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ABSTRACT

In this work, we investigated the transverse birefringence in PMMA-based polymer optical fibre introduced in the drawing process. We proposed a simple theoretical model that attributes the induced transverse birefringence to three major factors: quenching effect, molecular alignment, and thermal expansion mismatch. Various experiments have been designed and performed to ascertain and identify the individual contribution of the three factors. In our experiments, polymer optical fibres are drawn under varying conditions and end their transverse birefringence is measured using the interferometric microscope method. These experiments have determined the respective contributions of the three factors and produced important findings agreeable to our theoretical model: the birefringence increases with the drawing speed ratio; the quenching-induced birefringence has profile of parabolic shape which can be removed by annealing; the profile of birefringence due to thermal expansion mismatch has an abrupt change at the core-cladding interface; and the birefringence induced by molecular alignment is constant across the fibre, and the magnitude is small.

Keywords: Polymer optical fibre, transverse birefringence, molecular alignment, quenching, thermal expansion mismatch

1. INTRODUCTION

It is well known that stretching of polymer materials could introduce significant transverse birefringence. This birefringence may result from a number of effects: stress, molecular alignment and so on. Polymer optical fibre drawing is partly a stretching process and hence it may introduce considerable transverse birefringence. This work is motivated to find out more about this birefringence and its relation to the drawing process. We are also interested to investigate the molecular alignment effect in fibre drawing, since it could be related to linear and possibly nonlinear optical properties of the polymer fibres.

Polymer-based optical fibre (POF, or plastic optical fibre) was first reported in 1960's. The interest in polymer optical fibre has increased significantly in recent years. Many research organisations all over the world have done extensive work with regard to the properties and applications of polymer fibres. The interest in polymer optical fibres is mainly related to their advantageous properties, such as better flexibility, larger numerical aperture, lower cost and lighter weight, over those of silica fibres, and their applications in a wide range of areas: home and office networks. local area networks, fibre sensing systems and photonic components.

With regard to the photonic components, it is expected that larger nonlinear optical (NLO) effects could be obtained from polymer optical fibres, since highly nonlinear organic chromophores could be easily doped or chemically attached to main chain of POFs. In particular, the second order nonlinear effect (that is, electro-optical effect) has been a very active topic of POF research. Materials with large EO effect could find many applications[1], such as high speed optical modulators, optical switch with low operation voltage and non-metallic non-contact high voltage sensors.

The EO effect in polymer optical fibres may only be introduced by the orientation of doped EO molecules / chromophores. EO chromophores randomly dispersed in a polymer matrix usually produce no net EO effect unless poled or orientated by applying a strong DC electric field across the polymer material at elevated temperature. Besides electric poling, there are other methods to achieve orientation in polymer material, such as cold drawing of thermoplastics at room temperature [2]. Recently a method called "mechanical poling" was proposed [3]. However, a valid question to ask how much molecular orientation effect (and possibly EO effect) can be achieved by the mechanical poling method.

One simple method to test the level of molecular orientation in a polymer optical fibre is to measure its birefringence, that is, the degree of refractive index asymmetry it exhibits that allows light in two orthogonal polarisation states to travel at different speeds through the material. Since the polymer fibre is axial symmetric and can be considered using cylindrical structure, the transverse birefringence is more important than the longitudinal birefringence. Transverse birefringence is the difference of refractive indices between the directions parallel and perpendicular to the fibre axis. It is commonly known that if the polymer molecules are aligned to the direction of the fibre axis, the transverse birefringence will increase. However, the anisotropic orientation of polymer molecules is not the only factor that can induces transverse birefringence in drawn polymer optical fibres. Previous studies by other researches have suggested various factors to explain the transverse birefringence in the drawn polymer fibre, including the quenching effect, thermal stress and residual stress, thermal expansion difference, and so on. These studies were taken from different prospects, but none of these models is complete and includes all factors.

Thus the purpose of this research is to construct and present a more complete model to describe and explain the polymer optical fibre transverse birefringence phenomena. It will also provide experimental data to examine this model. It is hoped that through the study, the amount of transverse birefringence caused by various factors can be separated and determined individually. With these data, the characteristics and behaviours of polymer optical fibres shall be better understood, which shall then lead to improvement in the fabrication and utilisation of polymer optical fibres. For example, the model and experimental results shall lead to the knowledge of the portion of transverse birefringence contributed by the orientation of polymer molecules. This result can then be used to predict the effect of molecular orientation during the polymer fibre drawing, and therefore to determine whether the mechanical poling method is a feasible way to obtain electro-optic effect in polymer optical fibres.

2. THEORETICAL MODEL

The model we propose consider only three main contributing factors, namely:
  I.   Quenching effect
  II.   Mismatch of thermal expansion between fibre core and cladding
  III.   Alignment of polymer molecules
The first and the second factors are due to the thermal stress inside the fibre, so the birefringence due to these two factors is called thermal stress birefringence. The third factor is not related to thermal stress, but related to the anisotropic properties of the material due to the orientation of polymer molecules, so it is called orientation birefringence.

2.1 Transverse birefringence due to the quenching effect

This quenching effect occurs during the drawing of both polymer and silica materials. For PMMA-based polymer materials, the birefringence is always negative [2]. Its absolute value increases as it gets closer to the side of the fibre. Because the stress-optical coefficient (SOC, will be defined in the following section) of PMMA is very small, some researches predicted that this quenching-induced birefringence would be too weak to be observed [6]. However the experimental method used here is sensitive enough to measure small amount of transverse birefringence, including the

amount of transverse birefringence due to the quenching effect.

This quenching-induced birefringence can be removed by annealing process [5, 7], in which the temperature of the fibre is raised to a certain level, and then the fibre is cooled down to room temperature gradually and slowly with very similar temperature across the whole cross section of the fibre. This will relax the internal thermal stress due to the quenching temperature gradient and therefore remove the birefringence caused by quenching effect.

2.2 Transverse birefringence due to thermal expansion mismatch

There are different material compositions between core and cladding sections of an optical fibre. This leads to a mismatch of thermal expansion level between these two sections. The fibre then becomes a composite cylinder, and no longer a simple one-layer cylinder. As a result, the stress profile across the fibre diameter is no longer a gradually varying curve, instead there exists an abrupt variation at the interface between the core and cladding sections due to the discontinuity of material compositions. This abrupt variation in stress exists in all the 3 components in the cylindrical axes (r, θ and z), and in turn causes abrupt variation in the refractive index in all 3 components.

To reduce this effect of thermal expansion mismatch, the chemical compositions of the core and cladding materials can be carefully chosen to match the material constants, so that their difference is sufficiently lower than the refractive index difference. Under this condition, the thermal stress effect due to the mismatch of expansion between core and cladding can be neglected.

2.3 Transverse birefringence due to molecular alignment

Thermal stress is not the only source that causes transverse birefringence in the mechanically drawn polymer optical fibre. Experiments on polymer materials by many researchers showed that after the annealing of polymer materials there is still certain amount of birefringence remained [7, 8].

In polymer fibre drawing process, the polymer matrix undergoes a chain stretching along the fibre axis. This will align the orientation of polymer molecules to the drawing (axial) direction. This mechanical anisotropy gives rise to optical anisotropy of the fibre in the form of transverse birefringence [9]. Another factor that causes the alignment of polymer molecules during the fibre drawing is the flow of polymer during cooling, which is subject to the gravity (usually the fibre is drawn vertically from the preform) and the drawing force.

It is obvious that the birefringence induced by molecular alignment only occurs on polymer fibres and not on silica fibres because silica fibres do not contain long polymer chains which have large polarisabilities.

2.4 Equation for transverse birefringence

Essentially, the transverse birefringence on drawn POF are caused by thermal stress and orientation stress:

$$n_{total} = \Delta n_{thermal\ stress} + \Delta n_{orientation} \tag{1}$$

When a fibre is drawn from preform at the furnace of the polymer fibre drawing rig, it is subject to a temperature much higher than its glass transition temperature, so it behaves like a rubber. The kinetic theory of rubber-like elasticity shows that there is proportionality between the birefringence Δn and the stress produced during axial extension σ [10, 11]. The ratio of Δn to σ is called the stress-optical coefficient (SOC). Hence:

$$\Delta n = \text{SOC}\ \sigma \tag{2}$$

And therefore

$$\Delta n_{total} = \text{SOC}\ (\ \sigma_{th} + \sigma_{o}\ ) \tag{3}$$

The stress-optical coefficient is independent of the extension ratio, but dependent to the material.

Since the polymer fibre has rubber-like behaviour during drawing process, the AFFINE deformation model for rubbers can be used [10]. With this model, the orientation birefringence of a uniaxially stretched rubber Δn_{o} is approximated by:

$$\Delta n_o = \frac{2}{45} \pi N_C \frac{(\overline{n}^2 + 2)^2}{\overline{n}} (p_1 - p_2) \left(\lambda^2 - \frac{1}{\lambda} \right) \qquad (4)$$

Here N_C is the number of polarisable units (chains) per unit volume, $\overline{n}$ is the mean refractive index of the material, λ is the draw ratio, and p_1 and p_2 are the polarisabilities of the random link along and perpendicular to its length respectively. The same theory also connects the orientation stress σ_o produced during uniaxial extension with λ by the expression [10]:

$$\sigma_o = N_C \, k \, T \left(\lambda^2 - \frac{1}{\lambda} \right) \qquad (5)$$

where k is Boltzmann's constant and T is the absolute temperature.
From Equations 3.25 and 3.26, the stress-optical coefficient of the material can be obtained:

$$\mathrm{SOC} = \frac{\Delta n_o}{\sigma_o} = \frac{2\pi}{45kT} \frac{(\overline{n}^2 + 2)^2}{\overline{n}} (p_1 - p_2) \qquad (6)$$

This SOC value can be used for thermal stress calculation too, since it is a material constant. In this model, the amount of birefringence caused by molecular alignment is the same across the diameter of the fibre since it does not depend on the distance to the fibre centre axis. The equation also shows that the orientation birefringence is related to the fibre drawing speed ratio via expression $\left(\lambda^2 - \frac{1}{\lambda} \right)$, which is not a simple linear or quadratic relationship.

For thermal stress related birefringence, which includes both quenching-induced birefringence and thermal expansion mismatch-induced birefringence, the internal thermal stress σ_{th} is the difference between the thermal stress in the radial direction σ_r and the stress in the axial direction σ_z, they can be further expanded
Therefore the overall equation for the transverse birefringence of mechanically drawn polymer optical fibre can be written as:

$$\Delta n_{total} = \Delta n_{thermal\ stress} + \Delta n_{orientation} \qquad (7)$$

The term for thermal stress $(\sigma_r - \sigma_z)$ can be expanded further using a concentric cylinder model as shown by Brugger [12] and Scherer [5]. For the case of coreless fibre, the expanded overall birefringence Δn_{total} at distance r to the fibre centre axis can be expressed as:

$$\Delta n_{total}(r) = \frac{2\pi}{45kT} \frac{(\overline{n}^2 + 2)^2}{\overline{n}} (p_1 - p_2) \left[\frac{1}{2} \left(1 + \frac{R^2}{r^2} \right) \frac{E\alpha\Delta T}{1 - \upsilon} + N_C kT \left(\lambda^2 - \frac{1}{\lambda} \right) \right] \qquad (8)$$

Here ΔT is the temperature change, R is the radius of the fibre, E is Young's modulus, υ is the Poisson's ratio, and α is the linear thermal expansion coefficient of the material. All these coefficients are assumed to be constant over the temperature range ΔT.

3. MEASUREMENTS OF TRANSVERSE BIREFRINGENCE

The POF preforms are fabricated using the "Teflon string inside cladding technique" developed by Photonics and Optical Communications Group, UNSW [13]. The outer diameter of the preform is about 13mm, while the core diameter is about 2 mm. The preform is then drawn into fibre with different drawing speeds while drawing temperature and feeding speed are kept constant (270°C and 0.51 mm/min respectively). The polymer composition of the fibre is: Cladding – PMMA+PEMA+PBzMA with refractive index ≈ 1.490, Core – PMMA+PEMA with refractive index ≈ 1.483. In order to study the effect of the mismatch of thermal expansion between core and cladding, some coreless fibres are drawn, which only contain cladding material.
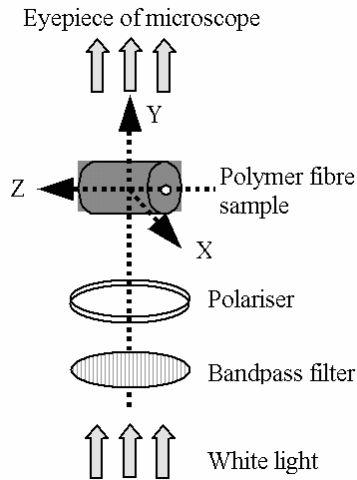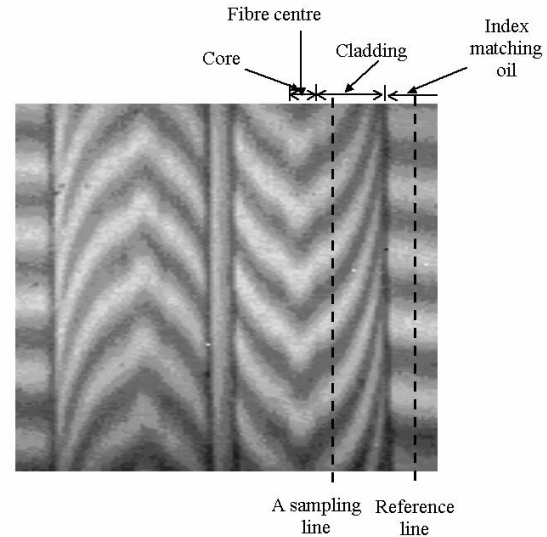
Figure 1. Measurement signal lightpath

Figure 2. A fringe pattern from interferometric microscope

A simple interferometric setup is used to measure the transverse birefringence of the drawn POF. To do so a piece of sample POF is immersed in oil with a refractive index that closely matches the index of the cladding of the fibre. White light from a halogen lamp is first passed through an optical narrow bandpass filter at 589nm and through a polariser, then through the fibre and oil sample transversely. A double image of the sample is formed using a Carl Zeiss Jena Interphako interference microscope through the shearing method. With this method, a Mach-Zehnder interferometer, positioned behind the microscope objective, is used to split the optical path into two. One path is shifted in the plane of the image before recombined when interference occurs. The optical arrangement of the signal path is shown in Figure 1. The interference of the two optical paths forms the fringe pattern that reveals the relative phase information of the fibre sample. Figure 2 is a typical interference fringe pattern.

The fringe pattern is recorded using an infrared camera, sampled and digitised by a digitiser, and then retrieved by computer. The azimuth of the polariser is aligned to the direction parallel to the fibre axis and perpendicular to the fibre axis, interference fringes are obtained respectively. A data processing program is used to calculate the phase delay profile of the fibre at each polarisation angle. Also, the dimension of fibre core and cladding diameters are measured from the microscope.

From the phase relay ($\Delta\phi$) profiles at 2 orthogonal polarisation angles, the birefringence profile of the drawn POF sample (Δn) can be calculated using the relationship:

$$\Delta n = \frac{\lambda \Delta \phi}{2\pi d} \tag{9}$$

where λ is the wavelength of the input light selected by the bandpass filter, and d is the thickness of the material measured, that is, the pathlength of the sampling ray inside the sample.

In order to study the amount of birefringence contributed by the quenching effect, annealing experiment is carried out on each sample. The transverse birefringence profile of each fibre sample is measured before and after the annealing process. During the annealing process, the fibre sample is heated to 80° C (below its T_g, which is measured previously to be about 101-106° C) for 2.5 hours in an oven. After that, the fibre sample is then cooled down gradually to room temperature, this cooling process it takes about 8 hours, which is much longer than a few seconds of cooling time during the drawing process. Therefore it is sufficient to relax the internal thermal stress due to quenching. The difference of the birefringence values measured before and after annealing experiment is the amount contributed by the quenching effect.

4. EXPERIMENTAL RESULTS AND ANALYSIS

4.1 Birefringence at different drawing ratios

The core and cladding transverse birefringence values with respect to fibre drawing speed ratios are measured. For the lightpath that goes through the core (such as A on Figure 3(a)), the birefringence portions due to the core and cladding are separated through calculation. Figure 3(b) shows the birefringence at A (due to cladding), total birefringence at B (which includes the birefringence values from both core and cladding), and the separated birefringence due to core only at A.

The result shows that the absolute value of the transverse birefringence in the drawn polymer fibre increases with the speed ratio of the drawing process. This agrees with the theoretical prediction. As fibre drawing ratio increases, the polymer molecules undergo larger mechanical "pulling" effect by the drawing motor, which then leads to a smaller angle θ between the chain axis and the fibre axis, and therefore larger value for the Hermans orientation factor. The resulting birefringence contributed by the molecular alignment is then increased. Faster fibre drawing ratio also leads to faster cooling of the surface of the fibre leaving the furnace. Therefore the internal temperature variation profile ΔT has larger gradient. This will increase the birefringence caused by quenching effect. Therefore the overall birefringence value increases with the drawing speed ratio.
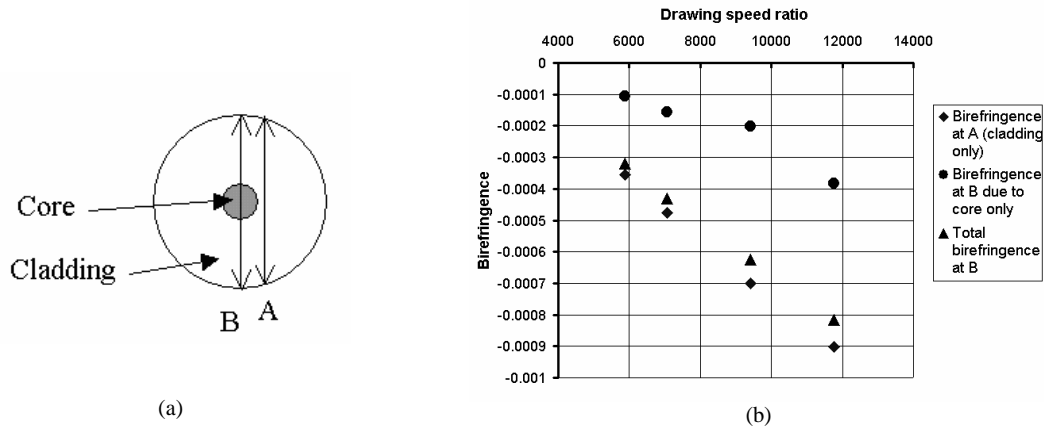

(a)   (b)

Figure 3. Birefringence at fibre core and cladding respectively at different drawing speed ratio

4.2 Transverse birefringence in polymer fibre

A piece of drawn optical fibre is selected. The drawing temperature for the selected section is 270° C, and the drawing ratio is 6000. The phase profiles at ordinary and extraordinary axes are measured using the interferometric microscope. The measured phase profiles are shown on Figure 4 (only the core region and the right side cladding region are shown, the left side cladding region is symmetrical). The phase angles are relative to the phase outside the fibre, that is, the phase angle at the surrounding index matching oil, which is a constant. From the curves, the core and cladding regions can be clearly identified. The x-axis has been normalised with respect to the radius of the fibre. Subtracting the phase profiles at these two orthogonal axes, the phase difference profile can be obtained. It is shown on Figure 5. It shows that there is a smaller phase difference at the core compared to the cladding region.

From the phase difference profile, the transverse birefringence of the fibre sample is calculated using the direct calculation method. Figure 5 is the average birefringence profile (i.e. the average value of the birefringence for both the core and cladding regions that the ray passes through). This is mainly referring to region B (same notation as in Figure 3(a)). As for region A, there is only cladding involved, therefore the average birefringence is same as the cladding birefringence.
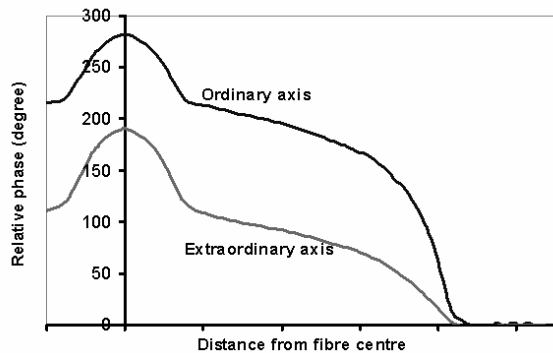
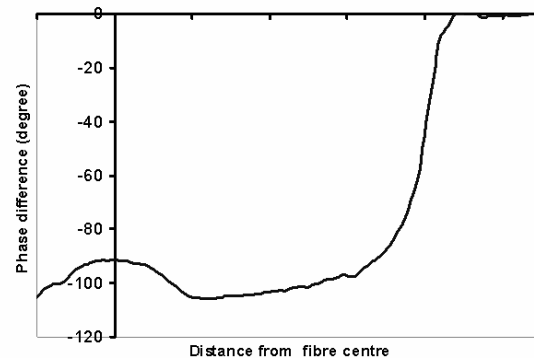Figure 4. Relative phase profiles for ordinary and extraordinary axes for polymer fibre with core before annealing

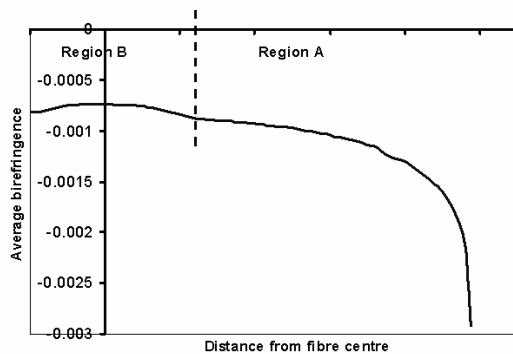Figure 5. Phase difference profile for polymer fibre with core before annealing

Figure 6. Average birefringence profile for polymer fibre before annealing for polymer fibre with core before annealing
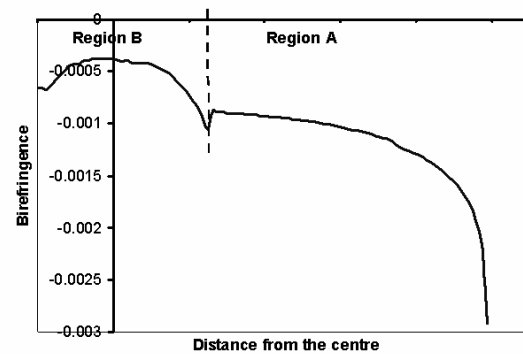

Figure 7. Final birefringence profile (after core/cladding separation) for polymer fibre with core before annealing

Using a separation equation, the individual amounts of birefringence due to core and cladding are obtained for region B. Figure 7 shows the final birefringence profile. For region A, the birefringence is the amount at the cladding; while for region B, the curve shows the birefringence in the core only.

This is the overall birefringence profile, which includes the birefringence components contributed by all of the three major factors described in the theoretical model. The data show that the transverse birefringence in the drawn polymer optical fibre is negative across the whole fibre. The birefringence is larger at the cladding, which starts from about -0.0009 at the core-cladding interface and increases towards the side of the fibre. At the core region the birefringence is smaller, and has a minimum value at the core centre, which is about -0.0004. These data show that the experimental set-up and method is very sensitive, and is able to measure very small birefringence values.

The sample is taken out of the index matching oil and annealed in the oven,. Then the sample is placed in the same index matching oil again and measured. Figure 8 shows the relative phase profiles, and Figure 9 is the phase difference profile. The average birefringence is calculated and shown on Figure 10. The final separated core and cladding birefringence profile is shown on Figure 11.

Compared with the data for the sample before annealing, it can be observed that the birefringence at the cladding is reduced after annealing (-0.0006 at the core-cladding interface), but at the core region the birefringence does not have significant change (still about -0.0004 at the fibre centre). Figure 12(a) shows the final transverse birefringence curves for the sample before and after the annealing, and the difference between them, that is, the amount removed by annealing. Figure 12(b) is the zoom-in curve of the birefringence removed by annealing. It can be observed that this birefringence difference is almost 0 at the fibre centre. Both the core and cladding profiles have parabolic shape (the data near the side of the fibre can be ignored due to the inaccuracy of the direct calculation method as discussed in previous

chapter), which agrees with the mathematical model. A parabolic curve is fitted onto the core region in Figure 12(b) and shows a good match.
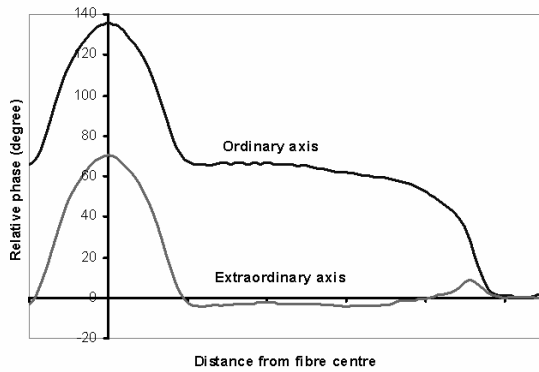

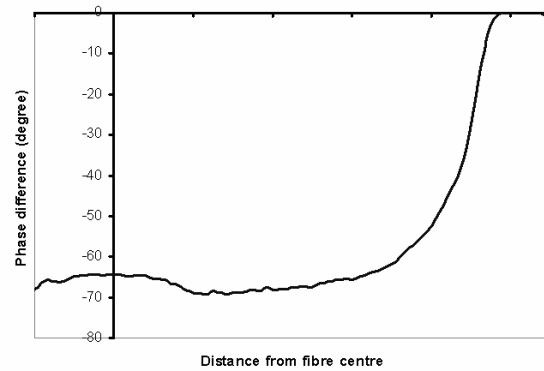Figure 8. Relative phase profiles for the annealed fibre with core

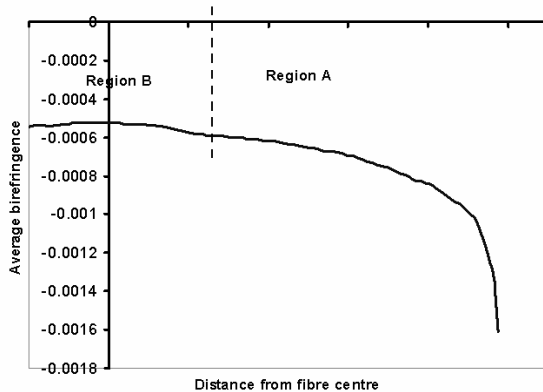Figure 9. Phase difference profile for the annealed fibre with core

Figure 10. Average birefringence for the annealed fibre with core
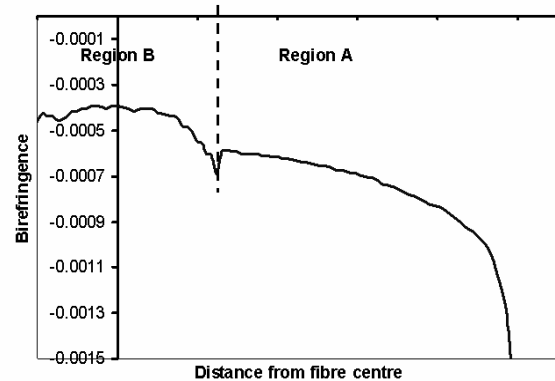

Figure 11. Final birefringence profile for the annealed fibre with core

According to the theoretical model, the difference between the birefringence values before and after the annealing process is the amount that is due to the thermal stress produced in quenching process of the fibre drawing, which is then relaxed by annealing. Therefore these experimental data show that the quenching during the fibre drawing process does not contribute significant birefringence at the fibre centre, but increases towards the side of the fibre. This behaviour of increasing birefringence has parabolic shape, the same shape as the temperature variation during the fibre drawing. The experimental result shows that the increasing rate in the core is faster than in the cladding. This is due to the different values for the material constants in core and cladding regions.

For comparison, polymer fibre without core has been made and tested. It has been observed that the birefringence caused by the alignment of polymer molecule (-0.0002) is smaller than the birefringence caused by the quenching effect during drawing, which is about -0.0003 at the fibre centre and increases towards the side of the fibre.

The same experiments are conducted on other polymer optical fibre samples with the same material composition. The measurement and calculation results are close to those data recorded above. This shows that this experiment method has good repeatability.

Experiments are also carried out to investigate the number of annealing steps required to sufficiently relax the internal thermal stress due to quenching in fibre drawing. The experimental results show that one annealing process is sufficient

to relax the internal thermal stress of the drawn POF samples.

5. CONCLUSIONS

We have studied theoretically and experimentally the drawing induced transverse birefringence in polymer optical fibres, based on a simple three-factor model. As the theoretical model expects, the behaviour of transverse birefringence due to the quenching effect demonstrates a parabolic shape. The behaviour of transverse birefringence due to thermal expansion mismatch shows an abrupt change at the core-cladding interface, however it is not a sharp peak as shown on the simulation curve. This is due to several possible factors, such as the mixing of chemical material around the core-cladding interface, and the difference between the actual material constants and the ones used in the simulation. The transverse birefringence due to the molecular alignment is constant across the fibre, except at the side of the fibre. This also agrees with the prediction based on the theoretical model. We have revealed that drawing affects significantly the transverse birefringence in polymer fibres. The induced transverse birefringence increases with the drawing speed. From our experiments, of these three factors, the molecular alignment contributes the least to the overall birefringence. This indicates that the orientation factor for the drawn polymer fibre sample is small.

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