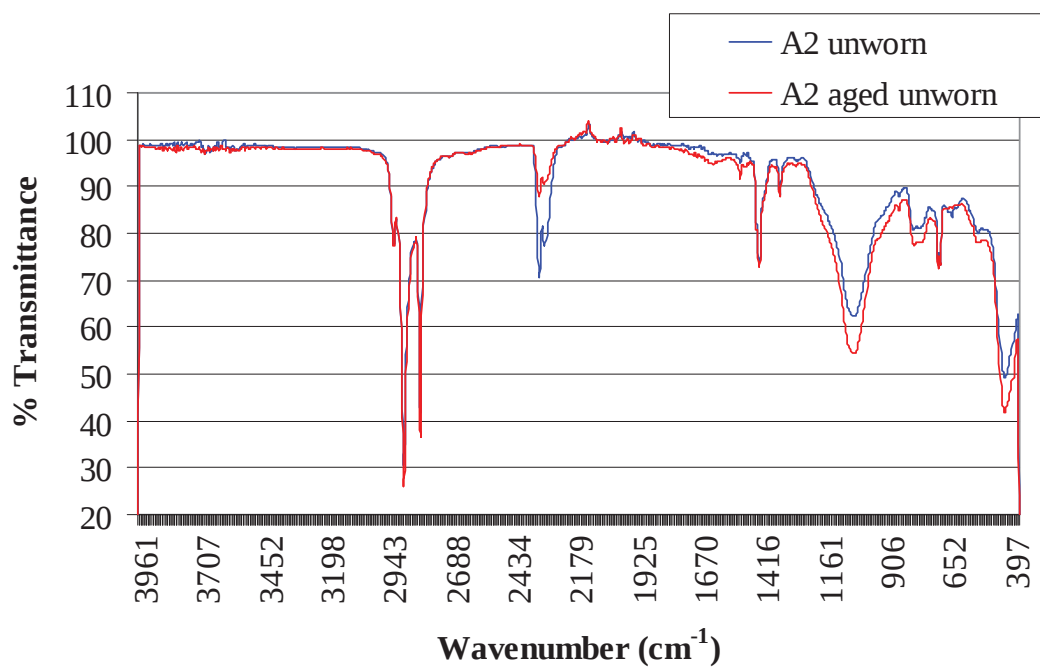


Figure 6.8 A2 spectra of unworn surface unaged and aged at 100°C for 1 month.

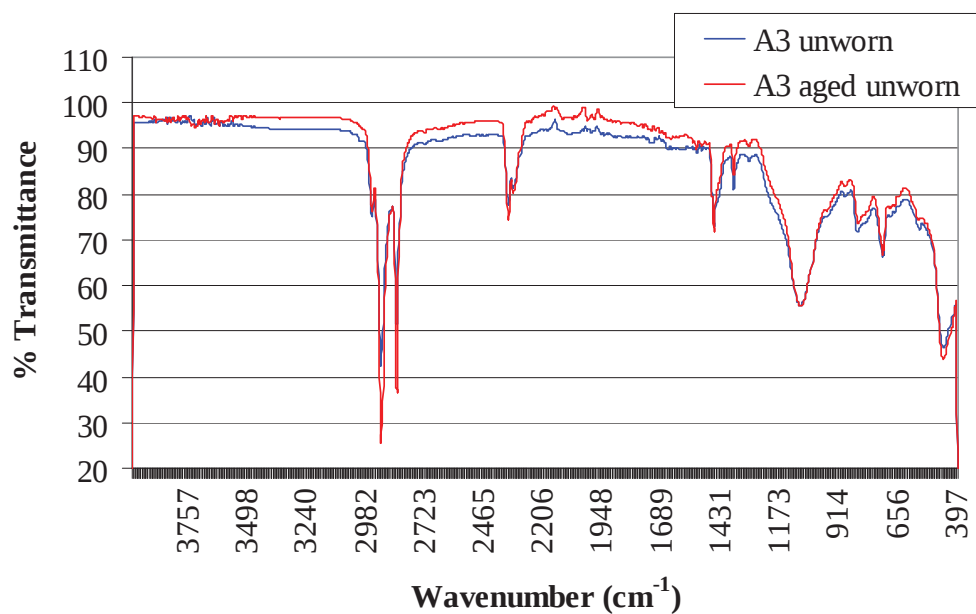


Figure 6.9 A3 spectra of unworn surface unaged and aged at 75°C for 1 month.

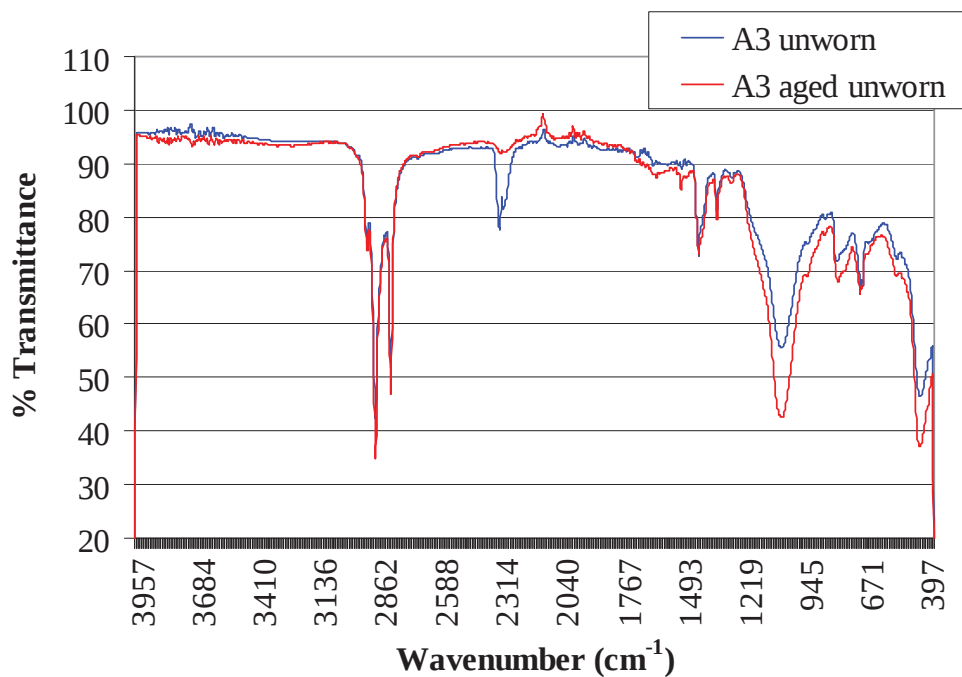


Figure 6.10 A3 spectra of unworn surface unaged and aged at 100°C for 1 month.

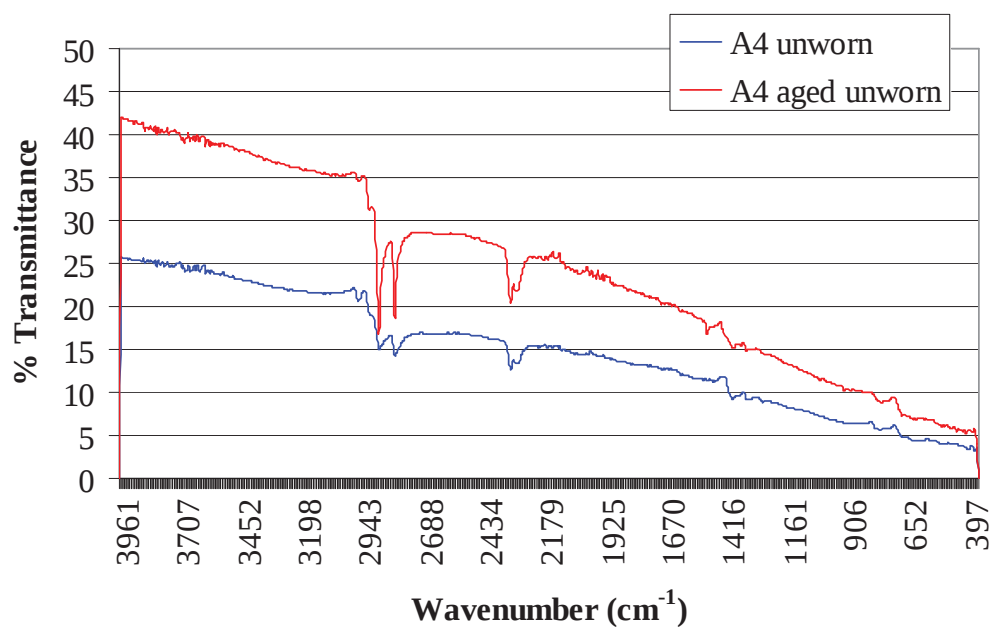


Figure 6.11 A4 spectra of unworn surface unaged and aged at 75°C for 1 month.

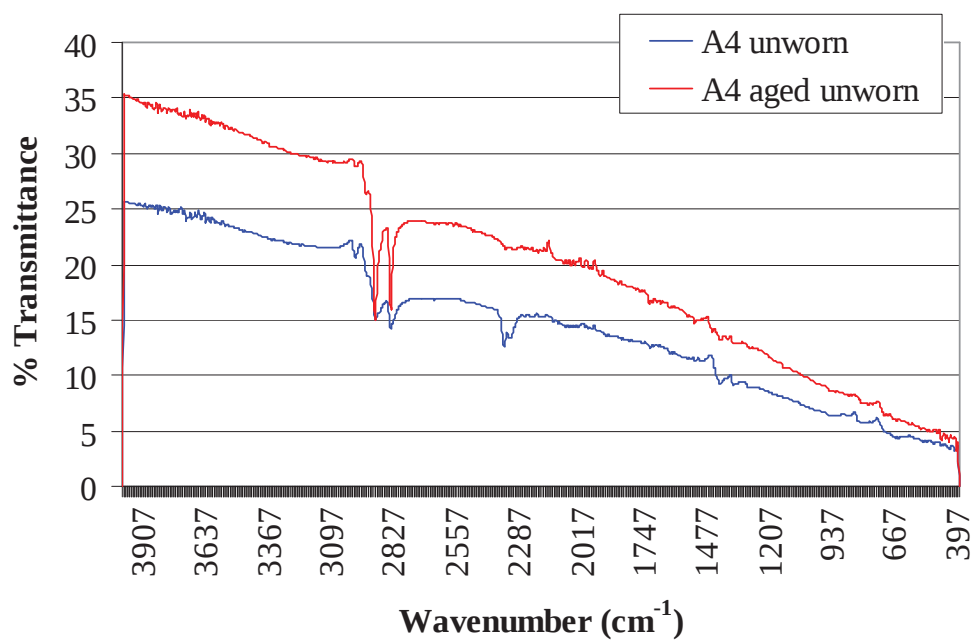


Figure 6.12 A4 spectra of unworn surface unaged and aged at 100°C for 1 month.

Table 6.2 Characteristic peaks of interest of unworn A1, A2 and A3 before and after aging at 75°C and 100°C for 1 month. Enlarged table located in Appendix 10.2.

Material	Wavenumber	Group Frequency	Origin	Functional Group	Assignment		Description	Peak Intensity	Unworn (%T)
A1	1539	1400-1500	C-C			stretch	C-C stretch (in-ring) aromatics	strong	76.85
	2916	2915-2935	CH ₂	Methylene C-H	asymmetric	stretch	Saturated aliphatic (alkane/alkyl) group frequencies	strong	57.71
A2	467							weak	51.52
	1095	950-1225					Aromatic C-H in plane bend	medium	64.05
	2846	2845-2865	CH ₂	Methylene C-H	symmetric	stretch	Saturated aliphatic (alkane/alkyl) group frequencies	strong	42.17
	2916	2915-2935	CH ₂	Methylene C-H	asymmetric	stretch	Saturated aliphatic (alkane/alkyl) group frequencies	strong	30.65
A3	463							weak	46.99
	1099	950-1225					Aromatic C-H in plane bend	medium	56.77
	2846	2845-2865	CH ₂	Methylene C-H	symmetric	stretch	Saturated aliphatic (alkane/alkyl) group frequencies	strong	51.57
	2916	2915-2935	CH ₂	Methylene C-H	asymmetric	stretch	Saturated aliphatic (alkane/alkyl) group frequencies	strong	42.38

The A1 material is a natural rubber formulation without reinforcing fillers such as carbon black and/or silica. The surface analysis revealed two characteristic peaks that are influenced by the aging test, at 1539cm⁻¹ and 2916cm⁻¹. The wavenumber of 1539cm⁻¹ is not identified in the literature and the wavenumber of 2916cm⁻¹ can be identified as belonging to the functional group CH₂ methylene C-H asymmetric stretch [15]. The surface of the unworn A1 has chemically changed as a result of the aging subsequent to the changes in the relative characteristic peaks.

Rubber formulations A2 and A3 behave in the same way when aged. These rubber materials are natural rubber based however, both use silica as the reinforcing agent. During the surface analysis calculations on the aged A2 rubber, there were four characteristic peaks that changed as a result of the aging test; 467cm⁻¹, 1095cm⁻¹, 2846cm⁻¹ and 2916cm⁻¹. The characteristic peak at 467cm⁻¹ is not identified in the literature and cannot be identified in this study. However, one can assume that at low wavenumbers of 400cm⁻¹ the functional group would be C-H bond. The characteristic peak of 1095cm⁻¹ can be identified as an aromatic C-H in plane blend. At the wavenumber of 2846cm⁻¹ is identified as CH₂ methylene C-H symmetric stretch. The characteristic peak at 2916cm⁻¹ is identified as CH₂ methylene C-H asymmetric stretch.

The A3 material is predominately a natural rubber with a polybutadiene polymer blend. Although being slightly different in chemistry to A1 and A2, the characteristic peaks of the spectrum remain similar to those of A2. The relative peak analysis established changes in four characteristic peaks as a result of aging of the A3 rubber. At the wavenumber 463cm^{-1} the characteristic peak showed significant change, however this wavenumber again cannot be identified by the literature. The assumed functional group would be considered as the C-H bond. The characteristic peak at 1099cm^{-1} can be identified as an aromatic C-H in plane bend. The final two characteristic peaks are located at the wavenumbers 2846cm^{-1} and 2916cm^{-1} . These characteristic peaks are identified as CH_2 methylene C-H symmetric stretch and CH_2 methylene C-H asymmetric stretch, respectively.

The data suggests that the A1, A2 and A3 rubbers undergo chemical changes during the aging process. By using this data on aging on the unworn surface of the rubber, we can then investigate whether there is a relationship between the erosive wear process and the aging process with reference to the chemistry of the rubber.

6.1.4 Erosive wear and the influence on rubber chemistry

The relationship of erosive wear on rubber chemistry was analysed in this study. There was a need to identify the chemical changes occurring during the erosive wear process. Using FT-IR spectrometry and relative peak method outline in Chapter 4.1.6.2, the surface chemistry of the rubbers was analysed before and after wear testing as well as before and after aging in order to find correlations with the wear application. Figures 6.13 and 6.14 show the FTIR spectra for the A1 rubber that has been aged at 75°C and 100°C respectively for one month before wear testing. As discussed earlier, the characteristic peaks analysis confirmed significant relative change at 1539cm^{-1} (C-C stretch (in-ring) aromatics functional group), 2361cm^{-1} (not defined in the literature) and 2916cm^{-1} (functional group CH_2 methylene C-H asymmetric stretch). As such, a chemical change is occurring during the erosive wear process through the relative change in characteristic peaks after wear testing. Although the characteristic peak at 2361cm^{-1} is defined in the literature as a H-S

(disulfide bond), N-S (sulfenamide bond) or C-H (methylene) [15]. Each of the rubber formulations are sulphur cured, consequently C-S bonds are present during the vulcanisation process and disulphide bonds are unpaired and left unreacted in the rubber matrix. These unreacted disulphide bonds in this case can pair up with H or N to form the H-S and/or N-S bonds.

New spectra peaks do not appear following aging but the relative intensities of the peaks at particular characteristic wavenumbers do fluctuate, accordingly. Tables 6.3 – 6.6 illustrate the characteristic peaks and relative increase and decrease in the intensities of the peaks as a result of aging and wear testing. Comparing the unworn A1 alongside the worn A1 resulted in one characteristic peak that displayed significant change in the relative intensity. This characteristic peak for the worn surface is identified as a disulfide, sulfenamide or methylene bonds and decreases in relative characteristic peak (% transmittance) by 27 percent. This change in relative peak intensity would suggest that the bonds are influenced by the wear process and could be the cause for the A1 degradation.

Analysing the A1 worn surface against the unworn aged surface shown in Table 6.4, three characteristic peaks are present in contrast to the one characteristic peak in the unaged sample. These characteristic peaks are identified as: 1539cm^{-1} (C-C), 2361cm^{-1} (H-S, N-S, or C-H bonds) and 2916cm^{-1} (CH_2). The aging of the A1 does not change the intensity of the characteristic peak at 2361cm^{-1} . The relative characteristic peak (% transmittance) decrease is comparable to the decrease in the unaged unworn and worn sample analysis data. This decrease can be specified at 27–30% relative characteristic peak (% transmittance) to the worn sample. However, at the characteristic peaks 1539cm^{-1} and 2916cm^{-1} the relative characteristic peak (% transmittance) of the worn sample increases in intensity in comparison to the unworn aged samples. At the aging temperature of 75°C , the relative intensity of these peaks increases by 32% and 13% respectively. And at the aging temperature of 100°C the relative intensities of these peaks increase slightly at 2% and 4% respectively.

Table 6.5 illustrates the FT-IR spectra of the A1 worn surface as a function of the A1 aged worn surface at 75°C and 100°C respectively. The characteristic peak at 2361cm^{-1} showed significant variation in the intensity during the analysis. At an aging temperature of 100°C, the relative intensity of the worn sample and the aged worn sample is comparable. The aged sample is 5% higher in relative characteristic peak (% transmittance) intensity than the unaged sample, leading to the assumption that the surface of the A1 worn sample is similar to that of a surface that has been aged. However, at the aging temperature of 75°C the intensity of the relative characteristic peak (% transmittance) increases by 27%. This relationship is similar to the result observed in the 75°C aged unworn A1 surface with the A1 worn surface where the intensity of the characteristic peak (% transmittance) also increases by 27% in the unworn sample.

In summary, the worn surface of the A1 rubber does not demonstrate signs of aging hence erosive wear cannot be correlated with aging. The data from Tables 6.3 and 6.4 illustrates this finding as such the erosive wear surfaces to the aged surfaces highlighted by the characteristic peak at 2361cm^{-1} .

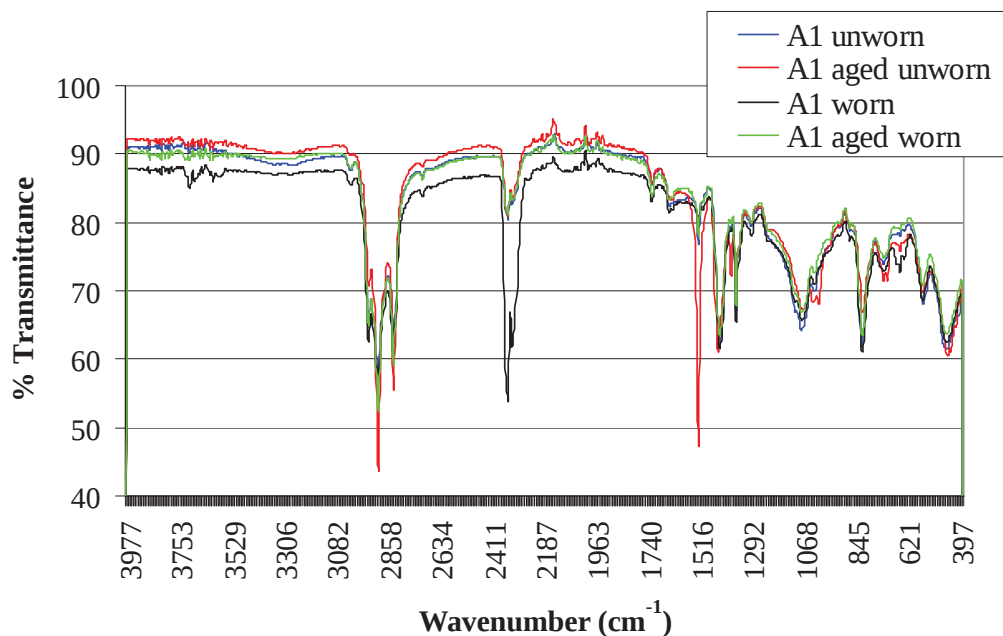


Figure 6.13 A1 unworn surface analysis overlay with worn, aged worn and aged unworn surface. Aging conditions: 1 month at 75°C.

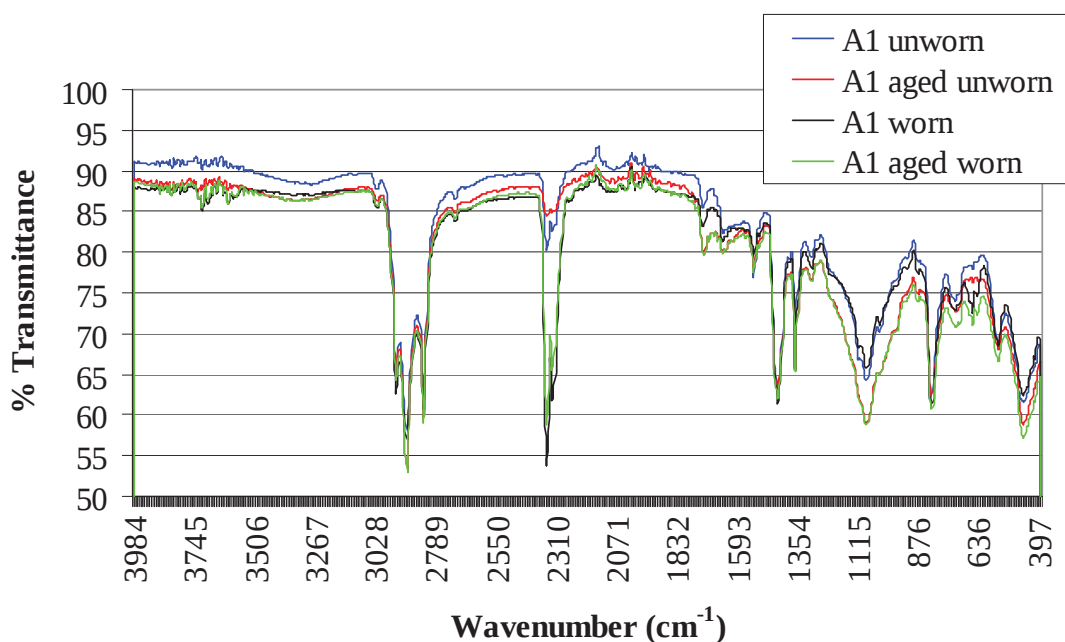


Figure 6.14 A1 unworn surface analysis overlay with worn, aged worn and aged unworn surface. Aging conditions: 1 month at 100°C.

The influence of erosive wear and aging on A2 rubber is shown in Figure 6.15 and 6.16. Similar to A1, no new spectra peaks form as a result of the erosive wear and aging conditions. However, the relative intensities of the characteristic wavenumbers increase and decrease due to these conditions leading to the assumption that the rubber chemistry is influenced due to wear. Comparing the A2 unworn rubber as a function of the worn rubber, four characteristic peaks for the worn surface displayed significant change in relative intensity. As mentioned earlier, the characteristic peaks of interest include the following wavenumbers: 467cm^{-1} , 1095cm^{-1} , 2846cm^{-1} and 2916cm^{-1} . The characteristic peak at 467cm^{-1} could not be identified from the literature. Characteristic peaks below 1000cm^{-1} cannot be identified due to the interference of external species and the infrared capability. At 1095cm^{-1} the relative transmittance of the worn surface is decreased by 23%. This would suggest that the aromatic C-H bonds are increased as a result of the wear testing. At the asymmetric and symmetric CH_2 bonds at wavenumbers 2846cm^{-1} and 2916cm^{-1} , the relative transmittance increases by 6% and 5% respectively. The variations in relative

transmittance in these characteristic peaks suggest that the rubber is undergoing a chemical change during the erosive wear process.

Table 6.4 illustrates the characteristic peaks of interest on the worn A2 surface as a function of the aged (75°C and 100°C for one month) unworn A2 surface. The characteristic peak at 467cm^{-1} shows relative differences between the samples, however this peak is not defined in the literature. The relative transmittance of the worn surface at 1095cm^{-1} decrease, by 30% and 15% compared to the unworn aged surface at 75°C and 100°C aging respectively. At this characteristic peak, the relative transmittance increase on the worn surface in relation to the unworn surface can be correlated with the relative increase in the unworn aged surface. Similarly with the asymmetric and symmetric CH_2 bonds at wavenumbers 2846cm^{-1} and 2916cm^{-1} , the relative transmittance increases by 16% and 11% respectively, at 75°C, and 12% and 10%, respectively, at 100°C. These higher observed values suggest the aging increases or decreases the relative intensity of the characteristic peaks in the unworn sample. However, the aging does not cause the chemical change of the rubber to the same effect as the erosive wear process.

Comparing the A2 aged worn surface as a function of the A2 worn surface, the relative transmittance of the aged worn surface show the same trends as the aged unworn surface to the worn surface. The relative intensity of the characteristic peak at 1095cm^{-1} decreases by 20% and 7% at aging temperatures of 75°C and 100°C, respectively. The decrease is not as significant as the comparison with the unworn aged sample and the worn surface, however, a similar trend is apparent. Similarly with the characteristic peaks at 2846cm^{-1} and 2916cm^{-1} , the relative intensities increases by 14% and 12% at 75°C and 8% and 9% at 100°C aging temperatures. This analysis and result suggests that aging influences the chemistry of the rubber but aging is not the source of chemical change during erosive wear.

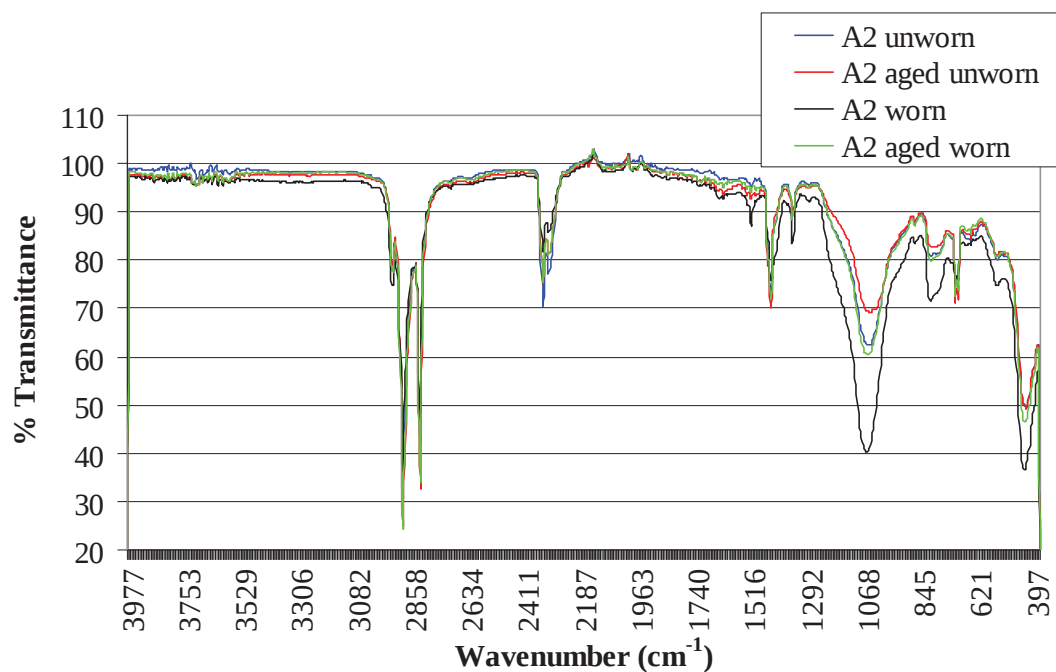


Figure 6.15 A2 unworn surface analysis overlay with worn, aged worn and aged unworn surface. Aging conditions: 1 month at 75°C.

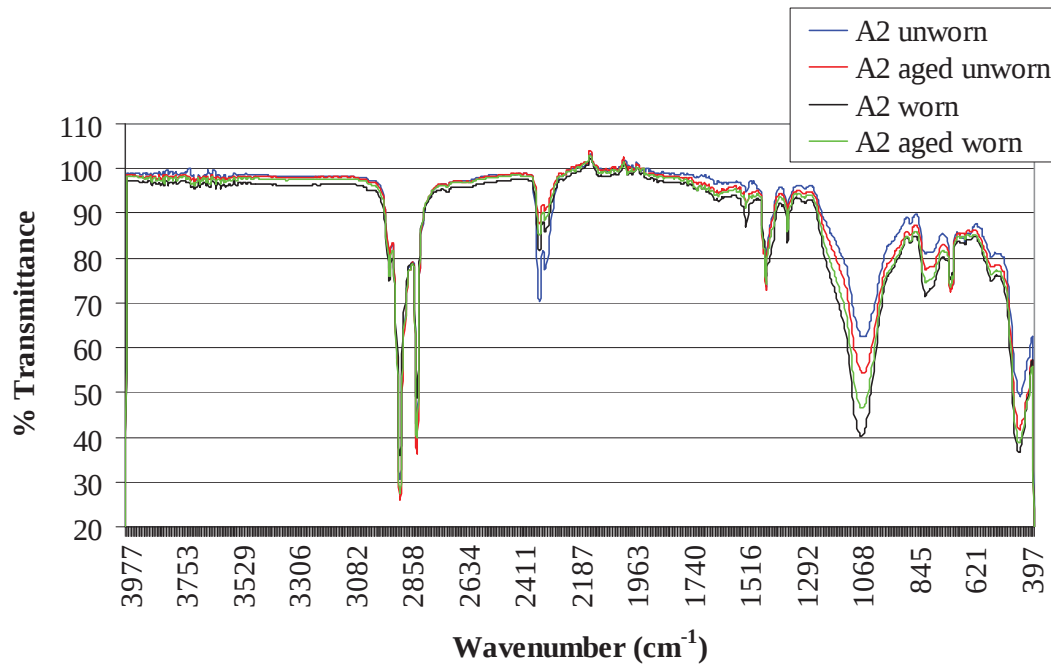


Figure 6.16 A2 unworn surface analysis overlay with worn, aged worn and aged unworn surface. Aging conditions: 1 month at 100°C.

The surface analysis of the worn and aged A3 samples are shown in Figure 6.17 and 6.18. Again, similar to A1 and A2 discussed earlier, new spectra peaks do not form during these aging conditions although the relative intensities of the peaks at characteristic wavenumbers do increase and decrease accordingly. Referring to Table 6.3 and the unworn as a function of the worn A3 surface, there are three characteristic peaks of interest in the spectra. The characteristic peak at wavenumber 463cm^{-1} is again present but cannot be identified. At 1099cm^{-1} , this wavenumber is identified in the literature as aromatic C-H bonds. The worn surface decreases in relative transmittance by 10%. At 2916cm^{-1} , the asymmetric CH_2 bonds decrease in relative transmittance by 5%. This data again suggest that the A3 rubber undergoes chemical change during the erosive wear process.

Table 6.4 shows the characteristic peaks of aged unworn A3 as a function of worn A3. The characteristic peaks of interest include the following: 1099cm^{-1} , 2846cm^{-1} and 2916cm^{-1} . At the 1099cm^{-1} peak, the relative transmittance intensity of the aged unworn sample in comparison to the worn sample decreases by 11% at 75°C and does not change significantly 100°C at an increase of 3% intensity. At the asymmetric and symmetric CH_2 bonds at wavenumbers 2846cm^{-1} and 2916cm^{-1} , the relative transmittance increases by 11% and 12% at 75°C , and 1% and 2% at 100°C . A similar observation to the A2 result suggests that degradation is occurring to the surface of the rubber during the erosive wear process.

Table 6.5 illustrates the characteristic peaks of aged worn A3 samples as a function of worn A3 samples. Similar trends are again shown in the relative intensities of the characteristic peaks as in A2. The relationship between the aged worn and the aged unworn as a function of the worn A3 is comparable at a different magnitude. The characteristic peak at 1099cm^{-1} the relative intensity of the aged unworn sample in comparison to the worn sample decreases by 8% at 75°C . However, the relative transmittance increases by 7% at 100°C . As discussed earlier, this data suggests that aging contributes to the chemical change of the rubber; however it is evident that the aged surface does not correlate with the erosive wear process.

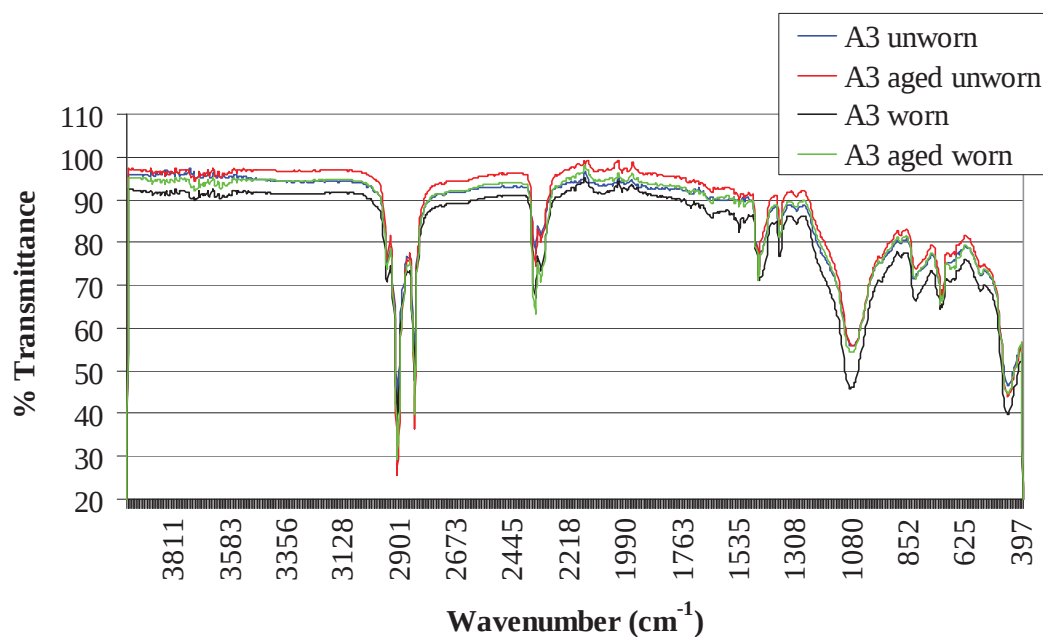


Figure 6.17 A3 unworn surface analysis overlay with worn, aged worn and aged unworn surface. Aging conditions: 1 month at 75°C.

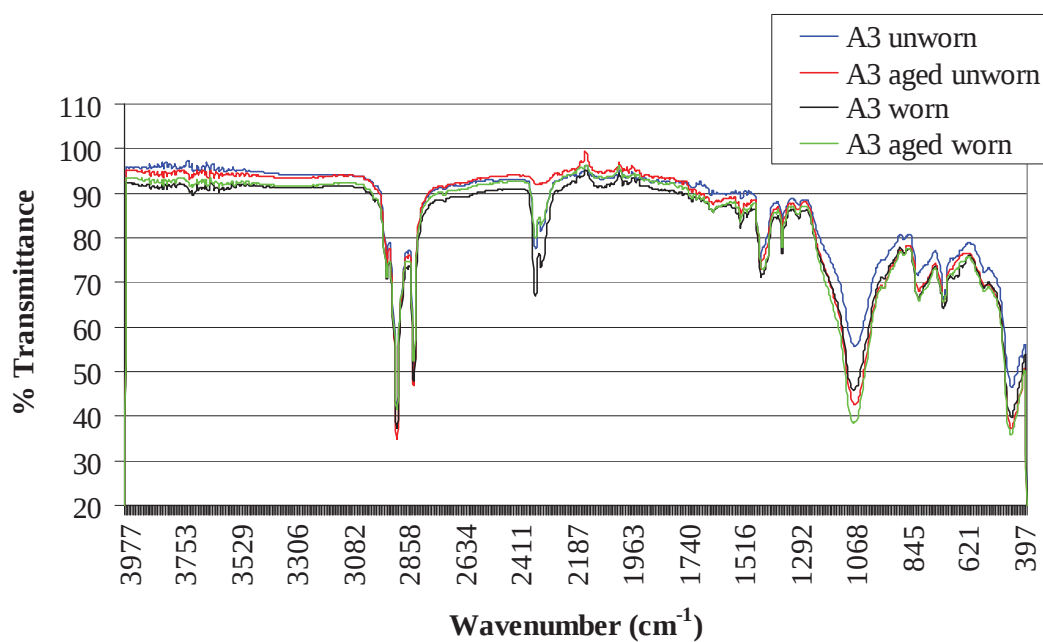


Figure 6.18 A3 unworn surface analysis overlay with worn, aged worn and aged unworn surface. Aging conditions: 1 month at 100°C.

The influence of aging on the unworn and worn surfaces of A4 is shown in Figures 6.19 and 6.20. The high level of carbon black loading in the A4 formulation affects the FT-IR reading and produces unclear spectra of the A4 rubber. As a result, the relative characteristic peaks and intensities of these peaks could not be accurately analysed. The FT-IR method of analysis uses infrared light to measure the level of absorbance and transmittance in the material. A4's high loading of carbon black causes the infrared light from the FT-IR to be absorbed directly into the carbon black, resulting in a drift or inaccurate spectra for identifying the characteristic chemical bonds in the material. For this limitation in the test method the chemical change from wear testing on the A4 material could not be discussed further in this thesis.

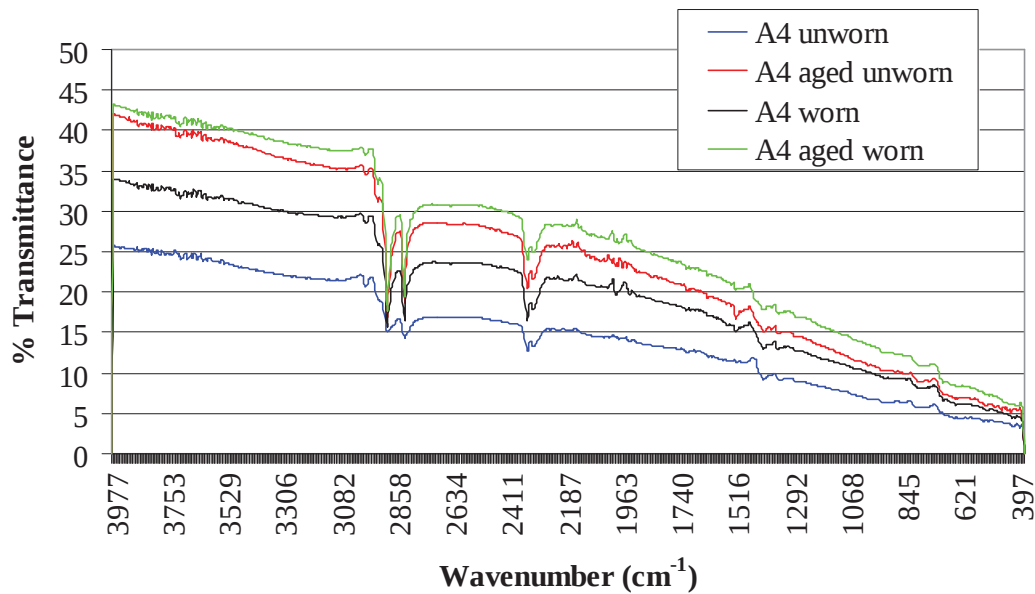


Figure 6.19 A4 unworn surface analysis overlay with worn, aged worn and aged unworn surface. Aging conditions: 1 month at 75°C.

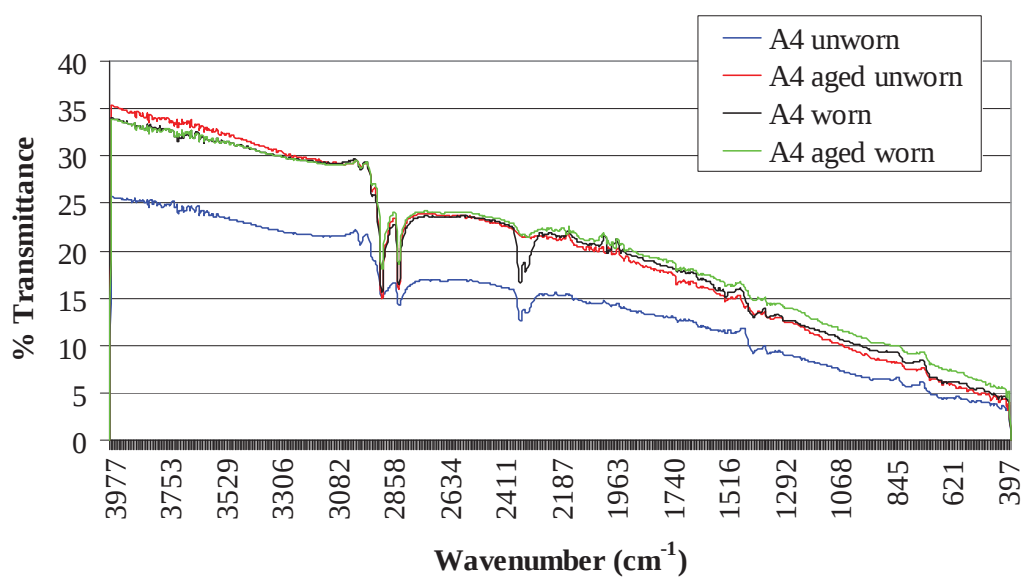


Figure 6.20 A4 unworn surface analysis overlay with worn, aged worn and aged unworn surface. Aging conditions: 1 month at 100°C.

Table 6.3 Relative characteristic peaks of interest for the comparison between unworn vs. worn A1, A2 and A3 samples. Enlarged table located in Appendix 10.2.

Material	Wavenumber	Group Frequency	Origin	Functional Group	Assignment		Description	Peak Intensity	Unworn (%T)
A1	2361						Either H-S, N-S or C-H bonds	strong	80.35
A2	467							medium	51.52
	1095	950-1225					Aromatic C-H in plane bend	medium	64.05
	2846	2845-2865	CH ₂	Methylene C-H	symmetric	stretch	Saturated aliphatic (alkane/alkyl) group frequencies	strong	42.17
	2916	2915-2935	CH ₂	Methylene C-H	asymmetric	stretch	Saturated aliphatic (alkane/alkyl) group frequencies	strong	30.65
A3	463							medium	46.99
	1099	950-1225					Aromatic C-H in plane bend	medium	56.77
	2916	2915-2935	CH ₂	Methylene C-H	asymmetric	stretch	Saturated aliphatic (alkane/alkyl) group frequencies	strong	42.38

Table 6.4 Relative characteristic peaks of interest for the comparison between unworn A1, A2 and A3 after aging at 75°C and 100°C for 1 month vs. unaged worn A1, A2 and A3. Enlarged table located in Appendix 10.2.

Material	Wavenumber	Group Frequency	Origin	Functional Group	Assignment		Description	Peak Intensity	Aged Unworn 75°C (%T)
A1	1539	1400-1500	C-C			stretch	C-C stretch (in-ring) aromatics	strong	47.3
	2361						Either H-S, N-S or C-H bonds	strong	81.0
	2916	2915-2935	CH ₂	Methylene C-H	asymmetric	stretch	Saturated aliphatic (alkane/alkyl) group frequencies	strong	43.5
A2	467							medium	51.6
	1095	950-1225					Aromatic C-H in plane bend	medium	70.9
	2846	2845-2865	CH ₂	Methylene C-H	symmetric	stretch	Saturated aliphatic (alkane/alkyl) group frequencies	strong	32.7
	2916	2915-2935	CH ₂	Methylene C-H	asymmetric	stretch	Saturated aliphatic (alkane/alkyl) group frequencies	strong	25.1
A3	463							medium	44.4
	1099	950-1225					Aromatic C-H in plane bend	medium	57.1
	2846	2845-2865	CH ₂	Methylene C-H	symmetric	stretch	Saturated aliphatic (alkane/alkyl) group frequencies	strong	36.9
	2916	2915-2935	CH ₂	Methylene C-H	asymmetric	stretch	Saturated aliphatic (alkane/alkyl) group frequencies	strong	25.7

Table 6.5 Relative characteristic peaks of interest for the comparison between worn A1, A2 and A3 after aging at 75°C and 100°C for 1 month vs. unaged worn A1, A2 and A3. Enlarged table located in Appendix 10.2.

Material	Wavenumber	Group Frequency	Origin	Functional Group	Assignment		Description	Peak Intensity	Aged Worn 75°C (%T)	Aged Worn 100°C (%T)	Worn (%T)	Aged 75°C Worn - Worn (%T)	Aged 100°C Worn - Worn (%T)
A1	2361						Either H-S, N-S or C-H bonds	strong	81.0	58.8	53.82	27.22	4.96
A2	467							medium	48.4	40.4	37.69	10.72	2.71
	1095	950-1225					Aromatic C-H in plane bend	medium	61.7	47.8	41.28	20.47	6.56
	2846	2845-2865	CH ₂	Methylene C-H	symmetric	stretch	Saturated aliphatic (alkane/alkyl) group frequencies	strong	34.4	40.2	48.62	-14.27	-8.46
	2916	2915-2935	CH ₂	Methylene C-H	asymmetric	stretch	Saturated aliphatic (alkane/alkyl) group frequencies	strong	24.4	27.6	36.11	-11.69	-8.51
A3	463							medium	45.1	35.9	39.94	5.16	-4.00
	1099	950-1225					Aromatic C-H in plane bend	medium	55.0	39.3	46.50	8.48	-7.23
	2846	2845-2865	CH ₂	Methylene C-H	symmetric	stretch	Saturated aliphatic (alkane/alkyl) group frequencies	strong	40.3	52.6	47.80	-7.47	4.81
	2916	2915-2935	CH ₂	Methylene C-H	asymmetric	stretch	Saturated aliphatic (alkane/alkyl) group frequencies	strong	29.5	41.5	37.34	-7.85	4.11

Table 6.6 Surface analysis of unworn vs. worn A1, A2 and A3 after aging at 75°C and 100°C for 1 month.
Enlarged table located in Appendix 10.2.

Material	Wavenumber	Group Frequency	Origin	Functional Group	Assignment		Description	Peak Intensity
A1	1539	1400-1500	C-C			stretch	C-C stretch (in-ring) aromatics	strong
	2361						Either H-S, N-S or C-H bonds	strong
	2916	2915-2935	CH ₂	Methylene C-H	asymmetric	stretch	Saturated aliphatic (alkane/alkyl) group frequencies	strong
A2	467							medium
	1095	950-1225					Aromatic C-H in plane bend	medium
	2846	2845-2865	CH ₂	Methylene C-H	symmetric	stretch	Saturated aliphatic (alkane/alkyl) group frequencies	strong
	2916	2915-2935	CH ₂	Methylene C-H	asymmetric	stretch	Saturated aliphatic (alkane/alkyl) group frequencies	strong
A3	463							medium
	1099	950-1225					Aromatic C-H in plane bend	medium
	1462 ?	1450-1470	CH			bend	Alkanes	weak
	2846	2845-2865	CH ₂	Methylene C-H	symmetric	stretch	Saturated aliphatic (alkane/alkyl) group frequencies	strong
	2916	2915-2935	CH ₂	Methylene C-H	asymmetric	stretch	Saturated aliphatic (alkane/alkyl) group frequencies	strong

6.2 *Physical Properties*

This chapter will outline the physical and viscoelastic properties of each rubber investigated in this study and discuss the correlations these properties have with the rubber chemistry and erosive wear. The physical and viscoelastic properties such as hardness, tensile strength, tear strength, resilience, shear storage modulus (G'), shear loss modulus (G''), and tan delta ($\tan \delta$) are important properties to consider in determining the material's erosive wear resistance. During the erosive wear process, shear stress and strain are induced onto the surface of the rubber causing material damage. The root cause of this damage stems from the energy build up and dissipation of energy will be discussed in detail in this section.

6.2.1 Hardness – Durometer A°

The hardness of the rubber is critical to the performance of the rubber in application. In some applications hardness is the key physical property for wear resistance, e.g. in highly abrasive applications a higher hardness rubber is required. Figure 5.10 shows the measured hardness values of the four rubber materials tested as a function of total wear loss following erosion wear testing. As discussed in an earlier section, the rubbers tested in this study have different formulations and chemistry. It is documented in the literature that carbon black will increase the hardness of the rubber to an optimum before decreasing [57]. The A1 is predominantly a natural gum base rubber with no reinforcing fillers other than a small amount of carbon black to add colour to the rubber. It was expected then to have the lowest hardness in comparison to the other tested materials. The rubber with the highest hardness was the A4 material, shown in Figure 5.10. A4 is a natural rubber and polybutadiene blend with high loading of carbon black. In this case the high level of carbon black loading has contributed to the A4 high hardness in comparison to the other rubbers in this study.

Due to the different formulation and chemistry of the rubbers analysed in this study, it was important to divide the rubber families into two groups when discussing the physical

properties and the erosive wear test results. A1 and A2 reside in the natural rubber family whereas A3 and A4 belong to the polymer blend of natural rubber/polybutadiene family. The hardness of the A1 and A2 rubber is comparable to the erosive wear loss similarly for the A3 and A4 rubbers. As the hardness of the rubbers increase, the erosive wear loss also increases. In the case of A1 and A2, the difference between the rubbers is that A1 is unfilled and A2 is filled with reinforcing silica therefore increasing the hardness of the material. With the A3 and A4 comparison, the A3 is not as highly filled with reinforcing fillers as the A4, hence the lower hardness and the lower erosive wear loss.

6.2.2 Resilience – Lupke test method

Figure 5.11 illustrates the resilience of the rubber materials as a function of the erosive wear loss of each rubber after wear testing. Resilience is a measure of rebound as the material is deformed or displaced under impacting force. Similarly to the hardness analysis, the rubbers need to be divided into the two groups when discussing the physical property and the erosive wear test results. The A1 has the higher resilience which has lower erosive wear loss in comparison to the lower resilient A2 rubber that has a higher erosive wear loss. The group consisting of natural rubber/polybutadiene blend exhibits a clear correlation with the theory of higher resilience results in lower wear loss. This is shown from the data in that A3 rubber has the higher resilience resulting in a lower erosive wear loss than the A4. The resilience of the rubber can also be correlated with the viscoelastic property $\tan \delta$. The resilience is relative to $1/\tan \delta$ and will be discussed further in a later chapter in this thesis.

6.2.3 Tensile Strength and Tensile Tear Strength

The tensile strength of the rubbers as a function of the wear loss is shown in Figure 5.12. Tensile strength is a property predominantly used for controlling the material quality and for determining degradation as a result of chemical and/or thermal exposure. There are no

clear trends between the tensile strength and the erosive wear loss in the rubbers analysed in this study.

The tensile tear strength of the rubbers is shown as a function of wear loss in Figures 5.13 and 5.14. The tear strength of a rubber is defined as the ability of the rubber to resist tearing at a localised point. Good dispersion of reinforcing agents such as carbon black or silica into the rubber matrix can influence the physical properties, such as tensile tear strength. A well dispersed filled rubber will require more energy for the tear to propagate through to failure, as the fracture line will deviate from its course many times past each filler. Whereas a poorly dispersed filled rubber will require less energy for the tear since large agglomerates are formed clearing a path for the fracture to propagate to failure. Figure 6.21 illustrates this concept.

The tensile strength and tear strength can also be correlated with crosslink density and the relationship can be seen in Figure 2.61 [53, 57]. Crosslink density is defined as the number of crosslinks per unit volume. A correlation could be found in this study where A4 has the highest tear strength and lowest tensile strength of all the rubbers. This finding correlates with Figure 2.61. This could also be the result of the conventional cure system that could cause very high crosslink density leading to strong stress concentrations occurring in the vicinity of the broken bonds.

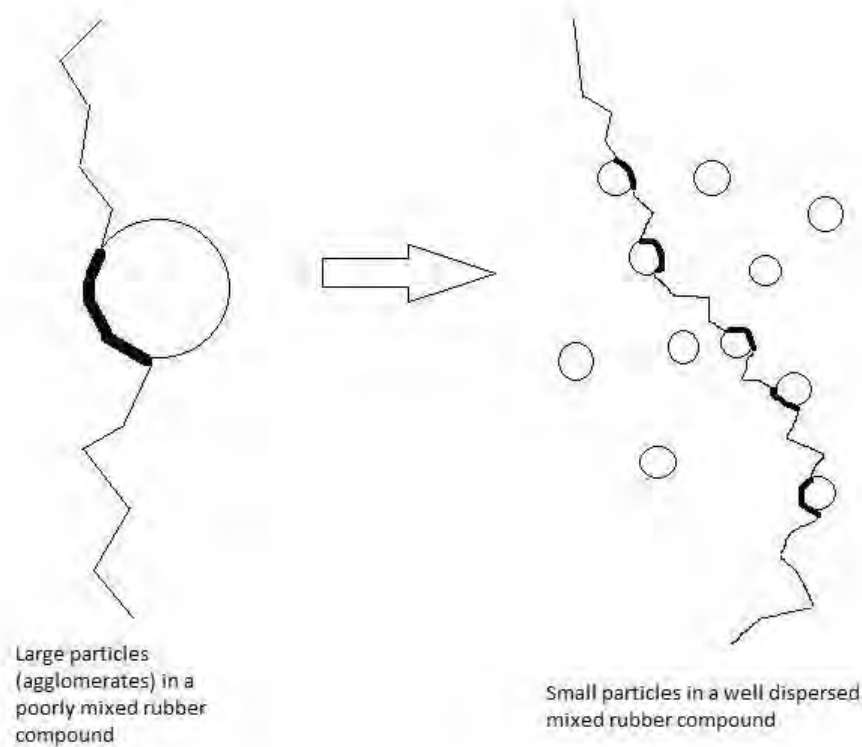


Figure 6.21 Large agglomerates in a poorly mixed rubber leading to lower tear strength in comparison to a well dispersed rubber compound.

In the erosive wear study, the analysis of the rubbers must be again grouped into two families, natural rubber and the blend of natural rubber and polybutadiene before correlations are made with the tear strength and wear loss. A1 and A2 make up the natural rubber family with A2 having a high reinforcing filler content resulting in a higher tear strength. However, in the case of the total wear loss, the A1 out performs the A2. Similarly with the natural rubber/polybutadiene blended rubbers of A3 and A4 where the A3 has lower tear strength yet the lower total wear loss. The lower total wear loss of the A3 in comparison to the A4 can then be attributed to the type of reinforcing agent, and the amount of reinforcing agent. In this case, A3 utilises Silica as the reinforcing agent while A4 has a carbon black reinforcing filler. The concentration of the filler is also important in this case. A3 has a lower total concentration of reinforcing filler as opposed to a high

concentration of carbon black in the A4 rubber. An additional cause for this lower total wear loss for the A3 rubber can also be identified by the level of polybutadiene loading. A3 has a significantly lower ratio of polybutadiene to natural rubber than A4. This increase of polybutadiene for A4 is the cause of the increase in wear loss. Polybutadiene is predominantly used for abrasion resistance whereas natural rubber is used for impingement/erosive wear applications. The natural rubber and polybutadiene blend is used for applications where a combination of abrasion and impingement wear is the driving wear mechanism. In the case of a centrifugal slurry pump, the nature of the wear is predominantly erosive; but it is a case of the best combination of chemistry and properties in A3 that produces a more erosion resistant material.

6.2.4 The influence of aging on physical properties

The physical properties of A1, A2, A3 and A4 are influenced by the wet and dry aging tests carried out in this study. The wet aging test with the conditions at 75°C in water for one month were used to simulate conditions the rubber would undergo in operation. Figure 6.22 illustrates the decrease in tensile strength of the rubbers during the wet aging process. It was observed at wet aging temperatures of 75°C, the tensile strength of the rubbers decreased in reference to the control samples. Previous studies have suggested that the aging effects on tensile strength are similar to the tear strength of rubbers [29]. Figures 6.23 and 6.24 show this trend where the wet aged samples decrease in tensile and tear strength after aging. At high aging temperatures, the amount of crosslinking increases restricting the mobility of the polymer chains. This restriction creates a polymer network that is incapable of dissipating much energy. The elastomer as a result becomes relatively brittle and fails in a brittle manner with low elongation and tear strength [29].

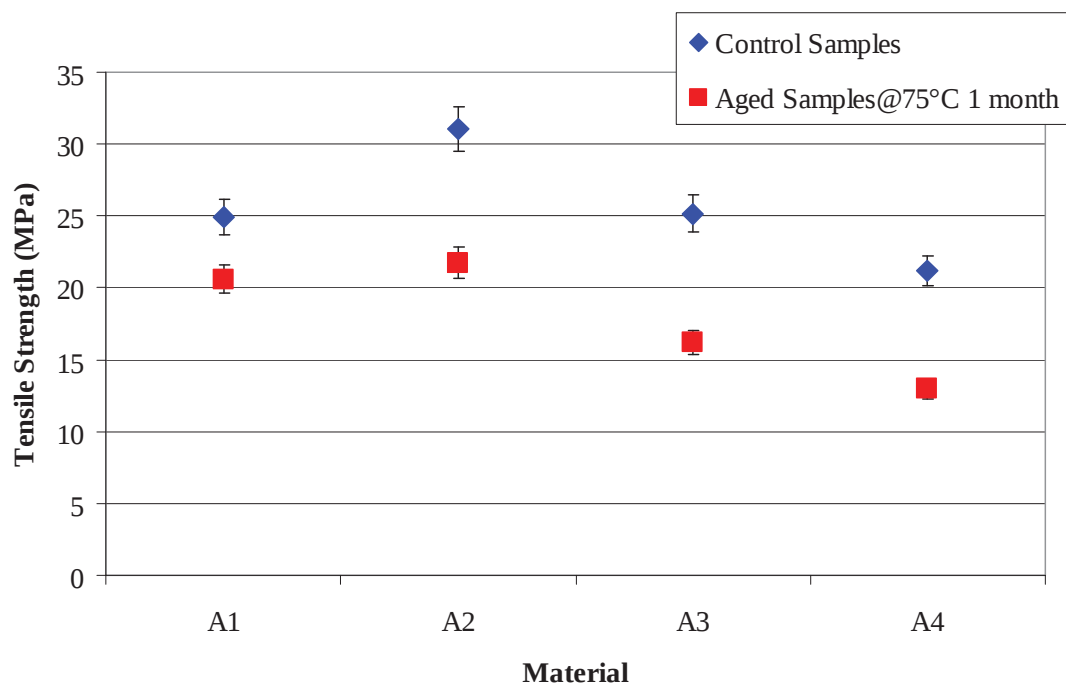


Figure 6.22 Tensile strength of control samples vs. wet aged samples at 75°C for 1 month.

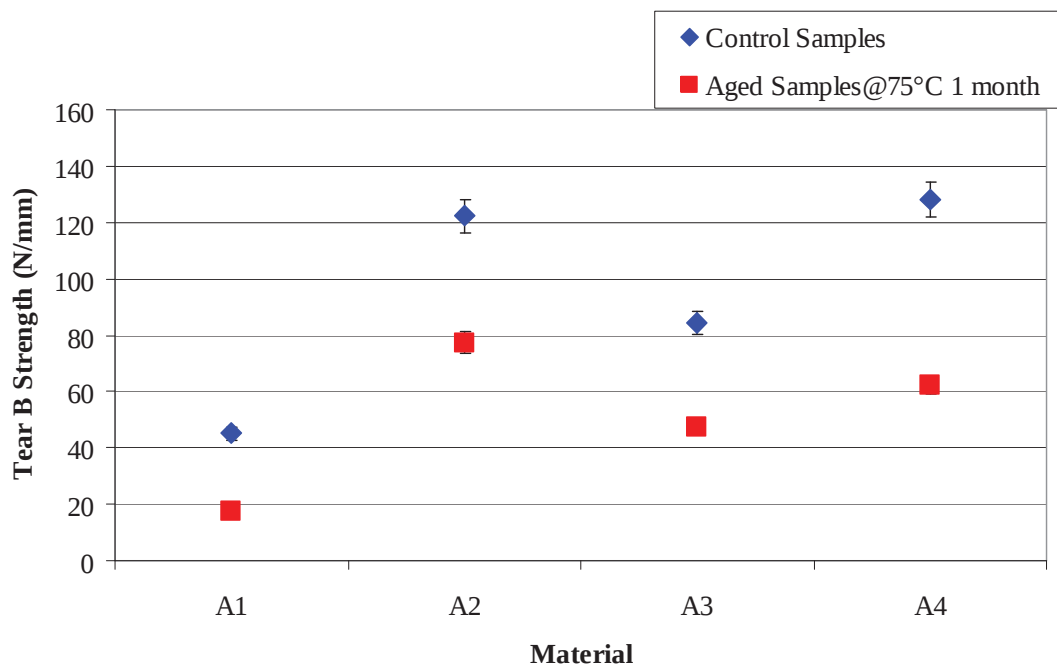


Figure 6.23 Tear B strength of control samples vs. wet aged samples at 75°C for 1 month

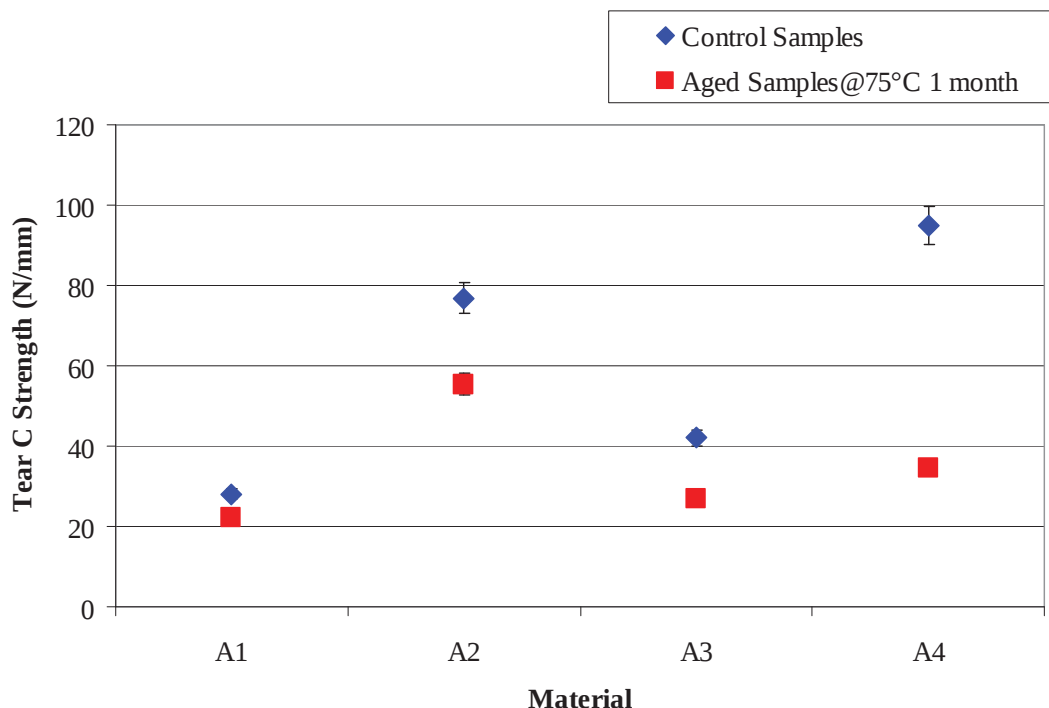


Figure 6.24 Tear C strength of control samples vs. wet aged samples at 75°C for 1 month

The hardness of the control samples increase after wet aging at 75°C, as shown in Figure 6.25. This increase in hardness of the rubbers is influenced by the crosslinking of polymer chains in the rubber matrix during the vulcanisation process. As discussed in the literature, Li and Koenig [52] suggest the free energy of polymer per monomer unit decreases as the temperature is raised during vulcanisation. Therefore, at a certain temperature the optimum vulcanisation reaction will occur and at temperatures about this point, long chain polymers are not possible. Crosslinking is the dominant reaction that occurs during the initial stages of aging [77]. As the rubber matrix becomes more highly crosslinked during the aging process, this leads to the increase in hardness of the rubbers analysed in this study.

Figure 6.26 shows the increase in wear loss of the analysed rubbers after wet aging at 75°C. This increase in wear loss can be correlated with aging which causes chemical change in the rubber shown from FT-IR surface analysis in Table 6.6. Although each rubber decreases in wear resistance by approximately 30 percent, the ratio of the wear loss remains constant between the rubbers tested. This suggests that wet aging of rubber at 75°C

degrades the natural rubber and natural rubber blended formulations relative to its control sample. However, as discussed earlier, the erosive worn surface of the rubber does not correlate with an aged surface, hence there is no direct relationship. However, this data does show that aging will decrease some physical properties and increase the erosive wear of aged samples, but aging is not the root cause of erosive wear.

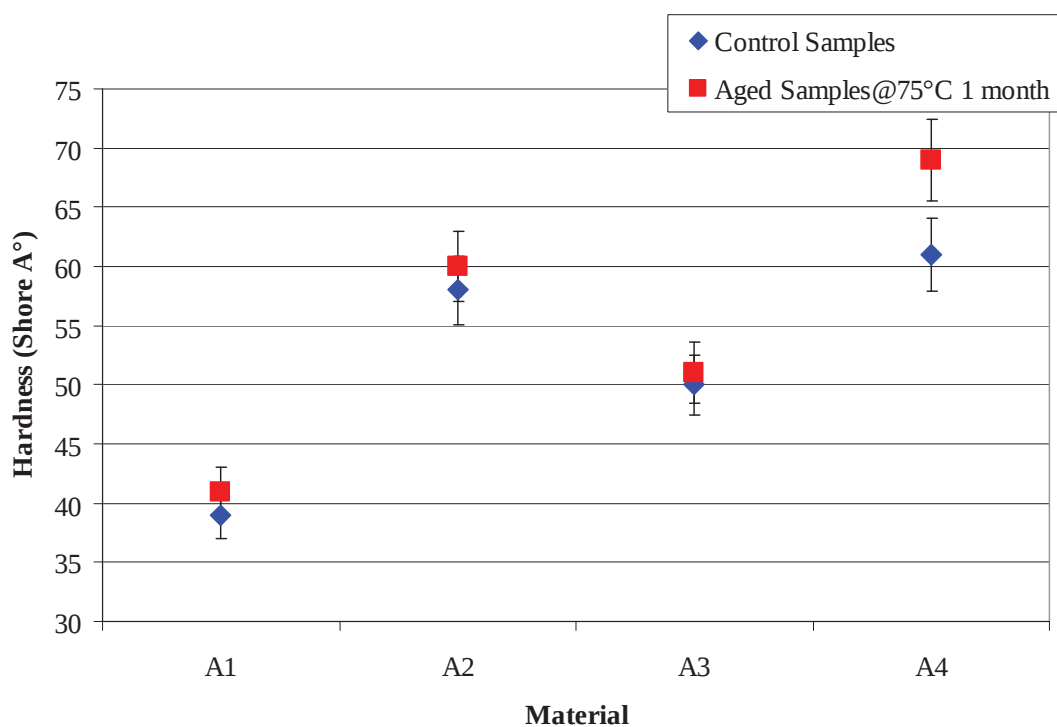


Figure 6.25 Hardness of control samples vs. wet aged samples at 75°C for 1 month

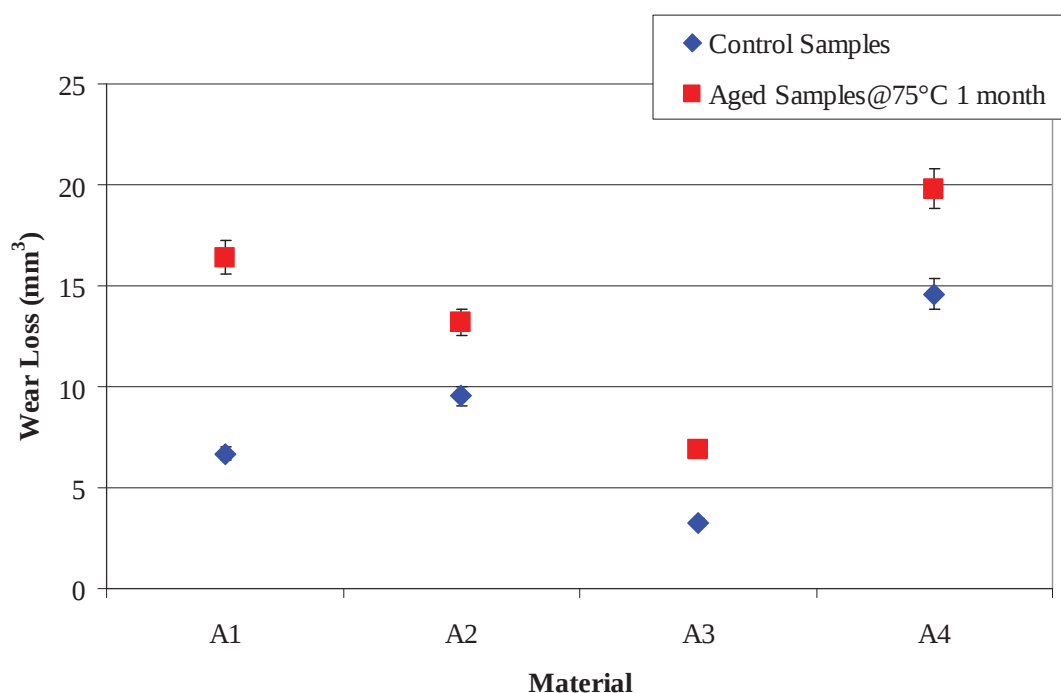


Figure 6.26 Wear loss of control samples vs. wet aged samples at 75°C for 1 month

Hot air aging tests were carried out at 75°C and 100°C for one month on the rubber samples. Figure 6.27 illustrates the effect of increased temperature on the tensile strength of the rubbers. At the hot air aging temperature of 75°C, the rubber exhibits similar decrease in tensile strength as in water. However, a much more severe decrease in tensile strength is observed at the hot air aging temperature of 100°C. At high temperatures, the natural rubber is exposed to oxidative degradation that can lead to the decrease in physical properties, seen in this study [52]. The extent of this degradation is dictated by the rubber chemistry and formulation. Rubbers with the inclusion of antioxidants and antiozonants will prevent or delay the polymer degradation. The rubbers analysed in this study all use the antioxidant 6PPD (N-(1,3-dimethylbutyl)-N'-phenyl-1,4-Benzenediamine), although at temperatures of 100°C the inclusion of 6PPD will not prevent the rubber from degradation, leading to a decrease in tensile strength. Considering the chemical change on the surface of the rubbers before and after aging shown in Table 6.2, it can be seen that a common functional group (methylene C-H) is influenced by the aging. This functional group could be the cause for the decrease in physical properties shown in Figures 6.27 – 6.29.

As discussed in the previous section, aging influences the tear strength of the rubber similarly to tensile strength. Figures 6.28 and 6.29 show similar trends in tear as tensile strength after aging. At 100°C the tear strength of the A1 material was almost unmeasurable. The crosslinking of polymer chains will increase with aging resulting in a decrease in tensile and tear strength. Further aging at high temperature beyond this point will result in these crosslinks breaking down. This is often referred to as rubber reversion [81]. After hot air aging, the rubber has reverted to some degree, particularly in A1 where the tensile and tear properties have decreased significantly.

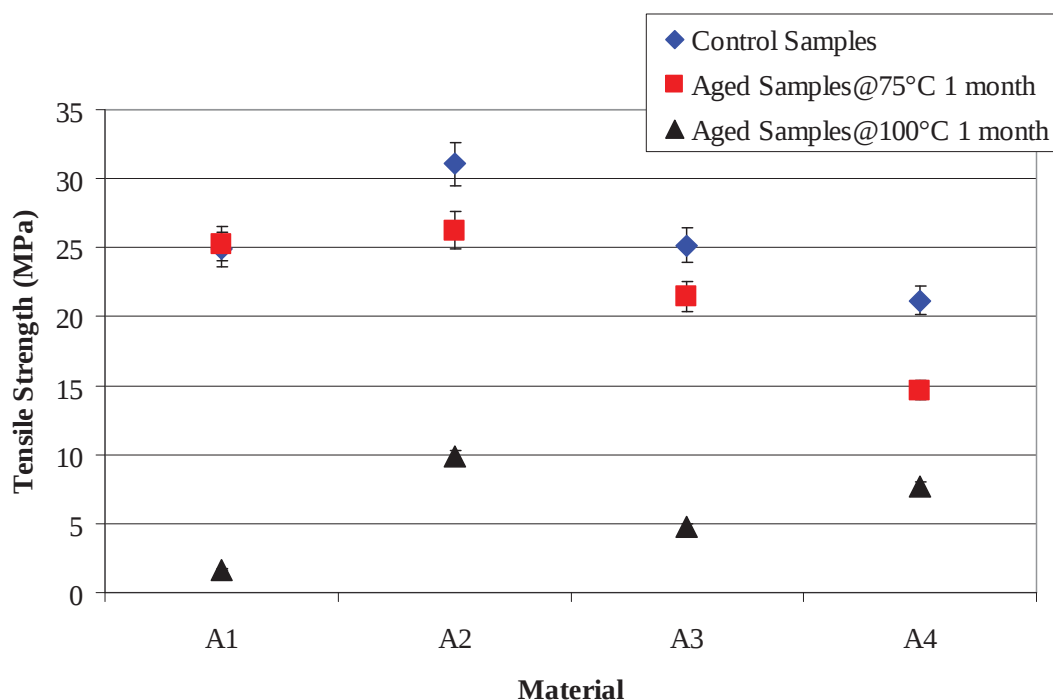


Figure 6.27 Tensile strength of control samples vs. air aged samples at 75°C and 100°C for 1 month

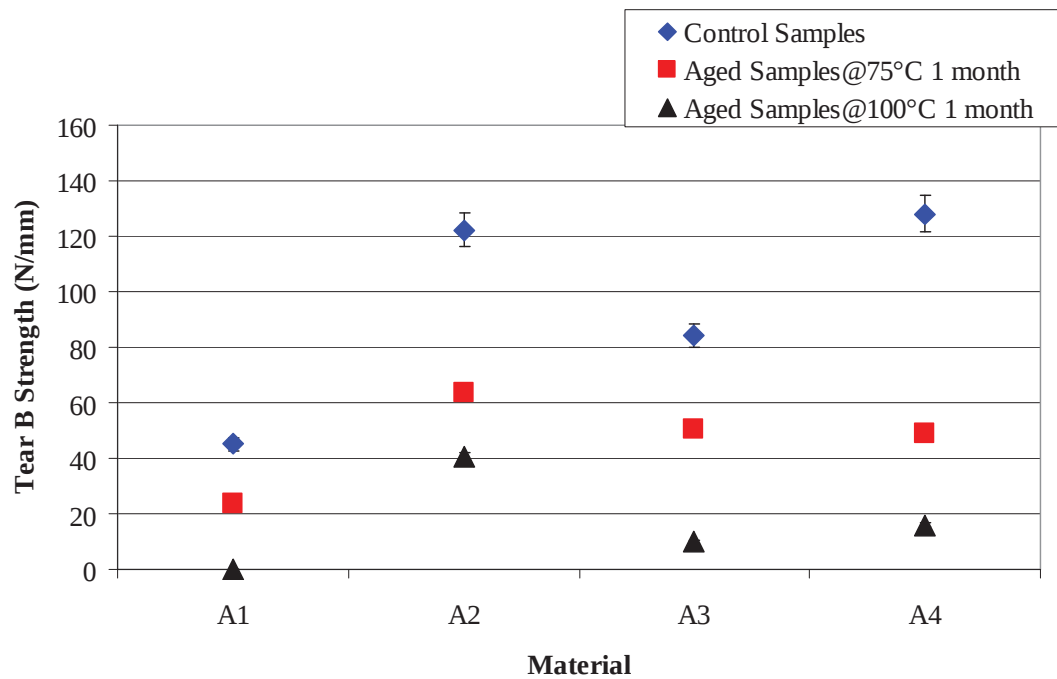


Figure 6.28 Tear B strength of control samples vs. air aged samples at 75°C and 100°C for 1 month

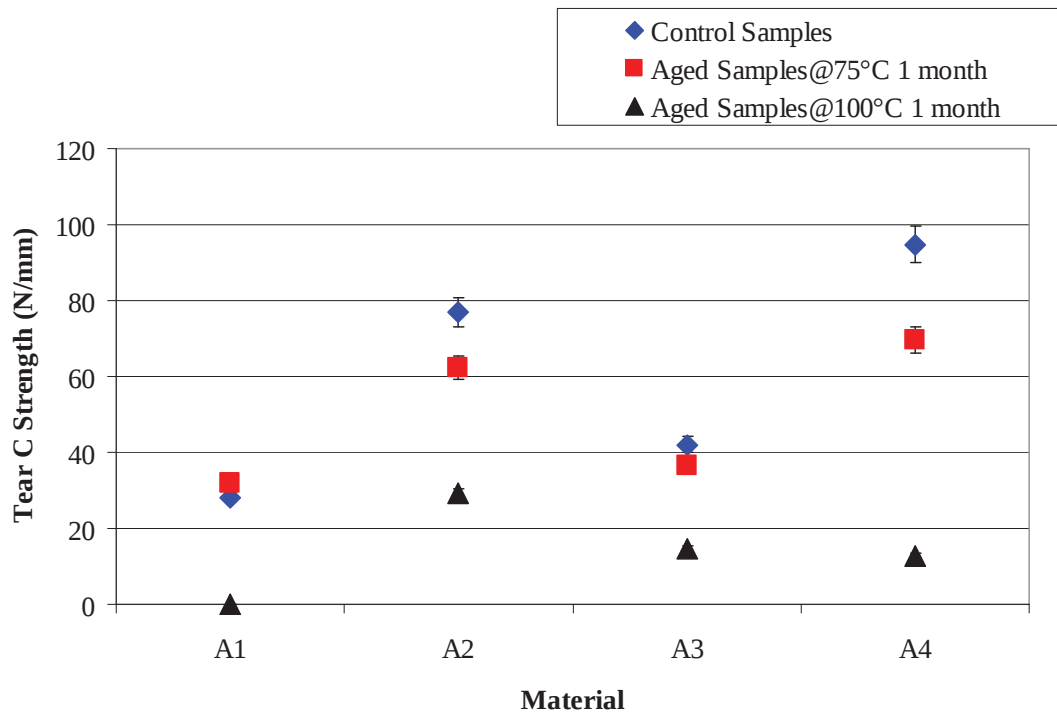


Figure 6.29 Tear C strength of control samples vs. air aged samples at 75°C and 100°C for 1 month

The hardness of the control samples after hot air aging is shown in Figure 6.30. The hardness increases for A4, similar to the wet aging results. This increase in hardness is the result of the polysulfidic crosslinks deteriorating from the heat aging. Polysulfidic bonds are found in conventional sulphur cured rubber compounds; in this case A4 is the only compound in this study which utilises a conventional cure system. Baranwal and Stephens [57] discuss the lower stability of polysulfidic to monosulfidic crosslinks by dissociation energy of bonds in these crosslinks. This reduction in polysulfidic crosslinks could be the cause of this increase in hardness for A4. The polysulfidic crosslinks could not be measured due to the limitations on the FT-IR instrument. The correlations between aging and the deterioration of the physical properties are shown in Figures 6.27 – 6.30.

The influence of hot air aging on the resilience of the rubbers is shown in Figure 6.31. A decrease in resilience can be seen in A1, A2 and A3 at the aging temperature of 100°C. This decrease is clear in A1 where a decrease in 25% resilience was observed. The A1 is an un-reinforced natural rubber compound which has a short mixing time during synthesis resulting in long polymer side chains [57]. The aging at 100°C clearly shows polymer degradation as a result of chemical bond scission [69] shown from the FT-IR analysis in Tables 6.2 – 6.6. Li and Koenig suggest the free energy of polymer per monomer unit decreases as the temperature is raised during the synthesis and application. Therefore, it can be seen from this data that at the aging temperature of 100°C the optimum polymerisation reaction temperature has been surpassed and long chain polymers are not possible [52]. As a result, premature polymer degradation has occurred with the A1.

Figures 6.32 – 6.34 illustrates the wear loss of the rubber samples influenced by the hot air aging test and its correlation with hardness and resilience. At the aging temperature of 75°C, the increase in wear resistance is minimal in comparison to the control samples. At the higher temperature of 100°C, the wear loss of each material is increased by at least 50%. A4 has the highest increase at 300% from the original control sample. Figure 6.33 shows the influence of hot air aging on wear loss and resilience of the rubbers. The resilience decreases for A1, A2 and A3 at the aging temperature of 100°C. As discussed earlier, the long chain polymers are broken down from the aging temperature through

chemical bond scission [69]. This leads to an increase in wear loss as the rubber is unable to absorb and rebound the impinging sharp particles through the slurry jet testing. However, A4 increases in resilience after hot air aging. This occurrence could be the result of the polysulfidic crosslinks increasing on the early stages of heat aging. The A4 is a conventional cure system which has a higher level of sulphur in the chemistry for vulcanisation. During vulcanisation, more polysulfidic crosslinks will form than in semi-efficient or efficient curing systems [57]. However, after the vulcanisation, unreacted sulphur can be left behind due to insufficient vulcanisation duration. On the onset of heat aging as polysulfidic crosslinks are being broken, the unreacted sulphur could replenish from these broken crosslinks to form more polysulfidic crosslinks, hence increasing the resilience. As mentioned above, the polysulfidic crosslinks could not be measured due to the limitations on the FT-IR instrument.

Figure 6.34 shows the influence of hot air aging on the wear loss and hardness of the rubbers. Again, it can be seen that the hardness of A4 increases with the increase in aging temperature, which then leads to an increase of wear loss due to a decrease in polysulfidic crosslinks. Figure 6.32 also shows a clear trend in the increase in wear loss for all rubbers from hot air aging. In the case of A4, the increase of wear loss is four times the control at 100°C aging temperature.

Heat aging will influence the physical and erosive wear properties as discussed above, however again there was no data to suggest that erosive wear results in a chemical change to the surface of the unworn and untreated surface. Although, this data does suggest that heat aging will influence the physical properties and reduce the erosive wear resistance of the rubber compounds.

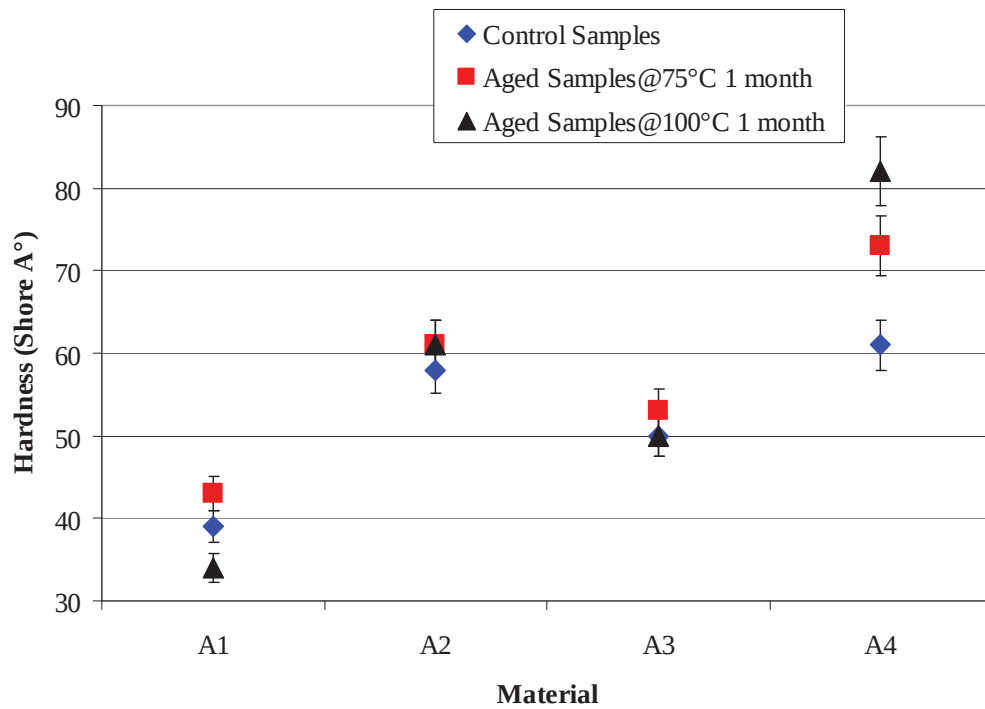


Figure 6.30 Hardness of control samples vs. air aged samples at 75°C and 100°C for 1 month

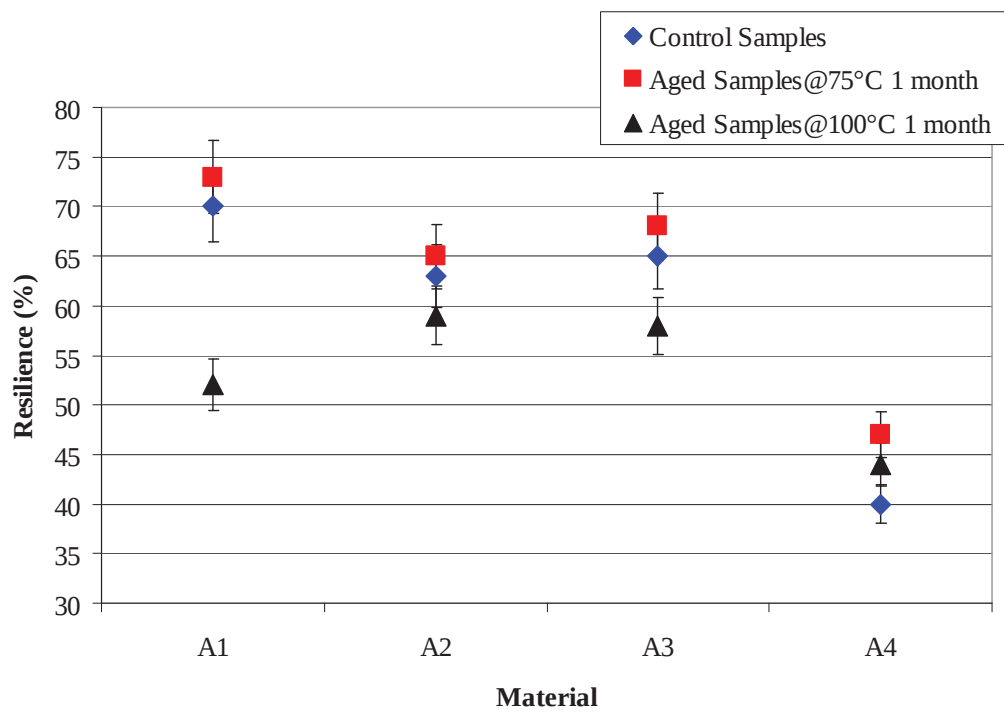


Figure 6.31 Resilience of control samples vs. air aged samples at 75°C and 100°C for 1 month

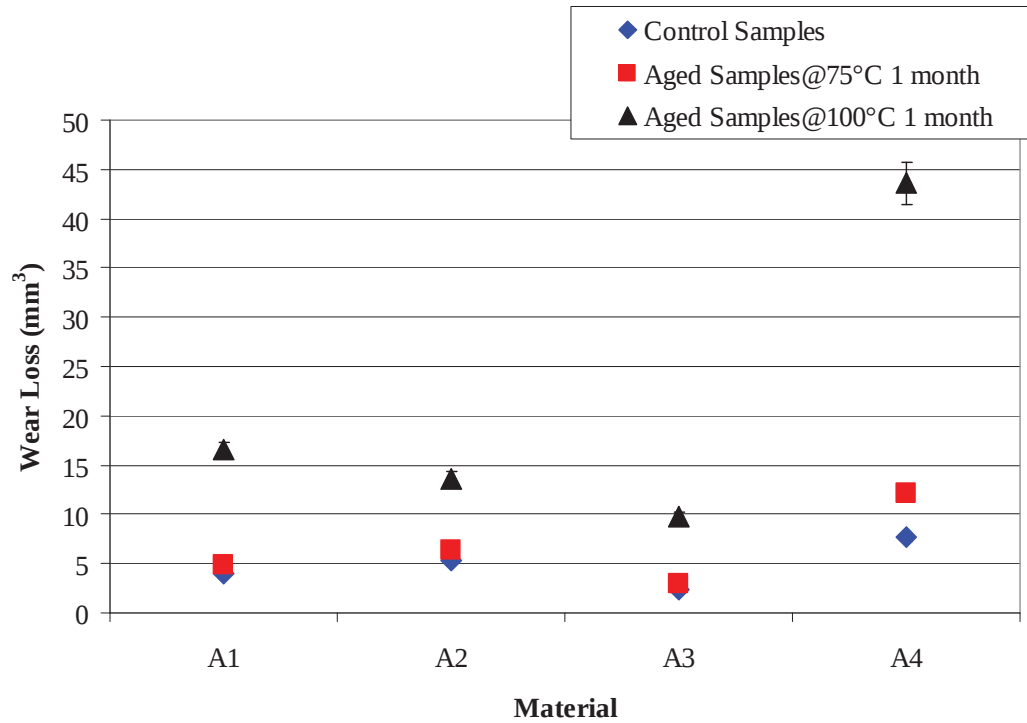


Figure 6.32 Wear loss of control samples vs. air aged samples at 75°C and 100°C for 1 month

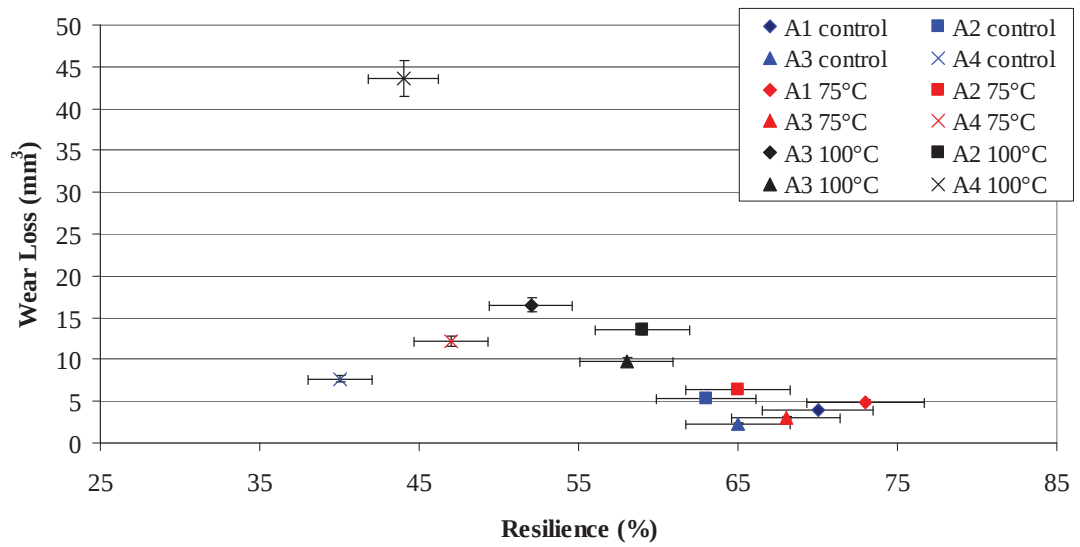


Figure 6.33 Wear loss vs. resilience of control and aged samples at 75°C and 100°C for 1 month

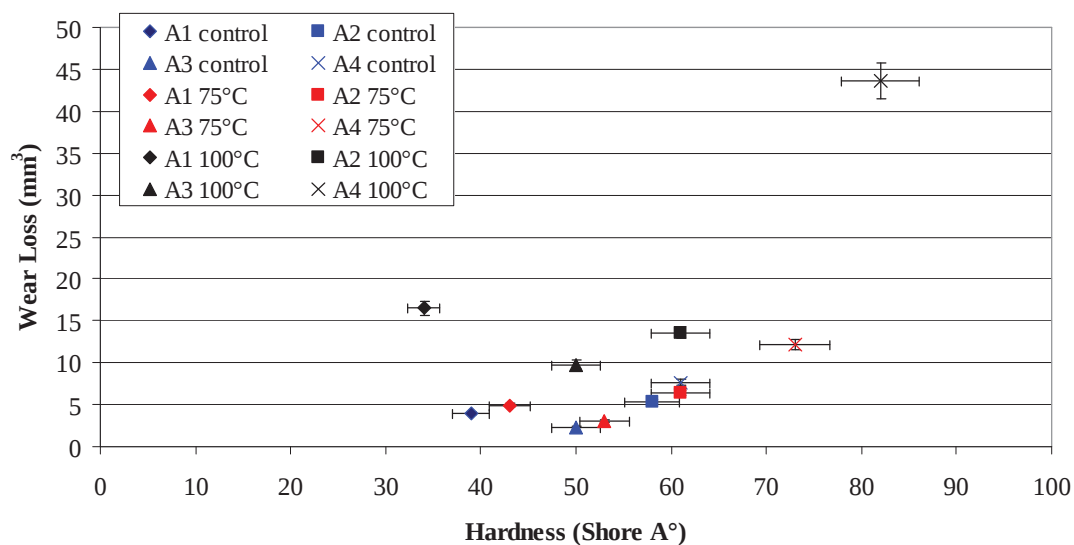


Figure 6.34 Wear loss vs. hardness of control and aged samples at 75°C and 100°C for 1 month

6.3 Viscoelastic Properties

The viscoelastic properties of elastomers are important to consider in the study of erosive wear in rubber pump lining applications. In this application, the rubber undergoes rapid cyclic deformations over a wide range of frequencies due to the impingement of slurry. The details of the viscoelastic property testing using the Rubber Process Analyser 2000 (RPA2000) are cited in the experimental chapter. Figure 5.15a shows the storage modulus (G') of the rubbers as a function of frequency. To recap, the storage modulus or elastic modulus (G') is defined as the ratio of shear stress to the shear strain with the addition of a small oscillatory strain. G' is essentially a measurement of the rigidity of the material and its response to shearing strains. G' can also be considered as the amount of energy that is stored by the material during dynamic testing. The A4 rubber has the highest G' at all frequencies tested. This result is expected as A4 has the highest hardness and highest reinforcing filler content. Conversely the A1 rubber has the lowest G' since it is a gum based rubber formulation with carbon black used only in small amounts for colouring. The

A1 also is the softest rubber out of the four, therefore suggesting a correlation of hardness with G' .

The loss modulus or viscous modulus (G'') as a function of frequency is shown in Figure 5.15b. G'' is defined as the amount of energy that is dissipated during dynamic testing usually as heat. The influence of a high level of carbon black reinforcement in A4 produces a high G'' . Baranwal and Stephens [57] discuss the effects of carbon black on the physical properties of the rubber. The carbon black used in A4 is highly bonded to the rubber molecules and has high surface area meaning it has high structure. The filler morphologies such as particle size and surface characteristics have a drastic effect on the physical performance of the rubber. The surface characteristics and active sites will determine the interaction between filler and polymer chains. Soltani and Sourki [109] discussed the effect of particle filler type on the rubber polymer particles. In carbon black loaded rubber compounds, the carbon black attaches itself to the polymer molecules through physico-chemical bonds. Each particle acts as a multiple crosslink between many polymer chains as well as acting as a rigid occupier in the rubber polymer network. Therefore, the high surface area and high structure carbon black used in A4 will impart higher levels of filler to the polymer network reinforcement, hence influencing the heat build-up, resilience and viscoelastic properties G' , G'' and $\tan \delta$. The carbon black in reinforced compounds also acts as a catalyst in vulcanisation, reducing the curing time. This behaviour is the result of carbon black's tendency to retain heat. These concepts are shown in Figure 5.15b where the G'' for A4 is much higher than the other rubber compounds. The A1, A2 and A3 compounds are not reinforced with carbon black, hence the lower G'' for these compounds. The A2 and A3 have similar G'' whereas A1 has a slightly lower value. These lower G'' values are not only attributed to the absence of carbon black in high loadings, but also to the different polymers, polymer blends, oil loadings and many other factors that may influence the relationships.

The characteristics of highly filled carbon black reinforced rubber compound such as A4 will influence the wear behaviour of the rubber, and will be discussed further in a later chapter in this thesis.

6.3.1 Aging influence on shear storage modulus G'

Aging tests using the RPA were carried out on the rubber samples at 75°C, 100°C and 150°C for 24 and 72 hours. As noted in the previous section, a number of physical properties degrade during the aging process, in particular the wear resistance of the rubber decreases at high aging temperatures. At lower aging temperatures the wear resistance did increase slightly, and the same can be seen to the elastic modulus (G') shown in Figures 5.16 (a – d). During the initial stages of aging at lower temperatures such as 75°C and 100°C, these temperatures are not high enough to cause polymer chain degradation. As discussed in a previous section, although the temperature is high enough for further crosslinking, resulting in an increase in physical properties such as tensile and tear strength, the temperature is not high enough to cause chain scission of the bonds. When the temperature does reach the point where chain scission occurs, the physical properties and wear resistance are decreased. The equivalent is seen with the shear storage modulus where it decreases and, with prolonged exposure to this higher temperature (150°C for 72 hours), the G' decreases further.

The storage modulus correlates with the aged wear loss data in the previous section. At the aging temperature of 150°C, G' decreases 50 percent in A1 with a similar effect on the wear resistance of the rubber. This concurrence is attributed to the formulation of A1, where a gum base rubber with few antioxidants is used to protect the rubber from aging. The A2 and A3 storage modulus aging graphs do not show nearly as much degradation as the A1. The decrease of G' from the control samples is 20 – 30 percent, again similar to the decrease in wear resistance of the rubber at the high aging temperatures. The G' of the A4 rubber behaves differently at high aging temperatures to the other rubbers shown in Figure 5.16d. The conventional cure system used in the A4 rubber could be the cause of this behaviour where at higher frequencies and at 150°C aging temperature, the G' has a steeper frequency gradient compared with the lower aging temperature G' . As discussed earlier, conventional cure systems have polysulfidic bonds that are weaker than monosulfidic

bonds found in efficient or semi-efficient cure systems. An explanation for the G' increasing for the 150°C aged A4 at high frequencies could arise from the polysulfidic bonds broken originally from the 150°C aging temperature. However, for the control and lower aging temperature samples, these polysulfidic bonds are not broken until the high frequencies are reached. The FT-IR analysis used in this study was unable to measure these polysulfidic and monosulfidic bonds due to the instrumental limitations.

6.3.2 Aging influence on shear loss modulus G''

The shear loss modulus (G'') as discussed earlier is defined as the amount of energy that is dissipated as heat during shear strain to the material. The inconsistency in the data points here, is attributed to the RPA's inability to measure small changes in G'' as frequency changes. This limitation from the RPA test data is shown in Figure 5.17 (a – c) where the data points are inconsistent at higher frequencies. Although the data from the RPA aging test is inconsistent, general trends can still be obtained from the data sets. The G'' of the rubbers analysed in this study, increases at high temperature. Aging causes the polysulfidic crosslinks to break, influencing the physical and viscoelastic properties. The elasticity and tensile properties of natural rubber are inherently linked to the polysulfidic crosslink content. The higher the polysulfidic bonds content the greater improvement in these properties [57]. With the high temperature aging at 150°C, these polysulfidic crosslinks are broken causing the G'' to increase. This concept is related to the G' where it was decreased as a result of heat aging. Heat aging has the opposite effect on the G'' in the rubber compounds investigated in this study.

The inconsistency in G'' from the RPA aging test is not as obvious in the A4 (Figure 5.17d) as the other rubbers as a result of the higher stiffness and highly reinforced rubber formulation leading to a lower relative error. The chemistry of the rubber is very different to the other rubbers as it was designed for impact and grinding applications rather than slurry pump applications. Hence the G'' of the rubber is 10 times the G'' of the A1, A2 and

A3 rubber compounds. The general trend is comparable to the other rubbers where at high aging temperature, the G'' increases from the control sample.

In comparing the G'' and the wear loss after aging, similarities can be seen in the trend of the graphs. The increase in aging temperature will increase the wear loss of the rubbers as discussed earlier. The G'' is also increased as the aging temperature is increased. To explain this further one must first consider the chemistry of the rubber and what occurs during aging. The polysulfidic crosslinking is likely to increase during aging which leads to unfavourable properties such as lower tensile and tear strength and a slight increase in hardness. These traditional physical properties are better understood by examining the dynamic viscoelastic properties of the rubber. As the particle of slurry attacks the surface of the rubber, the kinetic energy (can be considered as heat) is transferred to the rubber. The G'' affects the amount of energy the rubber will dissipate, therefore, a high G'' will be an indication on the amount of heat dispersed on the surface of the rubber. This energy or heat may cause the rubber to wear more quickly as shown in Figure 6.32 and correlates with the G'' in Figure 5.17 (a – d).

As discussed earlier, the chemistry of the rubber influences the viscoelastic and wear behaviour of the compound. The high level of carbon black loading in A4 increases the G'' significantly in comparison to the other rubbers analysed. A relationship can be made between the choices of reinforcing fillers used in this study. A4 is reinforced with carbon black, whereas A2 and A3 are reinforced with silica. A1 is a gum based rubber formulation and does not contain reinforcing agents other than 1% wt of carbon black used only as colouring. Figure 5.15b shows the significant increase in G'' of the A4 compared to the other rubbers. Figure 6.32 also shows a significant increase in the wear loss of the A4 in comparison to the other rubbers. An increase in G'' indicates a higher level of energy dissipation of the rubber where the carbon black has a key role.

In the case of A2 and A3, both silica reinforced compounds, the G'' is lower than A4, a carbon black reinforced compound shown in Figure 5.15b. Silica reinforced compounds have reduced heat loss, represented by the lower G'' whilst still providing the erosion wear

resistance. Therefore a case can be drawn from this study that silica filled rubbers are more erosive wear resistant than carbon black filled rubber compounds. And this is shown through the A4, which does not resist erosive slurry wear as well as the silica reinforced rubbers.

6.3.3 Aging Influence on Tan delta and Relationships with Resilience

The ratio of loss modulus (G'') and the storage modulus (G') is defined as the tan delta ($\tan \delta$). $\tan \delta$ is often referred to as the inverse of resilience of the rubber. The resilience is measured by the amount of rebound energy the rubbers exert when a standard weight is dropped from a known height. During testing, the rubber sample slightly increases in temperature indicating that the impact energy is dissipating through the rubber. The elastic nature of the rubber will provide the rebound energy to repel the standard weight. The relationship of $\tan \delta$ and resilience can be seen in the test results shown in this study. The A1 rubber has the highest resilience shown in Figure 5.11 where as, A4 has the lowest resilience value. Figure 5.15c illustrates the $\tan \delta$ of the rubbers where the A4 has the highest $\tan \delta$ and A1 the lowest. To better understand the trend one must consider the $\tan \delta$ and resilience equations:

$$\tan \delta = G''/G' \quad (6.1)$$

$$\text{resilience} \approx 1/\tan \delta = G'/G'' \quad (6.2)$$

The A4 rubber ratio between G'' and G' are much higher than the other rubbers which results in a high $\tan \delta$ value. This high G'' also indicates that the A4 rubber will dissipate more energy in the rubber when strain is applied. As discussed earlier, the high G'' and G' are attributed to the conventional cure system and the high loading of carbon black reinforcement in A4. The high level of sulphur in A4 results in a high proportion of polysulfidic crosslinks that will improve the tensile strength and elasticity of the natural rubber [57]. Furthermore the high loading of carbon black in comparison to A1, A2 and A3

increases the reinforcement in the rubber structure leading to a stiffer, more rigid rubber compound, hence the high G' . This high loading of carbon black in A4 will also improve the physical properties and abrasive wear resistance [57]. As discussed earlier, the high surface area carbon black used in A4 imparts higher levels of reinforcement through an increase in physio-chemical bonds between the filler particles and polymer chains, therefore a higher heat loss can be observed from the G'' [109]. In the case of the A1, the G'' is significantly lower and the G' remains high, consequently the low $\tan \delta$ for the A1 rubber in comparison to the A4. The resilience for the A1 is therefore high in comparison to the A4. Considering equation (2) and substituting values for G' and G'' , the high value for G' and the lower value for G'' results in high resilience for A1 and conversely low resilience for A4.

The aging influence on $\tan \delta$ is shown in Figures 5.18 (a – d). As discussed earlier, the high frequency testing of viscoelastic properties were reaching the resolution limits of the RPA2000. It can be seen in these graphs that high frequencies of more than 1000 cycles per minute produced significant scatter in G'' and consequently the $\tan \delta$. Although the scatter in the graphs is significant, the trend of each graph following aging is still evident. The $\tan \delta$ increases with high temperature aging similar to the G'' aging test results. The $\tan \delta$ can correlate with the molecular weight distribution and predict the long rubber molecular chains of the compound [57]. Highly masticated rubber compounds will have shorter molecular chains usually seen in highly reinforced rubber compounds. These highly reinforced compounds require long mixing cycles and high shear to blend the reinforcement into the rubber matrix at the cost of the molecular chains. The long molecular chains provides the rubber with its unique properties such as high resilience and viscoelastic properties. How the $\tan \delta$ and the long molecular chains influence the wear behaviour of the rubber will be discussed later.

6.4 *Wear Mechanisms*

A number of mechanisms are responsible for the wear of rubber pump liners in slurry transport applications. Due to the variable nature of wear in a slurry pump, the wear is typically a combination of erosion, abrasion, or a combination of each. The operation of the slurry pump influences the wear mechanism at different locations of the rubber pump liners. Figure 2.1 illustrates the components of a Warman AH heavy duty slurry pump. The slurry enters the pump and the first point of contact is the impeller. As discussed earlier, the impeller induces a centrifugal force on the slurry so it can be expelled through the discharge end of the pump. The impeller is exposed to impingement wear along with abrasion as the slurry is expelled through the vanes to the discharge. The rubber liners behave differently such that areas of the liner will have different wear mechanisms. Erosive wear is dominant throughout the liner; however, areas such as the cutwater impingement wear severely. At the cutwater the slurry that does not exit the pump through the discharge end is recirculated. Erosive wear is also the dominant wear mechanism for the throatbush as back pressure from the impeller causes the slurry to be forced back into the throatbush. In some cases, large aggregates are trapped between the impeller and the throatbush causing severe abrasive wear on the throatbush, but these are rarely seen if the process is well controlled and larger particles are screened.

In this chapter, the wear mechanisms will be discussed in relation to the rubber chemistry, physical and viscoelastic properties of the rubber in erosive wear. Thermal degradation will also be discussed in relation to rubber heat aging and its influence on the erosive wear resistance of rubber in slurry pump applications.

6.4.1 *Erosive wear*

Erosive wear is defined as wear that is caused by particles in a fluid system, impacting on the surface of the material causing material removal and damage [11, 16, 18, 22, 23]. Figure 2.17 illustrates the 3 main modes of erosive wear. The slurry jet erosion testing

carried out in this study does not include the sliding bed erosive wear mode due to test angle limitations although sliding bed erosion does occur in a slurry pump particularly in areas of the casing liner where impacting particles are compressed together moving tangentially along the rubber surface. Random and directional impacts are common erosive wear modes that can be characterised from the slurry jet erosion testing. Random impact erosive wear occurs when there are variations to the angle of impingement during the operation of the slurry pump. This can be the result of localised turbulent flow regimes that are common in application. Particles impinging on other particles could also be a cause for random impact resulting in erosive wear on the material. Directional impact erosive wear involves particles impacting on the surface of the material at a common angle. This wear mode is predominantly observed in impellers and areas of the casing liner where the slurry is expelled at a common angle. The most severe wear is often located in these areas of directional erosive wear; however the degree of wear is dictated by the angle of impingement.

The slurry jet erosion testing consisted of the following variables shown in Table 6.7. A wide range of variables were covered in this study to determine the influence of particle size, testing angle and material properties in erosive wear. In the next section, the erosive wear processes will be examined further with scanning electron microscope images of the worn surfaces to evaluate wear behaviour of the different rubber compounds. The wear trends are also investigated between the physical properties, rubber chemistry and the wear pattern on the surface of the rubber.

Table 6.7 Slurry jet erosion testing variables

Material	Particle size (μm)	Testing angle	Erodent material	Erodent shape
A1	1000	20°	Al ₂ O ₃	Sharp
A2	750	45°		
A3	500	60°		
A4	350	90°		
	200			

6.4.2 SEM analysis of wear scars and features due to particle impingement angles of attack

Slurry jet erosion testing was carried out on the A1, A2, A3 and A4 materials using the Eductor wear tester. The test conditions and variables are outlined in Table 6.7 with each sample analysed using the SEM to examine the wear scars and features due to the particle impingement angles of attack. The wear mechanism of the rubber is highly dependant on the angle of impingement. Figure 6.35 shows the SEM images of the rubbers after slurry jet erosion testing at an impingement angle of 20°. Enlarged figures of SEM images can be located in Appendix 10.3. The wear mechanism is considered as micro cutting. Micro-cutting is shown as long cuts on the rubber surface and is relatively directional to the jet stream. At 45° impingement, the wear mechanism is a combination of micro cutting and micro-gouging. The long micro-cuts on the rubber surface are now absent. Shorter cuts with deep gouges in some areas perpendicular to the jet stream replace the longer micro cuts. At 60° impingement, the wear mechanism is similar to the wear mechanism at 45°. The severity of the wear is lower as shown in Figure 5.6a, however, the combination of micro cutting and micro gouging wear behaviour remains. At the impingement angle of 90°, wear loss and material removal is minimal in comparison to low angles. The micro cutting is randomly orientated, with large crater formation in areas where the erodent has concentrated to form localised wear.

In reference to Figure 5.6a, A4 has the highest wear loss at all test angles. Although it is difficult to differentiate the amount of wear from the two dimensional SEM image, the wear scar trends of the different materials follow a similar path. The only exception is the A1 material where long micro-cuts and large micro-ploughs are seen in the SEM images. A1 is an unfilled natural gum based rubber without reinforcing agents. Reinforcing agents such as silica or carbon black will hinder the micro-cuts and gouges from propagating.

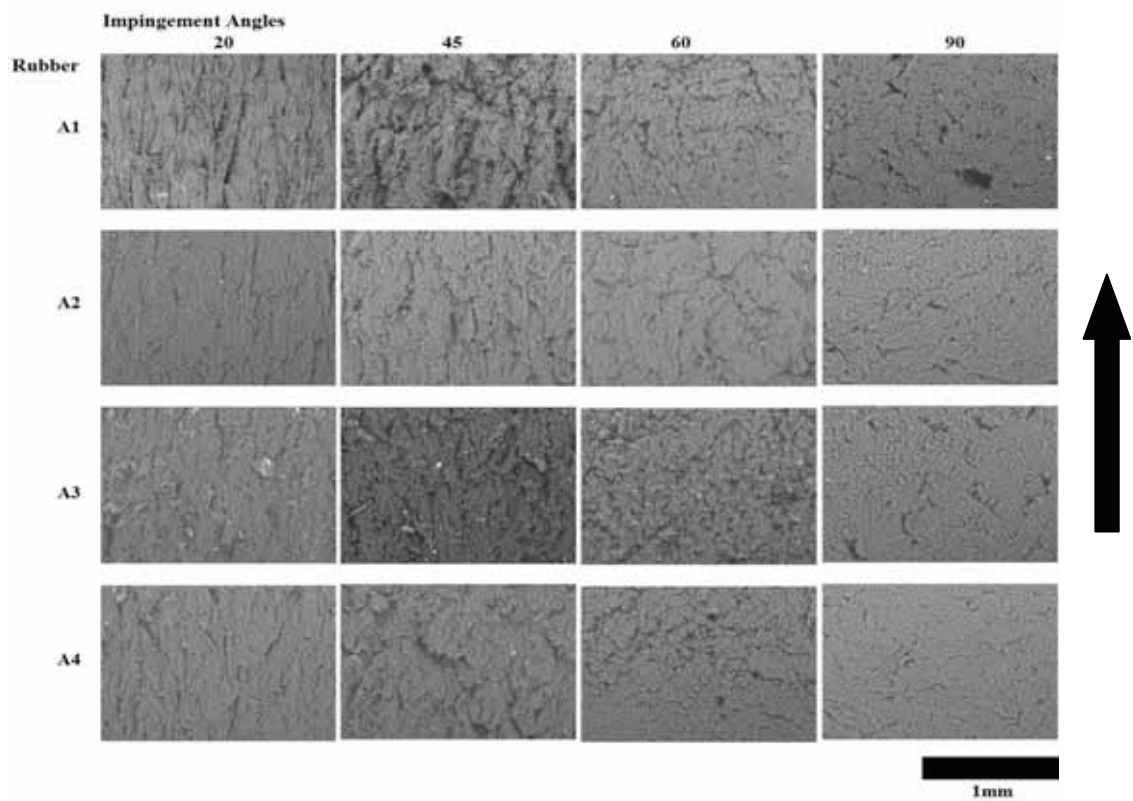


Figure 6.35 SEM images of wear scars of A1, A2, A3 and A4 at impingement angles of 20°, 45°, 60° and 90° with 1000µm Al₂O₃ particles. Wear direction indicated by an arrow. Enlarged figures located in Appendix 10.3.

The wear scars resulting from erosion at different particle sizes for each material tested in the slurry jet tester are shown in Figure 6.36 – 6.39. Similarly to the previous data, the wear scar features are dependant on the material. However, the extent of the wear decreases with decreasing particle size (Figure 5.5a). The A3 material differs slightly from the other materials in wear scar features. The micro cuts are shorter in length and are not dominated by the direction of the erosive jet stream during testing. The A3 formulation is made up of a natural rubber and polybutadiene blend along with silica filler used to reinforce the material. This has resulted in different wear scar features for the A3 as opposed to the other tested materials. Baranwal and Stephens [57] outline the benefits of using silica and silanes in passenger car tyres in reducing the rolling resistance to the road surface whilst retaining its wear resistance. This rolling resistance is correlated with $\tan \delta$ at 60°C. Studies have shown in dynamic testing on rubber compounds that silica and silanes content results in a lower $\tan \delta$, and by implication have an effect on erosive wear. Similarities are drawn to this study when comparing A4 with A3. As mentioned earlier, A4 is a carbon black reinforced compound whereas A3 is a silica and silane filled compound. Figure 5.15c shows a relatively higher $\tan \delta$ for A4 than for A3. Following this result, correlations can be seen with the erosive wear test data shown in Figures 5.6 (a – e) where A4 has the lowest erosive wear resistance and A3 the highest wear resistance. The A1 has the lowest $\tan \delta$ but it does not have the wear resistance of the silica filled rubbers; A2 and A3. The large cuts and gouges in the A1 material can be attributed to the absence of fillers in the formulation. However, since the natural rubber characteristic of the A1 results in a highly resilient and low $\tan \delta$ material, the wear loss remains small. The impinging particles damage the rubber initially to cause a cut or gouge, but the energy required to expand the wear is minimised by these properties.

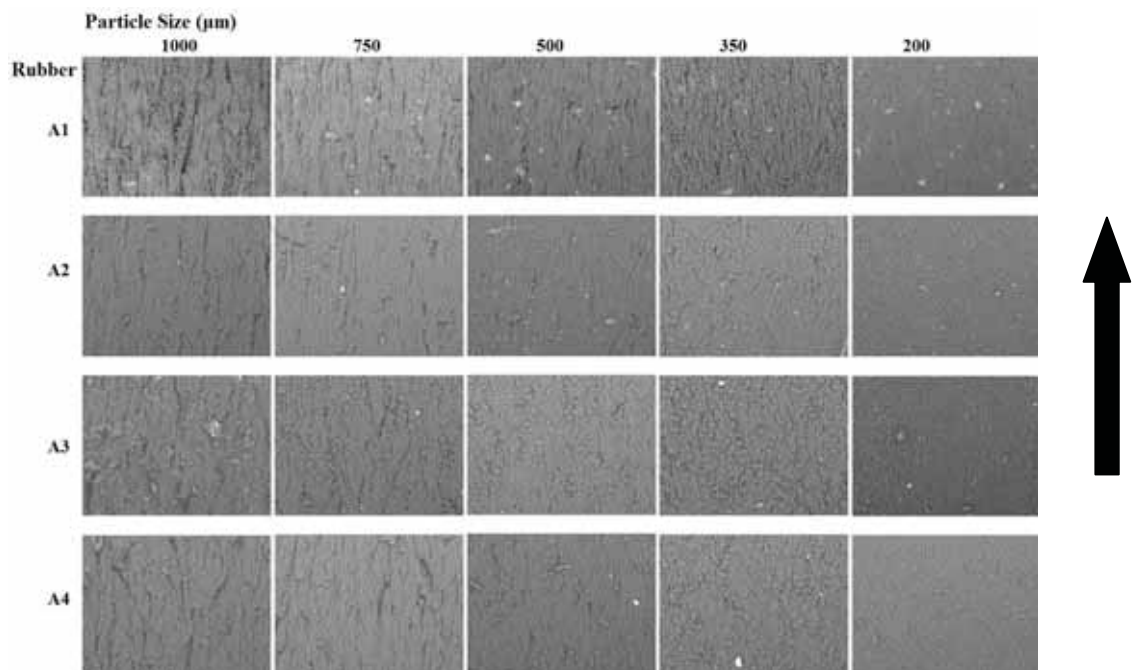


Figure 6.36 SEM images of wear scars of A1, A2, A3 and A4 at different particle sizes at impingement angle of 20°. Wear direction indicated by an arrow. Enlarged figures located in Appendix 10.3.

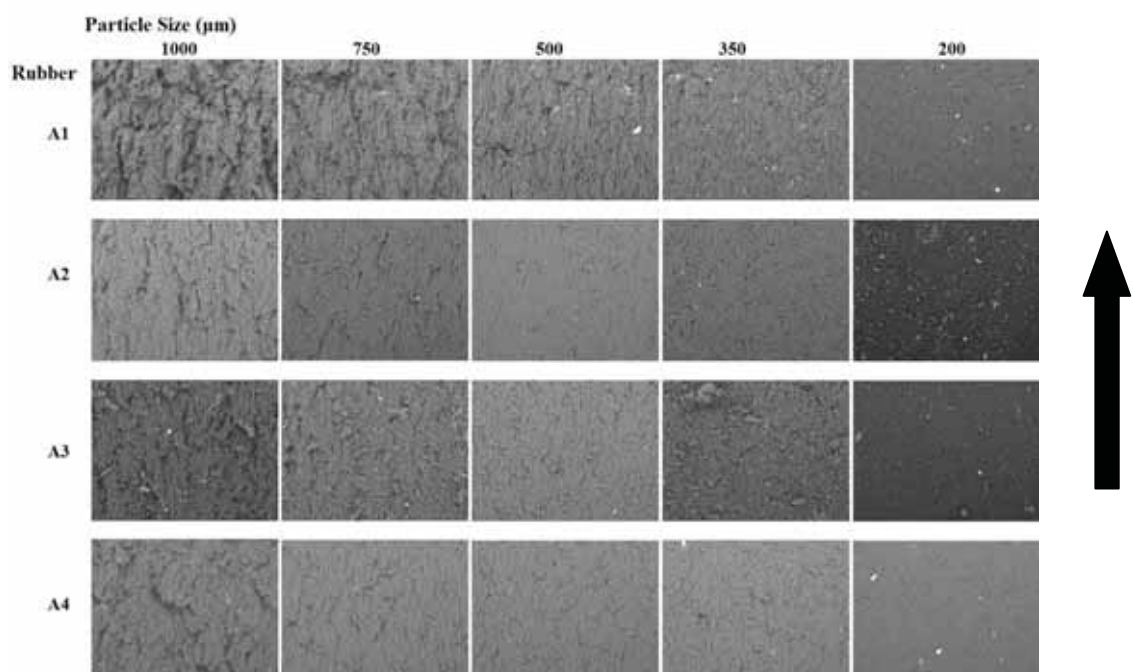


Figure 6.37 SEM images of wear scars of A1, A2, A3 and A4 at different particle sizes at impingement angle of 45°. Wear direction indicated by an arrow. Enlarged figures located in Appendix 10.3.

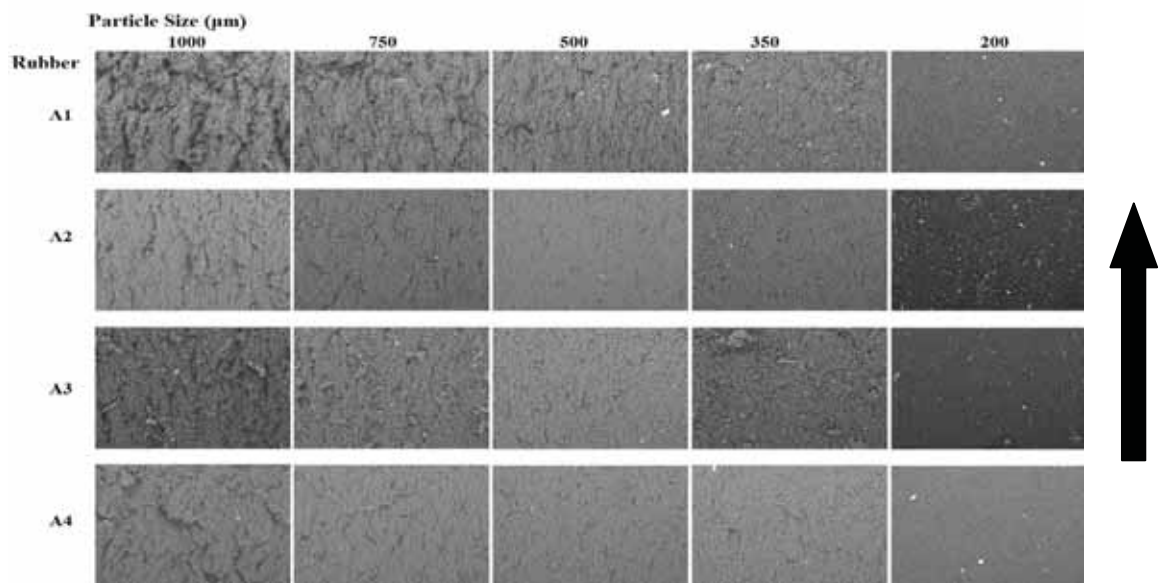


Figure 6.38 SEM images of wear scars of A1, A2, A3 and A4 at different particle sizes at impingement angle of 60°. Wear direction indicated by an arrow. Enlarged figures located in Appendix 10.3.

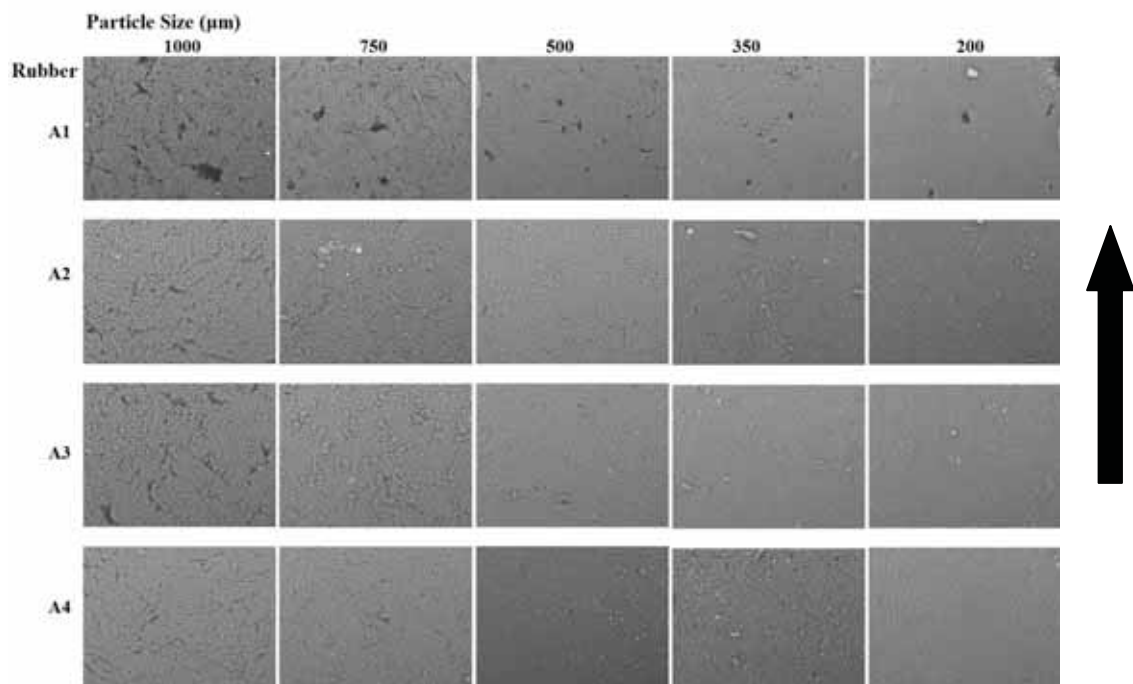


Figure 6.39 SEM images of wear scars of A1, A2, A3 and A4 at different particle sizes at impingement angle of 90°. Wear direction indicated by an arrow. Enlarged figures located in Appendix 10.3.

SEM images of aged worn samples of A1, A2, A3 and A4 are shown in Figure 6.40. The control and 75°C aged samples show similarities in wear scars. This observation is consistent with the wear loss of aged samples shown in Figure 6.32 where the control and aged samples at 75°C had similar wear losses. Furthermore at the aging temperature of 100°C, the SEM images show more micro-cutting and micro-gouging in each rubber. This increase in micro-cutting and micro-gouging can also be correlated with the wear loss of samples aged at 100°C. It is interesting to note that the wear behaviours of the rubbers do not change significantly up to the aging temperature of 75°C. However at higher temperatures of 100°C, the rubbers reach their temperature limit with physical properties and wear resistance reduced. Revisiting the chemistry of the rubbers using FT-IR (Table 6.5), it was found that at 100°C few C-H bonds after wear were chemically changed in the A2 and A3 rubbers. This could explain the increase in micro-cutting and gouging in the SEM images shown in Figure 6.40.

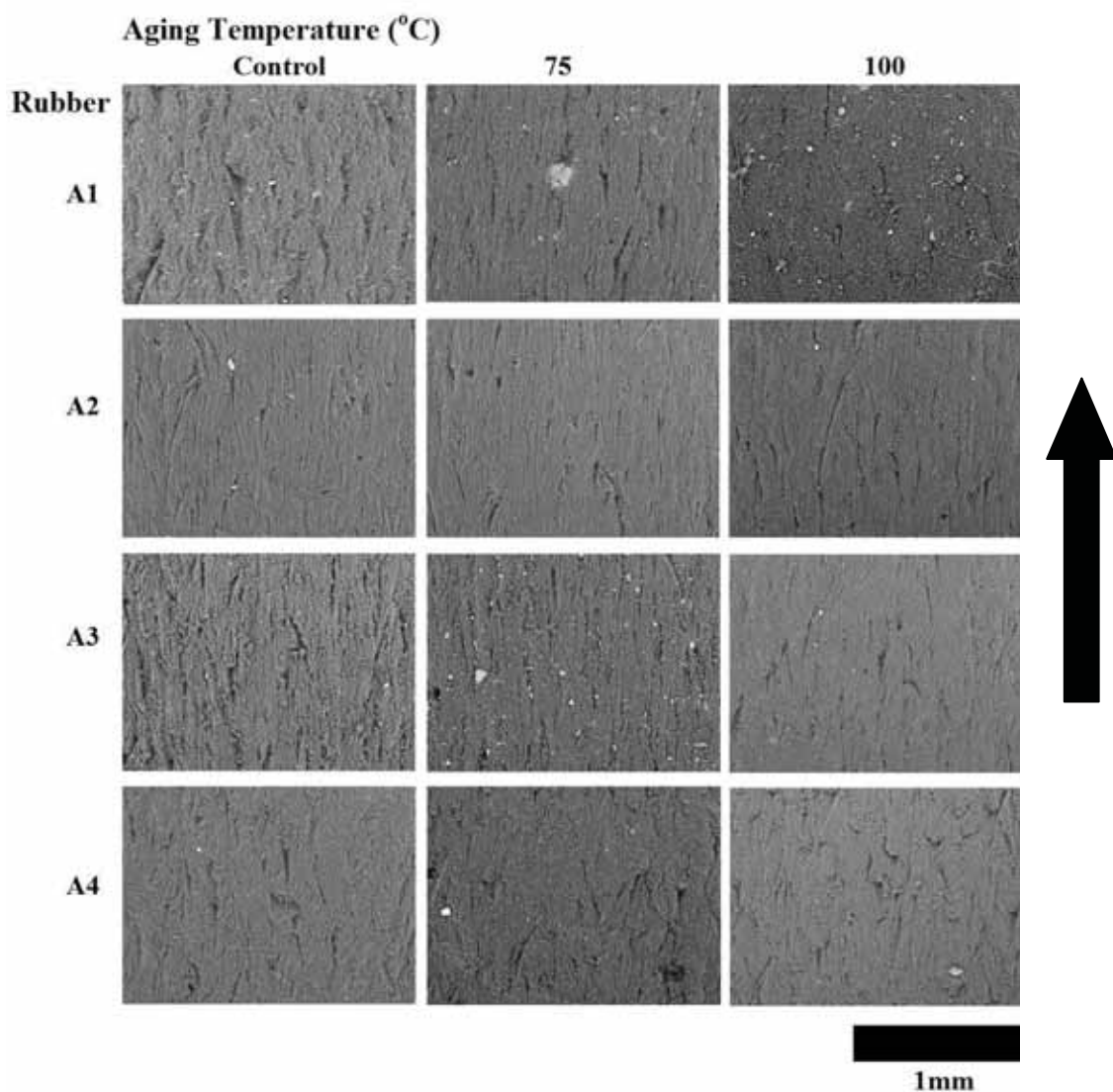


Figure 6.40 SEM images of wear scars of A1, A2, A3 and A4 at different aging temperatures wear tested at impingement angle of 20°. Wear direction indicated by an arrow.

6.4.3 Effect of physical properties on erosive wear

The physical properties of the rubber compounds in this study clearly correlate with aspects of erosive wear. Traditional methods of ranking elastomeric materials with performance have been primarily based on the material's physical properties such as, hardness, tear strength, resilience, tensile strength, etc. It is difficult to define one physical property that

defines erosive wear resistance. Rather it is a combination of properties that result in an erosion resistant material. In this study, the hardness and the resilience correlate well with the erosive wear testing. Figure 5.11 shows the resilience as a function of wear loss from slurry jet erosion testing. It can be seen that the lowest resilient rubber results in the highest wear loss. This data supports the theory of particle rebound where rubbers with high resilience will deflect or rebound the impinging particle without causing damage to the rubber itself. As the particle strikes the surface of the rubber, the rubber deforms as a result of the impact and returns the kinetic energy in the rebound process.

During the erosive wear process, it is also important to examine the angle of impingement. At low angles of particle impingement, the wear mechanism is predominantly cutting the surface of the rubber. A resilient unfilled rubber will resist this cutting to some extent, though a reinforced resilient rubber will resist this wear mechanism better than an unfilled rubber. At high angles of impingement, the resilience of the rubber influences the wear behaviour. In cases such as the A4 where there is low resilience, the rubber itself retains the energy of the impinging particles causing damage. In high resilience materials, the energy of the particles can be dissipated and rebounded in the direction of the flow. The data in Figure 5.11 reiterates the fact that not one physical property can define erosive wear resistance. A1 has the highest resilience but does not have the wear resistance of the A3 which has a lower resilience.

Hardness has the opposite influence where the highest hardness will result in the highest erosive wear loss, Figure 5.10. The hardness of the rubber is dependant on the amount of reinforcement in the rubber composition and the number of crosslinks that have resulted from the vulcanisation process. This observation is the opposite to the typical tribological behaviour of materials where higher hardness usually results in higher wear resistance. Rubber however, behaves differently in the slurry erosive wear applications where a higher hardness will result in higher wear loss. High hardness rubbers in slurry erosion applications will absorb the impact and hence the energy of the impinging particles causing damage to the material shown in Figures 6.30 – 6.34. Lower hardness rubbers tend to have higher resilience therefore lower $\tan \delta$ and lower erosive wear loss. As discussed earlier, the

A4 rubber has a high loading of carbon black reinforcement and a conventional cure system which leads to additional polysulfidic crosslinks in its chemistry. This higher carbon black loading and additional polysulfidic crosslinks lead to the higher hardness of A4. However, this increase in hardness is not favourable in slurry erosion wear resistance as shown in Figure 5.10. This combination of reinforcement and cure system increases the viscoelastic property $\tan \delta$ and will have a negative impact on the erosive wear resistance of the rubber.

Both A2 and A4 have a high level of reinforcing agents in the rubber composition leading to high hardness rubbers. High hardness rubbers do not perform well in erosive wear conditions as a result of the high loadings of reinforcing filler content. The hardness is inversely proportional to resilience, if the hardness is high then the resilience will be low. This is particularly important when discussing the erosion resistance of a rubber. For a rubber to be erosion resistant the resilience must be high enough to rebound the impinging particles and the hardness is required to resist surface damage from the sharp particles on initial impact. A combination of both hardness and resilience is required to have erosion resistance. The A3 material is the most erosion resistant in this study. A3 does not have the highest resilience or hardness, but the combination of the two properties results in the best erosion resistant material.

The tensile tear strength does not correlate with erosive wear data in this study. Tear strength is a measure of the rubber's ability to resist tear as a result of a nick or a cut. Figure 5.13 shows the tear strengths of the rubbers analysed in this study. As discussed earlier, the A2 and A4 compounds are highly filled with reinforcing agents, hence the high tear strength of the two compounds. With the introduction of a filler, the propagation of the tear is hindered by the reinforcement particle. The energy required to break through that particle or tear around the particle is greater than the energy required to tear through an unfilled rubber. Consequently the A1 compound results in low tear strength in comparison to the other compounds. Tear strength is commonly used as quality control measures to ensure the incorporation of reinforcing fillers are dispersed evenly throughout the compound. The wear mechanisms involved with erosive wear are significantly different to the controlled tensile tear test method. The tear test is essentially a tensile test where the

point of failure is at the initiation nick point. This initiation point will propagate to failure under high stress. The erosive wear mechanism is a cutting/gouging material removal process under low stress from multiple impacts from sharp particles. These micro-cuts and gouges do not propagate to failure, rather the cumulative effect of cuts and gouges lead to attrition and material removal. These unrelated wear mechanisms are shown clearly in Figure 5.13.

6.4.4 Viscoelastic properties' influence on wear behaviour

The definitions of the viscoelastic properties (G' , G'' , $\tan \delta$) were discussed. To recap, the storage modulus (G') is the amount of energy that is stored by the rubber when shear strain is applied. The loss modulus (G'') is the amount of energy that is dissipated as heat in the rubber when the shear strain is applied. $\tan \delta$ is the ratio of G''/G' and inversely related to resilience. The data shown in Figures 5.15 (a – c) demonstrates that the materials tested in this study have different viscoelastic properties which correlate to different erosive wear resistance. The A1 material has the lowest G' since it is predominantly a gum base rubber without any reinforcing agents. Reinforcing agents strengthen the rubber increasing the tensile strength, hardness and wear resistance. However as shown in this study, the wear resistance of a rubber is dependant on application. For applications where abrasion is the primary mode of wear, the hardness and reinforcing agent is critical. Whereas for slurry pump applications the primary mode of wear is erosive wear hence resilience and level of reinforcing agents are the determining factor.

The low value for the G' in the A1 material indicates that it will not store as much energy as the other rubbers when strain is applied. This is important, especially during the erosive wear process where particles are impinging the surface of the rubber at high velocities causing material removal. A high value for G' will result in more energy stored within the material and build up of internal stresses that can lead to bond scission and micro cracking of the elastomer. A high G' is commonly found in highly reinforced rubbers such as A4. In this case the G' for A4 is more than three times the G' of the A1 rubber, which is expected

due to the high level of reinforcement. The A4 is reinforced with carbon black, whereas the A2 and A3 materials are reinforced with silica. The carbon black reinforcing filler absorbs more energy than the silica reinforced materials resulting in the higher G' .

The loss or viscous modulus (G'') of A1, A2, A3 and A4 is shown in Figure 5.15b. It can be seen that A4 has the highest G'' in comparison to the other rubbers. This high value of G'' indicates that the A4 has a significant amount of energy converted to heat when strain is applied to the rubber. The high G'' contributes to the highest erosive wear loss of the A4 material. The heat dissipated in the surface of the rubber leads to molecular chain scission and decrease in physical properties. The heat aging tests confirm the materials decrease in erosive wear resistance and physical properties. Although each of the materials tested in this study are influenced by the heat aging tests, it is to varying degrees. This suggests that when comparing A4 with the other materials, the high G'' caused by the high filler loading of carbon black results in a material that has low slurry erosive wear resistance in comparison to the silica and natural rubber compounds.

Figure 6.41 shows the G'' of A1, A2 and A3 omitting the high value of G'' for A4. Both the A2 and A3 materials have similar G'' although different resistances to erosive wear testing. A1 has the lowest G'' highlighting the natural gum base rubber compound without reinforcing fillers hence maintaining the highly resilient and elastic material. Although the wear resistant ranking is not as apparent as the A4, further investigation into the material chemical composition and physical properties is important to discuss. The A1 has the lowest G'' , this indicates that it will dissipate the least amount of heat on the surface of the rubber in comparison to the other materials. However, this low value of G'' does not translate to erosive wear resistance. Baranwal and Stephens [57] outline the benefits of using reinforcing fillers in rubber compounds. The benefits include the increase in wear resistance of rubber compound used in wearing applications. The A1 material, although having a low G'' , does not have the reinforcement of fillers to resist the micro-cutting and gouging from the sharp hard impinging particles. An optimum level of filler reinforcement in the chemical structure of the rubber and low G'' is required to meet these criteria.

The A2 and A3 materials have similar G'' , however, different erosive wear resistance rankings. The polymer blend of natural rubber and poly butadiene plays a significant role in the erosive wear resistance of the material. The A2 is a purely a natural rubber compound and highly filled with silica as the reinforcing agent. This reinforcement of A2 does increase the hardness of the compound in comparison to the A3 compound. As discussed earlier, the hardness of the compound plays a significant part in erosive wear resistance of a material as the hardness is inversely related to resilience and hence the $\tan \delta$ value. The hardness vs. wear loss result from this study shown in Figure 5.10 illustrates this point. The harder materials did not have the wear resistance of the softer materials. The A3 material in this study possesses all the required physical and viscoelastic properties as well as chemical make up to be effective in erosive wear applications.

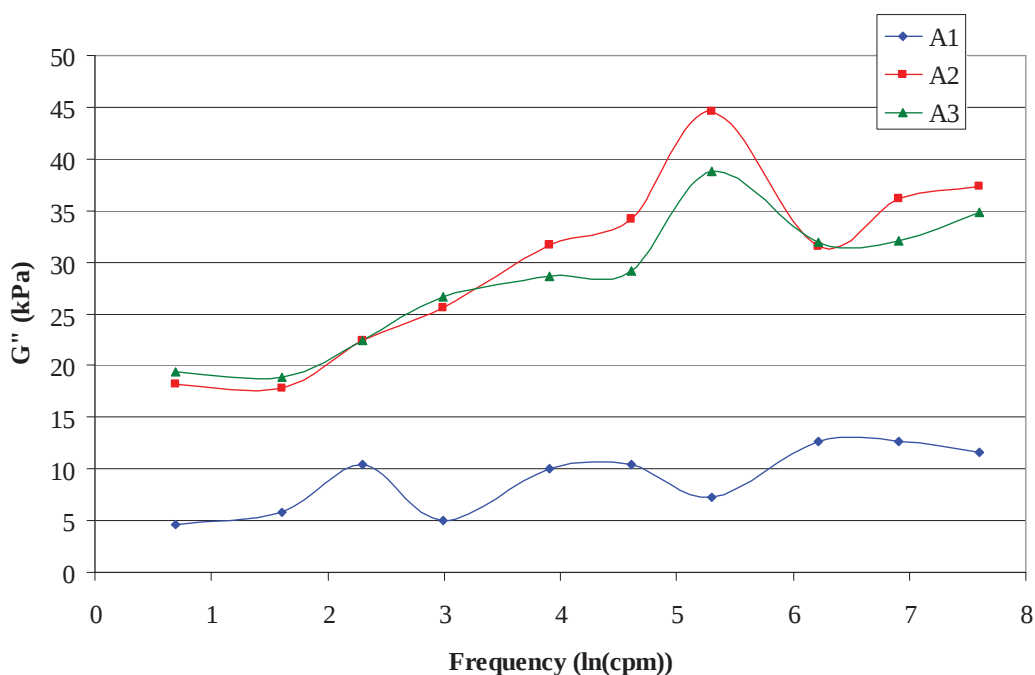


Figure 6.41 G'' of A1, A2 and A3 control samples using the RPA omitting A4.

The $\tan \delta$ of the A1, A2, A3 and A4 materials is shown in Figure 5.15c. Although the value of $\tan \delta$ is not an absolute number it has been used extensively in the literature to discuss rolling resistance and hysteresis in car passenger tyres. The higher the $\tan \delta$ translates to

higher rolling resistance and heat build up [57]. When determining the amount of erosive wear resistance a rubber has in relation to the $\tan \delta$, it is difficult to come to a conclusion since the level of hysteresis cannot be determined when comparing different rubber compounds. However, the ranking of erosive wear resistance can be measured in reference to the $\tan \delta$ as shown in Figure 5.15c. The A4 material has the highest $\tan \delta$, hence the highest erosive wear loss during testing. This high wear loss is attributed to the material's high level of reinforcing carbon black particles and relates back to the amount of energy that is stored (G') and dissipated as heat (G'') on the surface of the rubber. During the erosive wear process, a sharp particle will strike the surface of the rubber causing a deflection in the material and ultimately generation of heat. Since the A4 rubber has a high level of $\tan \delta$, this indicates that the resilience of the rubber is low as shown in Figure 5.15c. The rubber cannot rebound or return the impact energy of the impinging particle therefore causing damage to the surface. This eventually leads to high wear loss and low resistance to erosive wear. In contrast, the higher resilient materials A1, A2 and A3 have significantly lower $\tan \delta$ values. The resilience of these rubbers are higher than the A4 and conversely the energy from the impinging particle does not store or dissipate as heat on the surface of the rubber to the same level as the A4 compound. The end result is that less material is removed from these low $\tan \delta$ materials from the erosive wear process.

6.5 Discussion of Hypotheses

In this study four rubber materials were investigated to determine the slurry erosion wear mechanisms involved in the application on slurry transport. Each rubber has its own unique properties and chemistry which are important to distinguish during the wear and chemical analysis. The A1 was a natural rubber based rubber with no reinforcing fillers, producing a soft rubber with high resilience and low $\tan \delta$. The A4 was a highly loaded carbon black reinforced rubber, with a conventional cure system that resulted in a hard rubber with low resilience and high $\tan \delta$. A2 and A3 are reinforced with silica and silane, with properties between A1 and A4. A3 was the most erosive wear resistance attributed to its silica reinforcement, high resilience, low storage and loss modulus leading to a low $\tan \delta$. There

was a correlation that could be made between the erosive wear and the $\tan \delta$. This was particularly evident comparing the A4 $\tan \delta$ with the A3. Testing showed that the $\tan \delta$ of A4 was four times higher than A3, correlating with the erosive wear loss for the A4 and A3. In this study, the viscoelastic properties were shown to relate to the rubber physical properties but also the erosive wear behaviour.

Chemical change as a result of erosive wear was not found in this study. FT-IR was used to analyse control, heat aged, slurry jet erosion tested samples. Some chemical characteristic bonds did show degradation as a result of heat aging. However, no results could be correlated with the control worn sample surfaces with the erosive wear surfaces. Heat aging did result in chemical change to the surface of the rubbers and influenced the wear resistance of each compound. At the aging temperature of 75°C, the erosive wear resistance of the rubbers did not show a significant decrease. However at 100°C, some physical properties, viscoelastic properties and erosive wear resistance were decreased. This study showed that chemical change does occur as a result of heat aging; however it is clear, noting the limitations of the FT-IR, that no chemical change was observed as a result of erosive wear.

The hypotheses for this project are outlined below:

Hypothesis 1: The physical and viscoelastic properties of the rubber will be influenced by the erosive wear process as a result of heat and time. Elevated temperature aging will cause the material properties to degrade. Aging occurs in the erosive wear of rubber pump lining materials used in minerals processing which leads to a decrease in the physical and viscoelastic properties of the rubber.

Response: The tensile properties of A1, A2, A3 and A4 are decreased by the heat aging in air and water. The slight increase in hardness for each rubber is caused by the higher degree of crosslinking which restricts the mobility of the polymer chains. This increase in hardness then leads to a decrease in erosion resistance. The decrease in erosive wear resistance is relative for each material, and hence it is difficult to correlate heat aging with the wear

process. Similarly the viscoelastic properties of the rubbers decrease with heat aging. At low aging temperatures (i.e. 75°C and 100°C) chain scission does not occur as there is not enough energy to cause polymer chain degradation. At high aging temperatures there are signs of reversion in the A1 material with the storage modulus (G') decreasing from the control by 50%. Again no direct correlation can be made between heat aging and erosion wear, although the physical and viscoelastic properties of each rubber and their wear resistance can be quantified in reference to heat aging.

Hypothesis 2: Chemical change such as hysteresis and chain scission of the polymer molecules occurs during the erosive wear process. The higher degree of hysteresis and chain scission will lead to an increase in wear rate during the pump operation. In particular the C=C bond and the sulphur bonds will be of interest. Crosslink density relates to the amount of vulcanisation that occurs during the processing of the rubber. The higher the degree of crosslinking will result in a higher wear rate of material during the erosive wear process.

Response: Chemical change on the surface of the rubber can be attributed to the erosive wear process. Although the C=C bond did not show signs of degradation during the erosive wear testing and aging tests, other characteristic bonds of each of the rubber compounds showed signs of degradation. The A1 material showed signs of chemical degradation of the H-S (disulfide bond), N-S (sulfenamide bond) and C-H (methylene) bond after heat aging. The H-S and N-S bonds are weak bonds in the chemical backbone of the rubber structure, as such the degradation of these bonds during the aging process was expected. The A2 and A3 rubbers did not have signs of chemical degradation in the H-S and N-S, rather the aromatic C-H bond showed signs of degradation. This could be attributed to the silica reinforcement used in A2 and A3 as opposed to the natural unfilled gum based structure of the A1 material. The physical properties were affected by the heat aging causing an increase in erosive wear. Heat aging at higher temperatures causes the unreacted sulphur in the rubber to react with the carbon bonds hence increasing the crosslinking in the rubber structure. This higher level of crosslinking leads to lower erosion wear resistance shown by the chemical degradation data of A1 and the heat aging wear results.

Hypothesis 3: Particle attack on the surface of the rubber will result in cutting and gouging that will lead to failure of the material. This particle attack will also lead to chemical change and aging on the surface of the rubber. This will result in a decrease in the material properties. By using methods of wear testing, this will best simulate the erosive wear conditions experienced in the field.

Response: Particle attack on the surface of the rubber as a result of slurry erosion wear leads to cutting and gouging of the rubber surface. Each material had different levels of wear shown in SEM images and the severity of the wear was dependant on material, particle size and angle of impingement. The angle of impingement that exhibits the highest wear was at low angles of 20° whereas at high angles (i.e. 90°) the wear was significantly lower. It is important to note the wear mode of the rubber at impingement angles of 20° differs from the higher angles. At 20° long cuts shown on the surface of the rubber. However at higher angles, the wear mode of the scar is predominately gouging; in some cases deep pits and valleys have formed. Extensive aging tests on the rubber suggested that aging influences the performance of the rubber in slurry erosion resistance. However, the erosive wear process itself did not age the surface of the rubber as shown from the chemical testing of the rubber spectrum since no new functional groups were discovered from the aged samples when evaluating with the erosive worn samples. Chemical change on the surface of the rubbers was significant in a number of characteristic bonds after the erosive wear process. To quantify the role of these bonds to the rubber wear performance is unknown, although links to the material properties and wear behaviour of the rubber was discussed in this research.

7 Conclusions

Erosive wear is the predominant wear mechanism in rubber lined slurry pump applications. This study highlighted many aspects of erosion wear and its influence on material properties and chemistry. Firstly, the slurry erosive wear did not appear to cause significant aging on the surface of the rubber as a result of particle impingement. The erosive wear caused damage on the surface of the rubber and characteristic chemical bonds were broken, however this surface damage could not be correlated with an aged surface. Secondly, the mode of wear is highly dependant on the angle of impingement. The predominant wear mechanism for low angle impingement erosion wear is micro cutting. At higher angles of impingement, the wear mechanism becomes a combination of micro cutting and gouging. The severity of the gouging is dependant on the material and is seen in slurry with larger particle sizes. Thirdly, the viscoelastic properties of the rubber can predict the erosive wear resistance of the rubber. Although the testing could not provide an absolute number for this wear resistance, a relative result for slurry erosive wear resistance of comparative materials was defined.

The chemistry of the surface of the rubber following the heat aging was found to cause chemical degradation to a number of rubber characteristic bonds. The degradation to these bonds caused the rubber to wear at an increased rate as opposed to an unaged sample. Although the heat aging of the rubber influenced the wear resistance and the physical properties of the rubber, no relationship with erosive wear and aging could be established from the results of this study. This trend was shown when comparing the FT-IR spectra of a worn unaged rubber surface in comparison to an aged rubber surface. No correlations could be found with the two surfaces. Furthermore, a relationship could be made between the unworn aged surfaces and worn aged surfaces and the unworn surface and worn surface. This relationship was shown by the similar changes in the characteristic chemical bonds of the rubber before and after testing irrespective of the heat aging. The chemistry of the rubber compounds also influenced the wear and aging behaviour of the rubber. Reinforced and unreinforced rubber would result in different characteristic bonds being affected. In the

case of the, A1 material, the H-S, N-S and C-H bonds were degraded significantly as a result of the erosion wear. The reinforced rubbers A2 and A3 did not show signs of degradation at these bonds; rather the chemical degradation was shown in methylene (C-H) saturated alkane/alkyl functional groups. Although no correlation could be made with erosive slurry wear and aging of the rubber surface, a relationship was established between erosive wear and the influence of reinforcing agents in rubber compounds.

The wear modes of the rubber material as a result of the slurry jet erosion testing differ from impingement angle and particle size. As discussed in the literature [1, 3, 10, 18] the lower the impingement angle of the slurry, the higher the wear loss of the rubber pump lining material. In this study the 20° angle of impingement was shown to result in the highest amount of wear loss. At this low angle of impingement, the wear mode on the surface of the rubber was predominantly long micro cuts causing material to be removed. This attrition of the rubber was observed in all of the four rubber compounds tested in this study. The severity of the wear was dependant on the material formulation. It was found that the A4 material which is highly reinforced with carbon black was the least resistant to erosion wear. At higher angles of impingement, the worn surface of the rubber exhibits signs of micro gouging and ploughing. Although the worn surface of the rubber appears to be relatively damaged, the quantity of material loss in the wear process was not to the same level as that of the low angle of impingement. The erosive wear process did not show any evidence of surface aging on the rubber surface. With this in mind, the wear mode of the rubber is then attributed to the rubber formulation and its physical properties. In a slurry pump application, the erosive wear mode is predominant throughout the pump liner and various parts such as the impeller and the throatbush. The random impingement of the particles in the operation of the slurry pump does not change this outcome since the wear loss of each material is relative to the impingement angle. As such, the material performance in a slurry pump application can be defined by a limiting factor of the low angle slurry impingement wear study. A4 has the lowest erosion wear resistance at low angles therefore it will not perform well in slurry pump applications. Whereas, A3 has the highest erosion wear resistance at low angle, hence it will perform well in a slurry pump application. Based on these test results and outcomes of this study, future high erosive wear

resistant slurry pump liner rubber materials can be developed to increase productivity and longevity of current slurry transport systems.

The viscoelasticity of the rubber compounds demonstrated important characteristics in determining the erosive wear resistance in slurry pump applications. Traditionally only the physical properties of the rubber compounds are explored to determine if a rubber material will be suitable for a slurry erosion application. In this study, correlations between physical and viscoelastic properties were made for each rubber compound. The storage modulus (G'), loss modulus (G'') and $\tan \delta$ could be used to determine the relative erosive wear resistance of the rubbers. The significance of these properties and their link to erosive wear was shown through testing. The A4 was found to have the lowest erosive wear resistance yet it had the highest G' , G'' and $\tan \delta$. The high values for these viscoelastic properties are unfavourable to the rubber's erosion resistance. A large G' results in more energy stored on the surface of the rubber rather than rebounding and transferring the energy back to the impinging particle. The large G'' results in more energy dissipating as heat on the surface of the rubber causing damage. G' , G'' and $\tan \delta$ for the A3 material were significantly lower than the A4. As such the erosive wear resistance of the A3 material was far superior to that of the other materials. The relationship between $\tan \delta$ and resilience is also shown in this study. $\tan \delta$ has previously been defined as the inverse of resilience e.g. A4 has the lowest resilience and the highest $\tan \delta$. The test data show that A3 has far superior erosion wear resistant rubber compared to A4, A1 and A2. By using the viscoelastic properties of the A3 material, the erosive wear resistance can be ranked relative to the other materials. Following this research, a model can be used to develop future high wear resistant materials for the slurry transport application in the minerals processing industry.

8 Future Work

The main purpose of this research was to establish a fundamental understanding of the erosive wear mechanisms occurring in the rubber slurry pump liners in minerals processing applications. Although many objectives were met in this study, a number of aspects were not investigated due to time or equipment constraints. It is then recommended that future study should be undertaken in the following areas:

- Testing of other rubbers other than natural rubber (NR) compounds i.e. synthetic rubbers, composite rubbers, polyurethanes.
- Chemical analysis of specific formulation additives to the rubber and identifying the effect of these additives to the chemistry of the rubber i.e. Chemical analysis of the NR and identifying all the characteristic peaks and chemical bonds in that structure. Then analysing the NR + reinforcing agent and continuing to add the additives until the whole spectrum of each additive is identified and known. See section 4.6.
- Investigating the influence of abrasive wear of rubber in the slurry transport minerals processing applications such as OTR (off the road) truck tyres, conveyer belts, mill lining systems, pipes and hoses, etc.
- Wear testing natural rubber or synthetic rubber under elevated temperatures.
- Testing of rubber compounds using different abrasive media and liquid other than water.
- Investigation of the C=C double bond and the C-S bond if chain scission occurs at these characteristic bonds during the erosive wear process.

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10 Appendix

10.1 FT-IR relative peak data for worn and unworn samples

Relative Peaks of Unworn vs Worn A1

A1	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	
Wavenumber	% Transmittance																																
478.3	61.87	63.22	1.00	1.00	0.90	0.92	0.83	0.86	1.00	1.02	0.96	0.96	0.78	0.81	0.92	0.97	0.99	1.03	0.81	0.80	0.75	0.77	0.72	0.76	0.77	1.17	0.99	1.04	1.07	1.11	0.96	1.01	
570.9	68.43	68.56	1.11	1.08	1.00	1.00	0.92	0.94	1.11	1.11	1.06	1.04	0.86	0.87	1.02	1.05	1.10	1.12	0.89	0.86	0.83	0.84	0.80	0.82	0.85	1.27	1.10	1.13	1.19	1.20	1.06	1.10	
748.3	74.36	73.19	1.20	1.16	1.09	1.07	1.00	1.00	1.20	1.19	1.16	1.11	0.93	0.93	1.11	1.12	1.19	1.19	0.97	0.92	0.90	0.90	0.87	0.88	0.83	1.36	1.19	1.21	1.29	1.29	1.15	1.17	
837.0	61.79	61.71	1.00	0.98	0.90	0.90	0.83	0.84	1.00	1.00	0.96	0.94	0.77	0.79	0.92	0.94	0.99	1.00	0.80	0.78	0.75	0.76	0.72	0.74	0.77	1.15	0.99	1.02	1.07	1.08	0.95	0.99	
1095.4	64.32	65.83	1.04	1.04	0.94	0.96	0.87	0.90	1.04	1.07	1.00	1.00	0.81	0.84	0.96	1.01	1.03	1.07	0.84	0.83	0.78	0.81	0.75	0.79	0.80	1.22	1.03	1.08	1.11	1.16	0.99	1.05	
1315.3	79.74	78.47	1.29	1.24	1.17	1.14	1.07	1.07	1.29	1.27	1.24	1.19	1.00	1.00	1.19	1.20	1.28	1.28	1.04	0.99	0.96	0.96	0.93	0.94	0.99	1.46	1.28	1.29	1.38	1.38	1.23	1.25	
1373.1	67.12	65.50	1.08	1.04	0.98	0.96	0.90	0.89	1.09	1.06	1.04	0.99	0.84	0.83	1.00	1.00	1.08	1.07	0.87	0.82	0.81	0.80	0.78	0.79	0.84	1.22	1.08	1.08	1.16	1.15	1.04	1.05	
1446.4	62.40	61.43	1.01	0.97	0.91	0.90	0.84	0.84	1.01	1.00	0.97	0.93	0.78	0.78	0.93	0.94	1.00	1.00	0.81	0.77	0.75	0.75	0.73	0.74	0.78	1.14	1.00	1.01	1.08	1.08	0.96	0.98	
1539.0	76.85	79.49	1.24	1.26	1.12	1.16	1.03	1.09	1.24	1.29	1.19	1.21	0.96	1.01	1.14	1.21	1.23	1.29	1.00	1.00	0.93	0.97	0.90	0.96	0.96	1.48	1.23	1.31	1.33	1.40	1.19	1.27	
1666.3	82.68	81.58	1.34	1.29	1.21	1.19	1.11	1.11	1.34	1.32	1.29	1.24	1.03	1.03	1.23	1.25	1.32	1.33	1.08	1.03	1.00	1.00	0.97	0.98	1.03	1.52	1.33	1.34	1.43	1.43	1.28	1.30	
1743.4	85.66	83.13	1.38	1.31	1.25	1.21	1.15	1.14	1.39	1.35	1.33	1.26	1.07	1.06	1.28	1.27	1.37	1.35	1.11	1.05	1.04	1.02	1.00	1.00	1.00	1.57	1.34	1.37	1.48	1.46	1.32	1.33	
2360.6	80.35	83.82	1.20	0.85	1.17	0.78	1.08	0.73	1.30	0.87	1.25	0.82	1.01	0.69	1.20	0.82	1.29	0.88	1.05	0.68	0.57	0.66	0.94	0.65	1.00	1.00	1.29	0.99	1.39	0.95	1.24	0.85	
2850.4	62.35	60.70	1.01	0.96	0.91	0.89	0.84	0.83	1.01	0.98	0.97	0.92	0.78	0.77	0.93	0.93	1.00	0.99	0.81	0.76	0.75	0.74	0.73	0.73	0.78	1.13	1.00	1.00	1.08	1.07	0.96	0.97	
2916.0	57.71	56.93	0.93	0.90	0.84	0.83	0.78	0.78	0.93	0.92	0.90	0.86	0.72	0.73	0.86	0.87	0.92	0.93	0.75	0.72	0.70	0.70	0.67	0.68	0.72	1.06	0.93	0.94	1.00	1.00	0.89	0.91	
2958.4	64.78	62.54	1.05	0.99	0.95	0.91	0.87	0.85	1.05	1.01	1.01	0.95	0.81	0.80	0.97	0.95	1.04	1.02	0.84	0.79	0.78	0.77	0.76	0.75	0.81	1.16	1.04	1.03	1.12	1.10	1.00	1.00	
Wavenumber of Interest																									2360.6								

Figure 5.30 Relative peak data for unworn and worn A1

Relative Peaks of Unworn vs Worn A2

A2	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn			
Wavenumber	% Trans	% Transmittance	466.7	466.7	729	729	833.1	833.1	898.7	898.7	1095.4	1095.4	1315.3	1315.3	1377.0	1377.0	1461.9	1461.9	1539.0	1539.0	1670.1	1670.1	2846.6	2846.6	2916.0	2916.0	2958.4	2958.4	2958.4	2958.4			
466.7	51.52	37.69	1.00	1.00	0.70	0.50	0.64	0.52	0.58	0.45	0.80	0.91	0.54	0.41	0.58	0.45	0.70	0.50	0.54	0.43	0.53	0.40	1.22	0.78	1.68	1.04	0.66	0.50	0.50	0.50			
729.0	73.20	75.23	1.42	2.00	1.00	1.00	0.90	1.05	0.82	0.89	1.14	1.82	0.76	0.81	0.83	0.90	1.00	0.99	0.77	0.87	0.75	0.81	1.74	1.55	2.39	2.08	0.94	1.00	1.00	1.00			
833.1	80.99	71.86	1.57	1.91	1.11	0.96	1.00	1.00	0.91	0.85	1.26	1.74	0.85	0.78	0.92	0.86	1.10	0.95	0.85	0.83	0.83	0.77	1.92	1.48	2.64	1.99	1.04	0.96	0.96	0.96			
898.7	89.03	84.64	1.73	2.25	1.22	1.13	1.10	1.18	1.00	1.00	1.39	2.05	0.93	0.92	1.01	1.01	1.21	1.11	0.94	0.97	0.92	0.91	2.11	1.74	2.90	2.34	1.15	1.13	1.13	1.13			
1095.4	64.05	41.28	1.24	1.10	0.88	0.55	0.79	0.57	0.72	0.49	1.00	1.00	0.67	0.45	0.72	0.49	0.87	0.54	0.67	0.47	0.66	0.44	1.52	0.85	2.09	1.14	0.82	0.55	0.55	0.55			
1315.3	95.78	92.47	1.86	2.45	1.31	1.23	1.18	1.29	1.08	1.09	1.50	2.24	1.00	1.00	1.08	1.11	1.30	1.22	1.01	1.06	0.99	0.99	2.27	1.90	3.12	2.56	1.23	1.23	1.23	1.23			
1377.0	88.42	83.57	1.72	2.22	1.21	1.11	1.09	1.16	0.99	0.99	1.38	2.02	0.92	0.90	1.00	1.00	1.20	1.10	0.93	0.96	0.91	0.90	2.10	1.72	2.88	2.31	1.14	1.12	1.12	1.12			
1461.9	73.49	75.95	1.43	2.02	1.00	1.01	0.91	1.06	0.83	0.90	1.15	1.84	0.77	0.82	0.83	0.91	1.00	1.00	0.77	0.87	0.76	0.81	1.74	1.56	2.40	2.10	0.95	1.01	1.01	1.01			
1539.0	94.92	86.95	1.84	2.31	1.30	1.16	1.17	1.21	1.07	1.03	1.48	2.11	0.99	0.94	1.07	1.04	1.29	1.14	1.00	1.00	0.98	0.93	2.25	1.79	3.10	2.41	1.22	1.16	1.16	1.16			
1670.1	97.22	93.23	1.89	2.47	1.33	1.24	1.20	1.30	1.09	1.10	1.52	2.26	1.02	1.01	1.10	1.12	1.32	1.23	1.02	1.07	1.00	1.00	2.31	1.92	3.17	2.58	1.25	1.24	1.24	1.24			
2846.6	42.17	48.62	0.82	1.29	0.58	0.65	0.52	0.68	0.47	0.57	0.66	1.18	0.44	0.53	0.48	0.58	0.57	0.64	0.44	0.56	0.43	0.52	1.00	1.00	1.38	1.35	0.54	0.65	0.65	0.65			
2916.0	30.65	36.11	0.60	0.96	0.42	0.48	0.38	0.50	0.34	0.43	0.48	0.87	0.32	0.39	0.35	0.43	0.42	0.48	0.32	0.42	0.32	0.39	0.73	0.74	1.00	1.00	0.39	0.48	0.48	0.48			
2958.4	77.68	74.92	1.51	1.99	1.06	1.00	0.96	1.04	0.87	0.89	1.21	1.82	0.81	0.81	0.88	0.90	1.06	0.99	0.82	0.86	0.80	0.80	1.84	1.54	2.53	2.07	1.00	1.00	1.00	1.00			
Wavenumber of Interest			466.7								1095.4												2846.6				2916						

Figure 5.31 Relative peak data for unworn and worn A2

Relative Peaks of Unworn vs Worn A3

A3	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn	Worn	Unworn
Wavenumber	Transmittance	% Transmittance	462.9	462.9	574.7	574.7	729.0	729.0	833.1	833.1	894.9	894.9	1099.3	1099.3	1315.3	1315.3	1377.0	1377.0	1461.9	1461.9	1523.6	1523.6	1539.0	1539.0	1662.4
462.9	46.99	39.94	1.00	1.00	0.64	0.58	0.71	0.62	0.66	0.60	0.59	0.52	0.83	0.86	0.53	0.47	0.58	0.52	0.65	0.56	0.52	0.47	0.53	0.49	0.52
574.7	73.25	69.15	1.56	1.73	1.00	1.00	1.10	1.08	1.02	1.04	0.91	0.90	1.29	1.49	0.83	0.81	0.90	0.90	1.01	0.97	0.81	0.81	0.82	0.84	0.82
729.0	66.37	64.26	1.41	1.61	0.91	0.93	1.00	1.00	0.93	0.97	0.83	0.83	1.17	1.38	0.76	0.76	0.82	0.84	0.91	0.90	0.73	0.75	0.75	0.78	0.74
833.1	71.70	66.54	1.53	1.67	0.98	0.96	1.08	1.04	1.00	1.00	0.89	0.86	1.26	1.43	0.82	0.78	0.88	0.87	0.98	0.93	0.79	0.78	0.81	0.81	0.80
894.9	80.17	77.16	1.71	1.93	1.09	1.12	1.21	1.20	1.12	1.16	1.00	1.00	1.41	1.66	0.91	0.91	0.99	1.01	1.10	1.08	0.88	0.90	0.90	0.94	0.89
1099.3	56.77	46.50	1.21	1.16	0.78	0.67	0.86	0.72	0.79	0.70	0.71	0.60	1.00	1.00	0.65	0.55	0.70	0.61	0.78	0.65	0.63	0.54	0.64	0.57	0.63
1315.3	87.84	84.85	1.87	2.12	1.20	1.23	1.32	1.32	1.23	1.28	1.10	1.10	1.55	1.82	1.00	1.00	1.08	1.11	1.21	1.19	0.97	0.99	0.99	1.03	0.98
1377.0	81.08	76.67	1.73	1.82	1.11	1.11	1.22	1.19	1.13	1.15	1.01	0.99	1.43	1.65	0.92	0.90	1.00	1.00	1.11	1.08	0.89	0.90	0.91	0.93	0.90
1461.9	72.83	71.22	1.55	1.78	0.99	1.03	1.10	1.11	1.02	1.07	0.91	0.92	1.28	1.53	0.83	0.84	0.90	0.93	1.00	1.00	0.80	0.83	0.82	0.87	0.81
1523.6	90.74	85.53	1.93	2.14	1.24	1.24	1.37	1.33	1.27	1.29	1.13	1.11	1.60	1.84	1.03	1.01	1.12	1.12	1.25	1.20	1.00	1.00	1.02	1.04	1.01
1539.0	89.03	82.28	1.89	2.06	1.22	1.19	1.34	1.28	1.24	1.24	1.11	1.07	1.57	1.77	1.01	0.97	1.10	1.07	1.22	1.16	0.98	0.96	1.00	1.00	0.99
1662.4	89.69	86.30	1.91	2.16	1.22	1.25	1.35	1.34	1.25	1.30	1.12	1.12	1.58	1.86	1.02	1.02	1.11	1.13	1.23	1.21	0.99	1.01	1.01	1.05	1.00
1739.6	91.21	88.64	1.94	2.22	1.25	1.28	1.37	1.38	1.27	1.33	1.14	1.15	1.61	1.91	1.04	1.04	1.13	1.16	1.25	1.24	1.01	1.04	1.02	1.08	1.02
2846.6	51.57	47.80	1.10	1.20	0.70	0.69	0.78	0.74	0.72	0.72	0.64	0.62	0.91	1.03	0.59	0.56	0.64	0.62	0.71	0.67	0.57	0.56	0.58	0.58	0.57
2916.0	42.38	37.34	0.90	0.93	0.58	0.54	0.64	0.58	0.59	0.56	0.53	0.48	0.75	0.80	0.48	0.44	0.52	0.49	0.58	0.52	0.47	0.44	0.48	0.45	0.47
2958.4	75.17	70.76	1.60	1.77	1.03	1.02	1.13	1.10	1.05	1.06	0.94	0.92	1.32	1.52	0.86	0.83	0.93	0.92	1.03	0.99	0.83	0.83	0.84	0.86	0.84
Wavenumber of Interest	462.9												1099.3												

Figure 5.32 Relative peak data for unworn and worn A3

10.2 FT-IR relative peak data of interest for worn and unworn samples

Table 6.2 Characteristic peaks of interest of unworn A1, A2 and A3 before and after aging at 75°C and 100°C for 1 month.

Material	Wavenumber	Group Frequency	Origin	Functional Group	Assignment		Description
A1	1539	1400-1500	C-C			stretch	C-C stretch (in-ring) a
	2916	2915-2935	CH ₂	Methylene C-H	asymmetric	stretch	Saturated aliphatic (alkane/alkyl)
A2	467						
	1095	950-1225					Aromatic C-H in plan
	2846	2845-2865	CH ₂	Methylene C-H	symmetric	stretch	Saturated aliphatic (alkane/alkyl)
	2916	2915-2935	CH ₂	Methylene C-H	asymmetric	stretch	Saturated aliphatic (alkane/alkyl)
A3	463						
	1099	950-1225					Aromatic C-H in plan
	2846	2845-2865	CH ₂	Methylene C-H	symmetric	stretch	Saturated aliphatic (alkane/alkyl)
	2916	2915-2935	CH ₂	Methylene C-H	asymmetric	stretch	Saturated aliphatic (alkane/alkyl)

Table 6.3 Relative characteristic peaks of interest for the comparison between unworn vs. worn A1, A2 and A3 samples.

Material	Wavenumber	Group Frequency	Origin	Functional Group	Assignment		Description
A1	2361						Either H-S, N-S or C-
A2	467						
	1095	950-1225					Aromatic C-H in plan
	2846	2845-2865	CH ₂	Methylene C-H	symmetric	stretch	Saturated aliphatic (alkane/alkyl)
	2916	2915-2935	CH ₂	Methylene C-H	asymmetric	stretch	Saturated aliphatic (alkane/alkyl)
A3	463						
	1099	950-1225					Aromatic C-H in plan
	2916	2915-2935	CH ₂	Methylene C-H	asymmetric	stretch	Saturated aliphatic (alkane/alkyl)

Table 6.4 Relative characteristic peaks of interest for the comparison between unworn A1, A2 and A3 after aging at 75°C and 100°C for 1 month vs. unaged worn A1, A2 and A3.

Material	Wavenumber	Group Frequency	Origin	Functional Group	Assignment		Description
A1	1539	1400-1500	C-C			stretch	C-C stretch (in-ring) a
	2361						Either H-S, N-S or C-
	2916	2915-2935	CH ₂	Methylene C-H	asymmetric	stretch	Saturated aliphatic (alkane/alkyl)
A2	467						
	1095	950-1225					Aromatic C-H in plan
	2846	2845-2865	CH ₂	Methylene C-H	symmetric	stretch	Saturated aliphatic (alkane/alkyl)
	2916	2915-2935	CH ₂	Methylene C-H	asymmetric	stretch	Saturated aliphatic (alkane/alkyl)
A3	463						
	1099	950-1225					Aromatic C-H in plan
	2846	2845-2865	CH ₂	Methylene C-H	symmetric	stretch	Saturated aliphatic (alkane/alkyl)
	2916	2915-2935	CH ₂	Methylene C-H	asymmetric	stretch	Saturated aliphatic (alkane/alkyl)

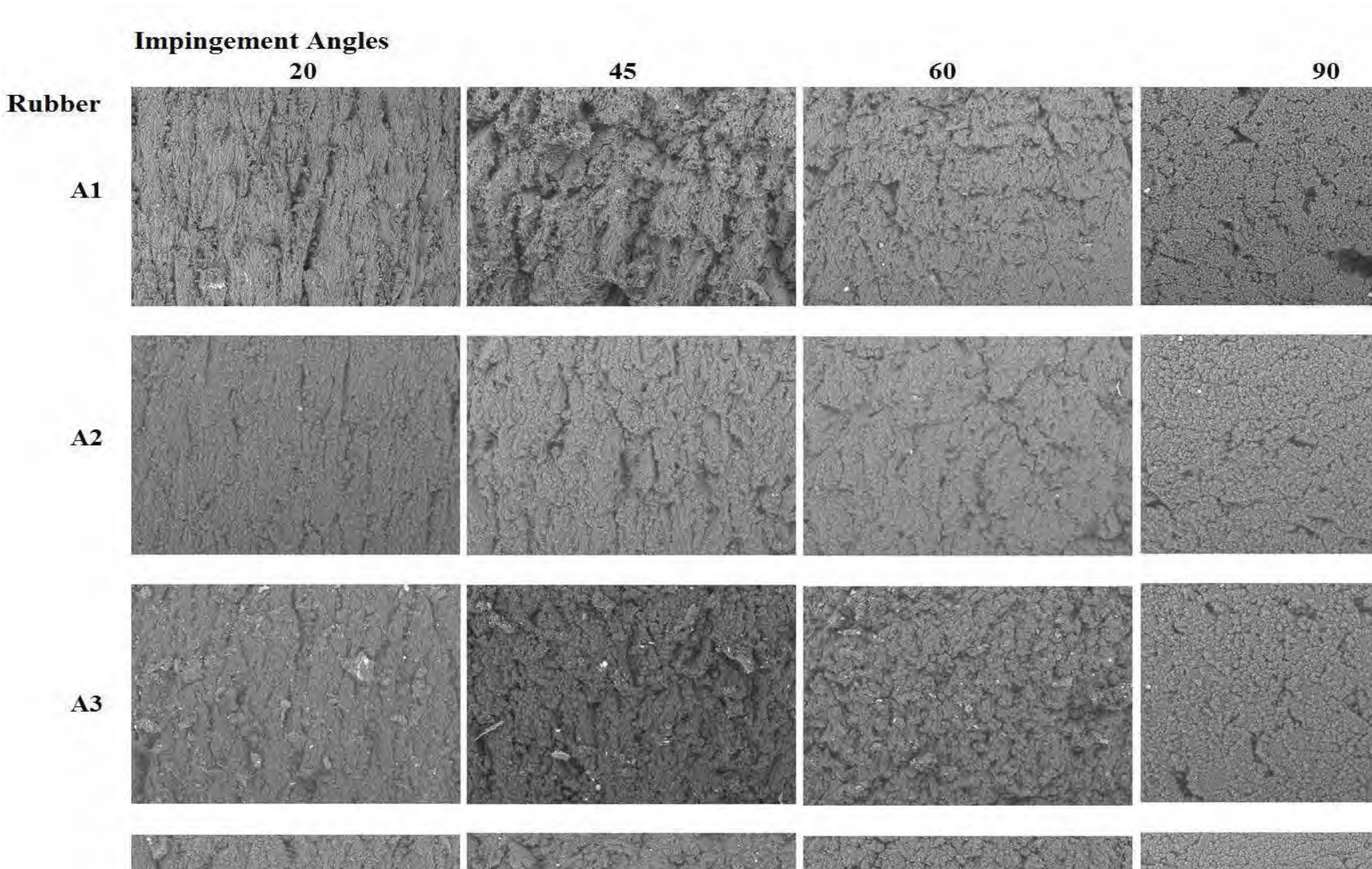
Table 6.5 Relative characteristic peaks of interest for the comparison between worn A1, A2 and A3 after aging at 75°C and 100°C for 1 month vs. unaged worn A1, A2 and A3.

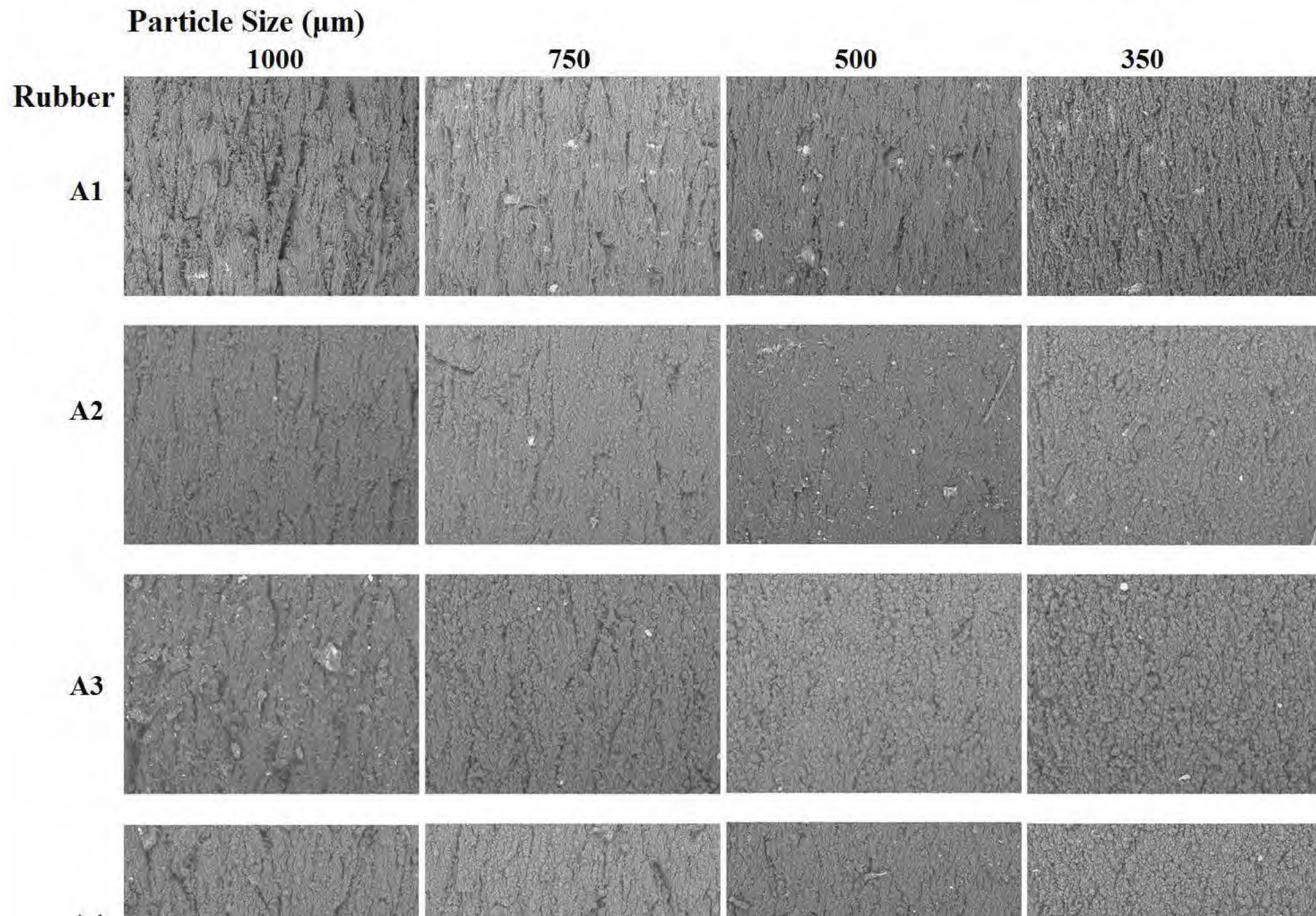
Material	Wavenumber	Group Frequency	Origin	Functional Group	Assignment		Description	Peak Intensity
A1	2361						Either H-S, N-S or C-H bonds	strong
A2	467							medium
	1095	950-1225					Aromatic C-H in plane bend	medium
	2846	2845-2865	CH ₂	Methylene C-H	symmetric	stretch	Saturated aliphatic (alkane/alkyl) group frequencies	strong
	2916	2915-2935	CH ₂	Methylene C-H	asymmetric	stretch	Saturated aliphatic (alkane/alkyl) group frequencies	strong
A3	463							medium
	1099	950-1225					Aromatic C-H in plane bend	medium
	2846	2845-2865	CH ₂	Methylene C-H	symmetric	stretch	Saturated aliphatic (alkane/alkyl) group frequencies	strong
	2916	2915-2935	CH ₂	Methylene C-H	asymmetric	stretch	Saturated aliphatic (alkane/alkyl) group frequencies	strong

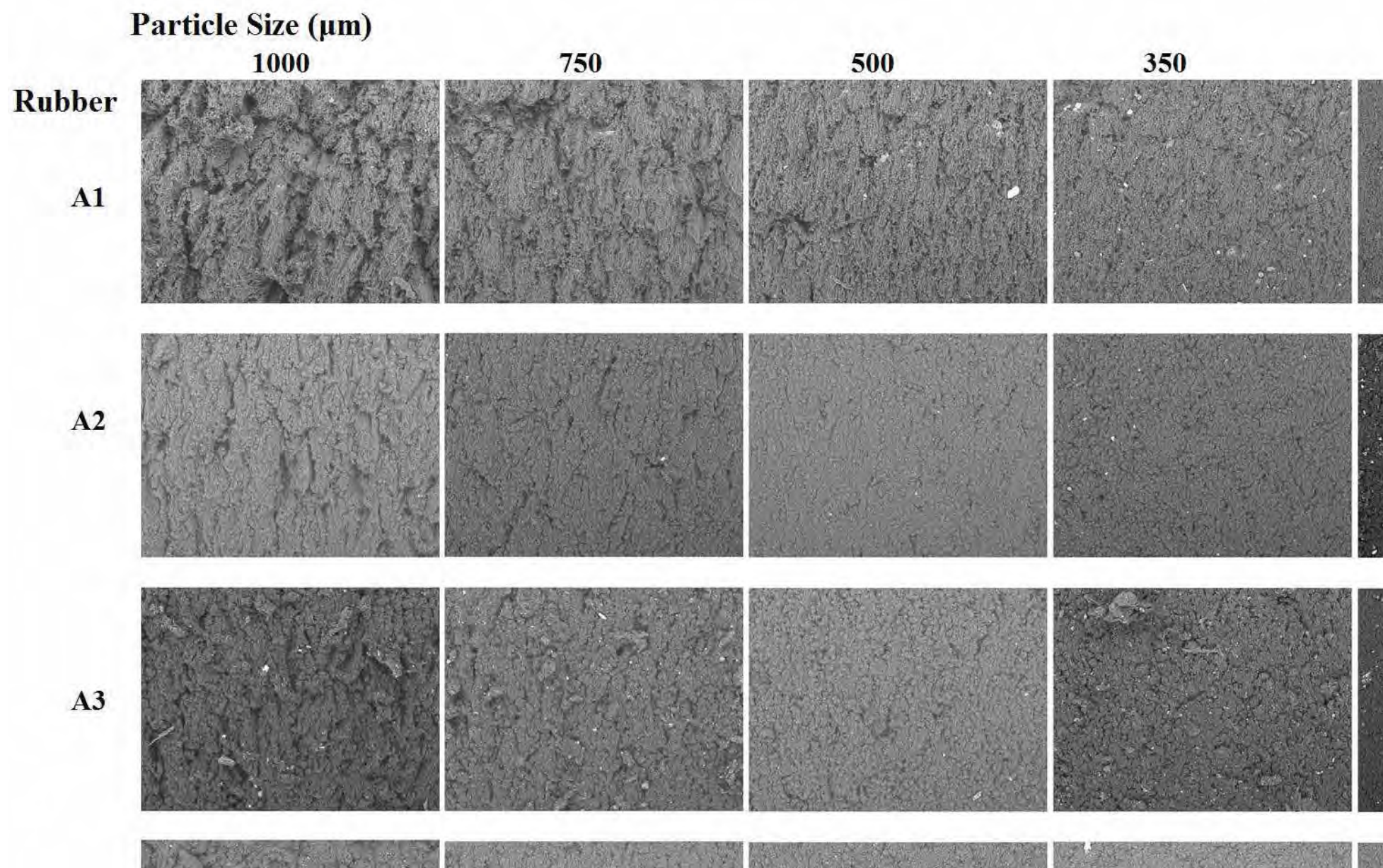
Table 6.6 Surface analysis of unworn vs. worn A1, A2 and A3 after aging at 75°C and 100°C for 1 month.

Material	Wavenumber	Group Frequency	Origin	Functional Group	Assignment		Description
A1	1539	1400-1500	C-C			stretch	C-C stretch (in-ring)
	2361						Either H-S, N-S or C-S
	2916	2915-2935	CH ₂	Methylene C-H	asymmetric	stretch	Saturated aliphatic (alkane/alkene)
A2	467						
	1095	950-1225					Aromatic C-H in plane
	2846	2845-2865	CH ₂	Methylene C-H	symmetric	stretch	Saturated aliphatic (alkane/alkene)
	2916	2915-2935	CH ₂	Methylene C-H	asymmetric	stretch	Saturated aliphatic (alkane/alkene)
A3	463						
	1099	950-1225					Aromatic C-H in plane
	1462 ?	1450-1470	CH			bend	Alkanes
	2846	2845-2865	CH ₂	Methylene C-H	symmetric	stretch	Saturated aliphatic (alkane/alkene)
	2916	2915-2935	CH ₂	Methylene C-H	asymmetric	stretch	Saturated aliphatic (alkane/alkene)

10.3 SEM images of unworn and worn samples







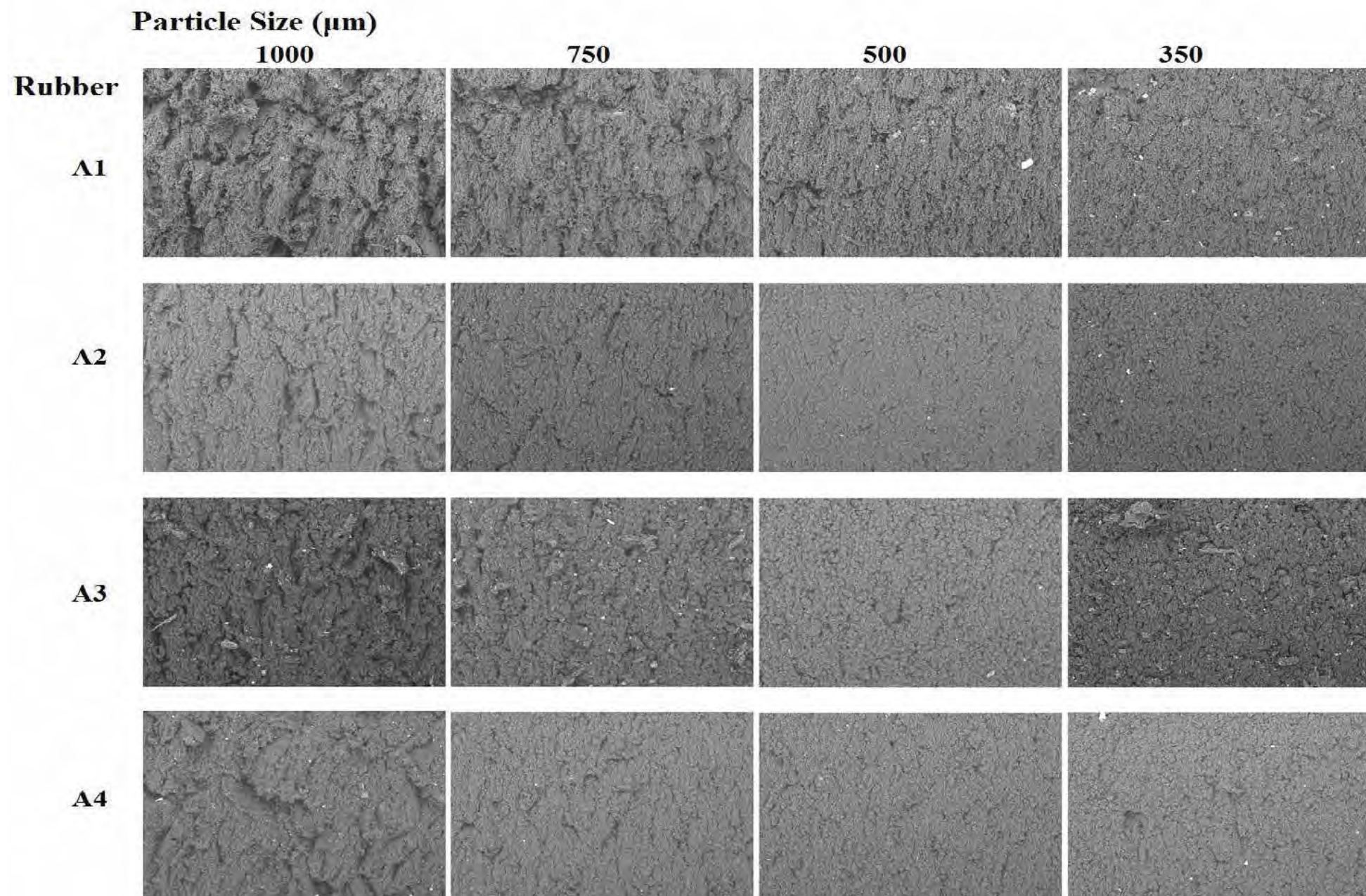


Figure 6.38 SEM images of wear scars of A1, A2, A3 and A4 at different particle sizes at impingement angle of 60°. Wear direction indicated by an arrow.

