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Publication details:

Proceedings of ACUN 5: Development in Composites: Advanced Infrastructural, Natural and Nano composites

pp. 352-358

0733423639 (ISBN)

Event details:

ACUN - 5 International Composites Conference

Sydney, Australia

Publication Date:

2006

DOI:

<https://doi.org/10.26190/unsworks/456>

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Flexural and impact properties of binary reinforced epoxy nanocomposites

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Abstract.

A binary system of nano-reinforcement was used to increase flexural strength, flexural modulus and impact strength of a bisphenol-A type epoxy resin. Montmorillonite and alumina particles were used as modifiers. Each modifier, by itself, was found to increase these properties and further the use of both was found to have a synergistic effect.

1. Introduction

Thermosetting polymers are widely used materials in mechanical, marine and aerospace industry. Epoxy resin is a polymeric material, which is liquid in its natural state and has the ability to convert to solid state via chemical reaction. Epoxies are composed of two parts, the resin which accounts for the majority of the material and the hardener which only occupies a minority of the total volume (within 1-5% vol).

The unique properties of epoxy resins are low specific weight and high resistance to degradation. Inferior properties of thermosetting polymer are very brittle, poor crack resistance, low impact strength and low modulus of elasticity. The push for better thermosetting polymer has led to the addition of nano-fillers in thermosetting polymer.

Perhaps the first investigations on polymer based nanocomposites were performed by Toyota researchers.¹ Researchers have carried out numerous studies in epoxy resin with the addition of nano-particles.²⁻⁵ These reinforcements include titanium oxides, carbon nanotubes, fly ash, calcium oxides, polymer layer smectite clay and alumina. Only polymer layer smectite clay and nano-alumina particles are able to improve the properties of epoxy resin without sacrifice of any of the inherent properties. However, no research on epoxy resin reinforced with both nano-alumina and nano-clay particles have been cited.

Meguid and Sun⁶ found that increases in strength were obtained up to around 5wt% alumina nano-particles. After that aggregation of particles resulted in strength decreases. The maximum strength was obtained at 3wt%. Wetzel et al.⁷ found maximum increases in flexural strength at

around 2-3wt% alumina nano-particles. They also found that the nano-alumina particles increased the flexural modulus gradually. Impact strength was also found to increase up to 1-2wt% reinforcement then gradually decrease.

The most widely used clay used for the reinforcement of epoxy resin is smectite or montmorillonite. These clays are used because of their intercalation chemistry. This allows the clay to be chemically modified for dispersal into the resin via exfoliation of the clay layers.

When clays are added to epoxy resin three possible outcomes may occur. If the clay structure remains unaltered then a "conventional" composite is obtained. In this case only very modest increases, if any, are obtained in mechanical properties. If the epoxy resin can insert itself between the clay layers, "intercalated" composites are achieved. If the individual clay layers are dispersed through the epoxy matrix an "exfoliated" composite is formed.

Juwano and Edward⁸ showed flexural modulus increases at 2.5 and 10wt% clay, with concomitant decreases at 5 and 7.5wt%. These decreases were put down to interactions between hydrophilic ions and the curing agent.

Ratna et al.⁹ showed that an 800% increase in tensile strength could be achieved at a 15wt% loading of clay particles for the system they investigated. The high ductility of their matrix allowed for platelet orientation.

Wetzel et al.⁷ have shown that synergistic effects are evident when a combination of nanoparticles and conventional microparticles

are combined, especially where friction and wear properties are important.

These increases in strength and fracture energy have been attributed to crack-particle interactions such as crack bowing, crack deflection, crack branching and crack blunting. Crack bowing

Evans¹⁰ discussed that line tension,¹¹ analogous to that found in the discussion of dislocations,¹² could be used to describe crack interaction with second phase particles. Evans found that an increase in fracture energy is obtained at low volume fractions (larger interparticle distances) and then decreases as the interparticle distance decreases or the volume fraction of particles increases. Strengthening will occur when the particles are deemed impenetrable, causing bowing of the crack front between the particles¹⁰

2. Experimental Procedure

The epoxy resin used in this study was a West System's bisphenol-A type 105 resin with West System's Type 205 hardener, a modified aliphatic polyamine. The chemical composition for the resin and the hardener are given in Table 1. The resin and hardener were mixed, at a ratio of 1 part hardener to 5 parts resin, using a rotary mixer, and then placed in a vacuum chamber to de-gas the resin prior to pouring into silicon rubber moulds.

Composites were made based on the same process. The particles were added to the epoxy resin, thoroughly mixed and degassed prior to addition of the hardener. The hardener was added slowly during stirring and the resulting mixture placed into a vacuum chamber for degassing prior to pouring into moulds and curing at room temperature.

The epoxy was cured at room temperature for 8 hours, then removed from the moulds and allowed to post-cure for 3 days before mechanical testing

West System Epoxy resin 105	
Bisphenol-A type epoxy resin	>50%
Benzyl alcohol	<20%
Bisphenol-F type epoxy resin	<20%

Ethylene glycol monobutyle ether	<0.3%
West System hardener 205	
Polyethylenepolyamine	< 25%
Reaction products of TETA with Phenol/Formaldehyde	< 25%
Triethylenetetramine (TETA)	< 15%
Hydroxybenzene	< 12%
Reaction Products of TETA and propylene oxide	< 12%
Tetraethylenepentamine (TEPA) in various concentrations	< 12%

Table 1. Chemistry of the Epoxy Resin Matrix.

The alumina nano-particles are from Alcoa thermally reactive aluminas made via sol-gel methods and are classified under superground CT 3000 SG. Particle size was quoted as 500-800nm with a surface area of 8.5 m²g⁻¹.

The clay is a surface modified montmorillonite which will disperse to the nano-scale in epoxy resin systems. It was purchased from Nancor and is designated I.30E Nanoclay. Particle size before dispersion is 8-10µm.

Flexure testing was conducted in accordance with ASTM D 790-03 (Standard method of test for flexural properties of plastic). Testing was performed in 3 point configuration. Flexural strength and flexural modulus were measured on specimens nominally 13mm wide by 4mm thick and the span was 75mm mounted flatwise in the test rig.

Impact testing was conducted in accordance with ASTM D 6110-97 (Standard test method determining the charpy impact resistance notched specimens of plastics). The specimen geometry was 120mm long, 12mm wide and 4.5mm thick.

All mechanical testing was performed at a crosshead speed of 2mm/min.

3 Results

3.1 Flexural Modulus

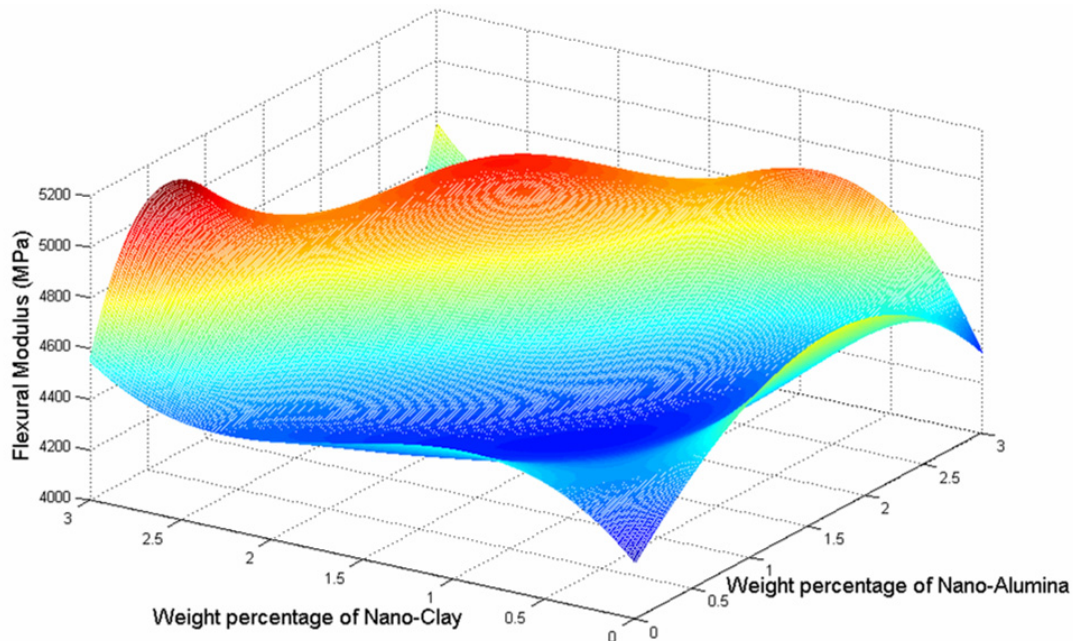


Figure 1. Flexural modulus as a function of reinforcement content

Figure 1 shows the variation in flexural modulus with particle content. The maximum flexural modulus occurs at 3% nano-clay and 1% alumina. A 24% increase from 4.1GPa to 5.1GPa is achieved. Other peaks are found at 2% nano-clay/2% alumina, and 1% nano-clay/3%alumina. Figure 1 also suggests that further peaks may be found at 4% nano-clay and 4% alumina (from trends in the graph). It appears then, that a total of 4wt% of particles seems to provide the maximum increase in stiffness.

The alumina particles have more of an effect on the stiffness than do the clay particles. At 2wt% clay the modulus is 4.5GPa and at 2 wt% alumina, 4.7GPa.

3.2 Flexural Strength

Figure 2 shows the variation in flexural strength as a function of reinforcing content. The strength increases from the pure epoxy strength of 65MPa to 92MPa for a composite containing 2% nano-clay and 2% nano-alumina, a 43% increase.

The shape of the curve appears to suggest a similar trend as modulus for the binary composites. That is, a combined particle of content of 4 wt% provides maximum increase in the properties.

As far as the individual particles' contribution is concerned, the clay particles cause larger increases in strength, compared to stiffness where it was the alumina particles providing the major contribution.

If only the nano-clay is considered, a peak in strength occurs at 2%, approximately 90MPa. The same percentage reinforcement gives a maximum for the alumina only composites of 75MPa.

3.2 Impact Strength

Figure 3 shows the impact strength as a function of reinforcement content. It can be seen that the nano-clay has a less of an effect on increasing the impact strength of the epoxy, an increase of 12% over the reinforcement content studied. The alumina on its own achieves a

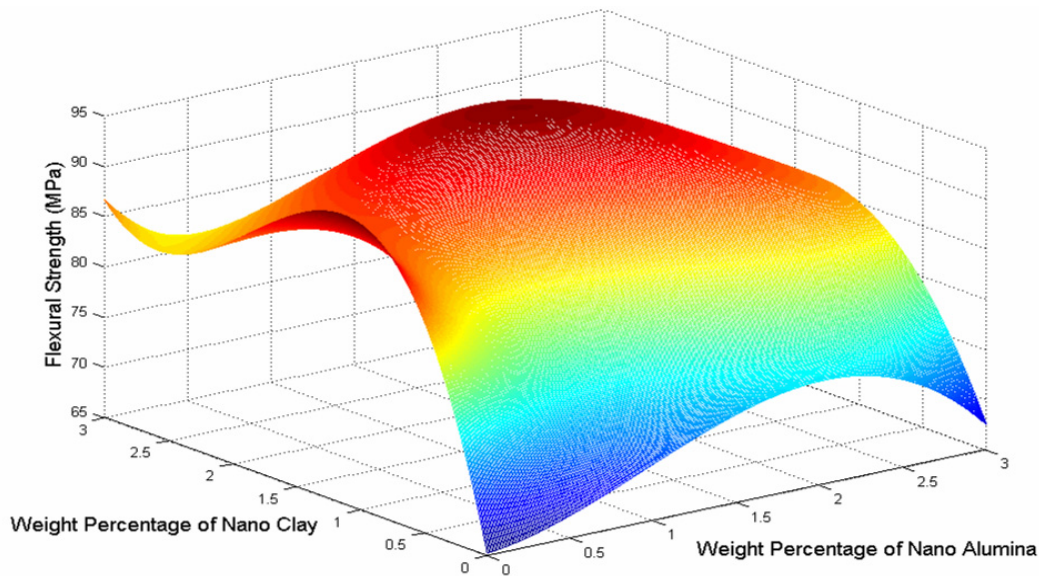


Figure 2. Flexural strength as a function of reinforcement content

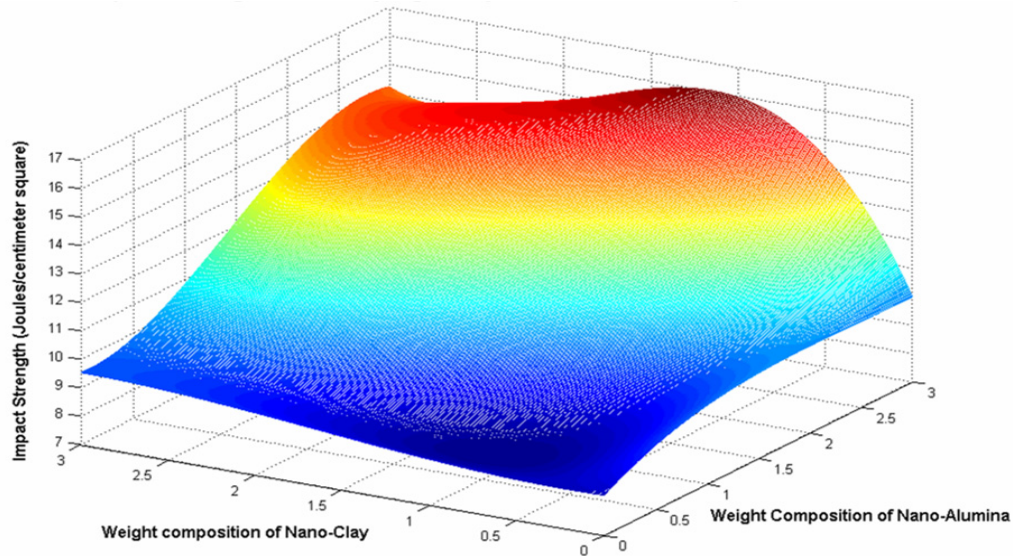


Figure 3. Impact strength as a function of reinforcing content

slightly better increase of 17% for the same content. The maximum increase of 88% is obtained with a combined reinforcement of 1wt% clay and 3wt% alumina. Again there appears to be an optimum condition of 4wt% total particle content.

For composites reinforced with a single phase the same trend of an increase in property to a maximum wt% then a decrease in not observed here. There is a gradual increase in impact strength with increasing particle content over the range studied.

4. Discussion

This paper looks at nanocomposites that have binary reinforcement phases. From the results presented it can be seen that the addition of two different particle types has a synergistic effect on the mechanical properties studied.

4.1 Single reinforcement phase composites.

The larger increase in stiffness for the alumina reinforced composites would be expected from a rule of mixtures approach, the alumina being much stiffer than the clay. The clay only composites show a slight peak at 1wt% a

decrease then another gradual increase, similar that observed by Juwano and Edward⁸. The larger drop in stiffness for the alumina only composites at above 2-2.5wt% need further study. Interfacial studies for the relative bonding between the epoxy resin and the two types of particles may help to explain this.

Single phase composites based on the clay and the alumina particles showed similar trends - an increase in strength followed by a decrease. This may be described by the penetration of the crack front through the particles and the work of Evans.

The clay provided larger increases in strength, suggesting the reinforcement morphology plays an important part in strengthening. The clay exists as platelets compared to the more equiaxed alumina particles. Two effects may result in the better performance of the clay

The shape of the particles, platelets, add increased energy consumption to crack growth due to crack twisting as well as deflection, and even the increased likelihood of crack deflection. Faber and Evans¹³ found that the more effective morphology for deflecting propagating cracks are disc shaped particles followed by spheres. They found that particle reinforced composites would have a maximum concentration of reinforcement over which overlapping particle would diminish toughness.

The second mechanism available for these platelets could be pullout and/or crack bridging, which could not be provided by the more equiaxed alumina particles.

The drop in strength at a clay content of 2.5wt% may be explained by the concept of crack penetration. Evans showed that as the interparticle spacing becomes smaller a critical value is reached where the particles or obstacles no longer behave in an impenetrable manner.

The larger increase in strength for the clay particles suggests that at least intercalation has occurred and perhaps true exfoliation. The smaller particles, being more finely dispersed throughout the matrix, would provide a more effective crack trapping network. The efficiency of this impenetrable network of obstacles is a function of the particle size to inter-particle distance ratio. A detailed microscopic study is to take place to investigate this.

Isik et al.¹⁴ found that the tensile strength and strain at break behaviour was dictated by the matrix. For example a maximum for these properties at 1 wt% montmorillonite content in an epoxy-montmorillonite system was achieved. In polyol modified nanocomposites, the tensile strength and strain at break decreased, in general, as the montmorillonite content increases. The same trend was found with impact strength.

Hauptert and Wetzel¹⁵ report that nanoparticles have a favourable effect on impact strength at low and also higher filler loadings. For small particles (around 10-25nm) maximum impact energy was obtained at 1-2vol%, whilst for larger particles (300nm) that maximum occurs at 4-5vol%. The impact energy for both particle sizes decreases at higher volume fractions. The authors explained the results in terms of stress concentrations around the inclusions. In their nanocomposites they conclude the stress concentration around the particles is expected to be small, because the impact strength is not weakened by the particle presence. They also reported that angular particles (CaSiO_3) increased brittleness due to localised stress concentrations.

Riley et al.¹⁶ found that the impact properties were enhanced when small, low-aspect-ratio particles are used. Large particles can act as flaws and high-aspect-ratio particles induce large stress concentrations near their edges. They also found that particle agglomerates remain as stress concentrators in the matrix. This appears to be the case here, with the alumina particle providing better impact resistant composites than those with only clay particles.

Hauptert and Wetzel also state that an increase in elastic modulus will result in a decrease in impact strength. In this study that was not the case. Comparison of Figures 2 and 3 reveal the same trends for elastic modulus and impact strength with particle addition.

4.2 Binary reinforcing phase composites.

When the two reinforcements are placed together in the composite the results are not so easily explained. The combined effect of the different particle morphologies appear to

interact and may contribute synergistically to the increases in stiffness, strength and impact strength above that of the single reinforcing phase composites.

The notion that it is a total particle content and not so much the inherent properties of the particles is difficult to explain. It may be that the ratios that provide this ridge across the graph in Figure 1 result from an efficient packing of the reinforcement. This may also help explain the similar trend in strength. A detailed fractographic study is to be undertaken to determine if this is the case.

The reduction in strength at higher weight fractions can be accounted for by the arguments for a single phase reinforcement, however the mechanisms involved would be more complex and require modelling. The reduction in stiffness at higher binary contents, i.e. on the far side of the ridge in Figure 1, could be explained by the introduction of critical size imperfections that allow chain movement.

The impact strength of the binary reinforced composites increase in impact strength with increasing alumina content for the range of clay reinforced composites and vice versa. Detrimental levels of particle content were not reached.

5. Conclusions

The data presented here shows that two reinforcement particle types of different size and morphology have a synergistic effect on the mechanical properties of the epoxy matrix investigated in this study. The combination of particles of different morphology and size provides real increases in the mechanical properties studied.

For this system a composite consisting of 2wt% alumina and 1.5-2wt% clay provides an optimum flexural and impact properties. Further microscopic and fractographic studies are required to determine the exact nature of the strengthening mechanisms and why a 4 wt% net reinforcement content provides better properties.

Authors' Biographies

Dr Greg Heness is a senior lecturer in Materials Science at the University of Technology, Sydney. Much of his research has been on particle reinforced metal matrix composites, including matrices that are superplastic, metal roll bonding, ceramic nano-coatings for biomaterial use and recently nanocomposites.

Mr W. Tam performed the experiments in this work as part of his Master's by coursework thesis. Mr Tam has found employment in Hong Kong and now resides there.

Dr Sri Bandyopadhyay is a senior lecturer in the School of Materials Science and Engineering at the University of New South Wales. He is renowned for his structure-property-fracture correlation research in polymers and composites. He has also established himself in the area of nanomaterials since 2000.

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