Birefringence of aramid fibres

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(Received 4 March 1991; revised 16 October 1991)

Values of refractive indices and birefringence of aramid fibres measured by different authors are commented on and a modified approach to the spectrophotometric method is proposed.

(Keywords: aramid fibres; birefringence; variable wavelength interferometry; spectrophotometry)

It has come to my attention that Roche *et al.*[1] stated at the end of one of their papers that 'Hamza and Sikorski[2], a few years ago, and Pluta[3], most recently, have measured values of the Kevlar® $n_{\parallel}$ index that are greatly in error because they assumed that the apparent achromatic fringe represented the true optical path difference (OPD)'. This statement is without foundation. Notwithstanding that researchers using interferometric techniques should know that, in general, such an assumption cannot be made, the statement displays a misunderstanding of my paper on the variable wavelength microinterferometry of textile fibres[3].

This new interferometric method, referred to as the VAWI method, does not require the position of the zero-order interference fringe and the achromatic fringe to be identified among the fringes displaced by an object under study. The VAWI method (or the VAWI-1 version described in ref. 3) employs monochromatic light of continuously variable wavelength. It functions especially well when the true OPDs are relatively large, and thus objects such as polymer fibres do not require an immersion liquid to be used for reducing the OPD if the mean refractive indices are measured at the centre of a cylindrical fibre.

Moreover, a single poly(*p*-phenylene terephthalamide) (PPT) fibre I measured[3] was more than 10 years old. As can readily be seen, its birefringence for $\lambda = 600$ nm is coincident with the results reported by Yang *et al.*[4] in 1982 (*Figure 1*). However, a very high spectral dispersion of birefringence reported by Hartshorne and Laing[5] is doubtful.

A small criticism can also be made against the assumption of Roche *et al.*[1] that the Cauchy expression applies to the spectral dispersion of birefringence of aramid fibres in a way similar to that used for the refractive indices of immersion oils.

At any rate, the discrepancies between the results of different authors (*Figures 1* and *2*) are very large, and thus it is useful to explain such a situation. In particular, it would be of interest to measure the same sample of aramid fibres using Roche *et al.*'s equipment and my VAWI-1 technique using a double-refracting microinterferometer Biolar PI (known as Pluta's polarizing interference microscope[6]).

In my earlier paper[3], it is important to note that the refractive index $n_{\perp}$ and its spectral dispersion (*Figure 2*) are determined very accurately due to the fact that a specific situation, referred to as the object-adapted interferometry in the interfringe domain, occurred. On the other hand, the values of $n_{\parallel}$ can suffer from an error, but $\Delta n_{\parallel}$ is not greater than 0.05 because the initial interference order $m_1 = 27$ was also possible (in the place of $m_1 = 28$ as shown in Table 5 of ref. 3). Consequently, the broken line in *Figure 2* can also be considered as the true dispersion curve for $n_{\parallel}$. Similarly, $m_1 = 13$ is also possible in the place of $m_1 = 14$ for the PPT fibre birefringence B (see Table 4 in ref. 3), and thus the broken curve in *Figure 1* may be lowered by $\Delta B = \sim 0.05$.

As far as the spectrophotometric method is concerned, the order of interference deduced from the slope of a plot of m as a function of $1/\lambda$ can certainly suffer from inaccuracy similar to that shown by Roche *et al.*[1]. However, I propose to use another approach. In principle, the equation $\mathrm{OPD} = m\lambda = d\,\Delta n$, given by Roche *et al.*, should be written as

$$\delta_1 = m_1\lambda_1 = B_1 d \qquad (1a)$$

$$\delta_2 = m_2\lambda_2 = B_2 d \qquad (1b)$$

$$\delta_3 = m_3\lambda_3 = B_3 d \qquad (1c)$$

$$\ldots \quad \ldots \quad \ldots$$

where $\delta_1, \delta_2, \delta_3, \ldots$ are the OPDs corresponding to wavelengths $\lambda_1, \lambda_2, \lambda_3, \ldots$ for which the minima of light intensity are measured by the spectrophotometer, d is the fibre thickness (or diameter) and $B_1, B_2, B_3, \ldots$ are the fibre birefringences (Δn), respectively. Equations (1b), (1c), ... may be written as

$$\delta_s = m_s\lambda_s = (m_1 + q_s)\lambda_s = B_s d \qquad (2)$$

where $s = 2, 3, \ldots$ and $q_s = 1, 2, \ldots$ (for $s = 1$, $q_s = 0$ and equation (1a) holds). The parameter q_s is referred to as the increment of the current interference order m_s with respect to the initial interference order m_1 when the light wavelength decreases from λ_1 to $\lambda_2, \lambda_3, \ldots$ Consequently, $m_s = m_1 + q_s$. It is recommended that the initial wavelength λ_1 (for which $m_s = m_1$, $q_s = 0$ and $B_s = B_1$) should be selected as large as possible in the longwave (red) region.

From equations (1a) and (2) we obtain

$$m_1 = q_s \frac{\lambda_s}{B_{s1}\lambda_1 - \lambda_s} \qquad (3)$$

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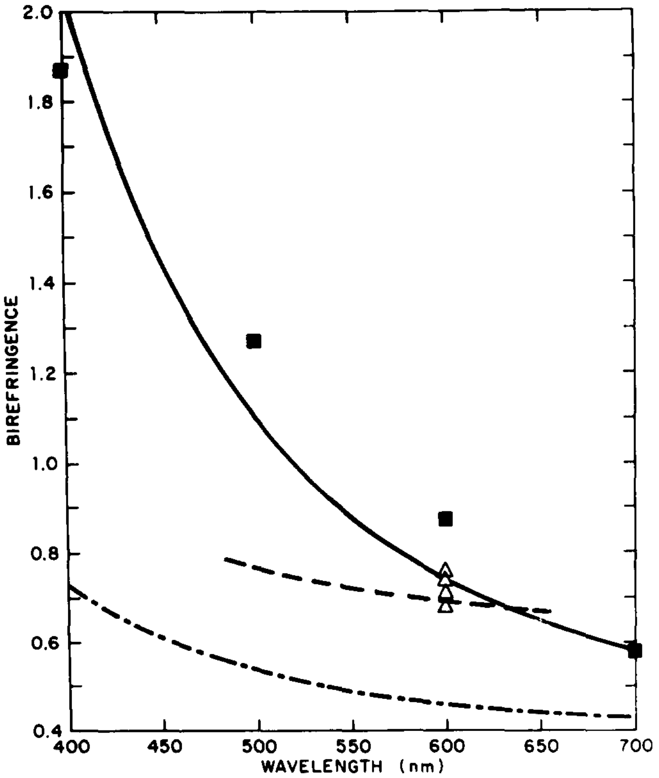

Figure 1 Comparison of interference and spectrophotometric birefringence dispersion data of aramid fibres (adapted from Roche *et al.*[1] and supplemented by the results in ref. 3): (■) reference 5; (△) reference 4; (– – –) inverse fourth order fit to interference data; (——) interference data augmented by correction term; (– – –) reference 3

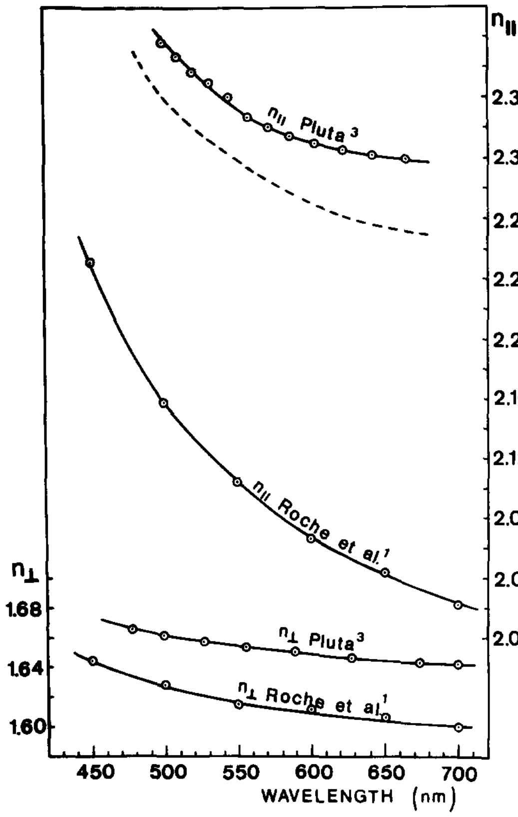

Figure 2 Comparison of interference refractive index dispersion data taken from Roche *et al.*[1] and Pluta[3]

where $B_{s1} = B_s/B_1$. As can be seen, equation (3) is identical to equation (6) derived for the VAWI-1 technique[3].

In the red spectral region the relationship between B and λ is more linear, so we can therefore assume $B_{s1} \sim 1$ and calculate the initial interference order m_1 from the relation

$$m_1 = q_s \frac{\lambda_s}{\lambda_1 - \lambda_s} \qquad (4)$$

In general, the approximate value for m_1 calculated from equation (4) will be slightly greater than the true value following from equation (3) if the spectral dispersion $B(\lambda)$ is normal and the dispersion coefficient B_{s1} is known a priori. For instance, if equation (4) gives $m_1 = 23.2$ in the red and/or orange region, the true initial interference order m_1 may be, at most, equal to 23.

The main goal of the above approach is to determine the birefringence of the fibre (or fibres) under study. We can distinguish two steps. The first is to read (or measure) the wavelengths $\lambda_1, \lambda_2, \lambda_3, \ldots$ for consecutive minima of light intensity, to which the current interference orders $m_s = m_1,\ m_1 + 1,\ m_1 + 2, \ldots$ correspond, and then calculate the initial interference order m_1 from equation (4) and take for m_1 the integer which is the nearest to but not greater than the value following from equation (4) applied to λ_1 and λ_s from the longwave region (see above). The second step is to calculate the optical path differences

$$\delta_1 = m_1\lambda_1,\ \delta_2 = (m_1 + 1)\lambda_2,\ \delta_3 = (m_1 + 2)\lambda_3, \ldots$$

and determine the birefringences $B_1 = \delta_1/d$, $B_2 = \delta_2/d$, $B_3 = \delta_3/d, \ldots$ if the fibre thickness (diameter) d is known or can be measured accurately. If there are any doubts, the initial order m_1 can also be verified by analysing the coefficient

$$B_{FC} = \frac{B_F}{B_C} = \frac{\delta_F}{\delta_C} \qquad (5)$$

where the subscripts F and C denote the spectral lines of wavelengths $\lambda_F = 486.1$ nm and $\lambda_C = 656.3$ nm. The relation $B_{FC} = \delta_F/\delta_C$ follows directly from equations (1a) and (2) if the subscripts 1 and s are replaced by C and F, respectively. An inaccurate initial interference order m_1, differing from its true value by at least unity (+1 or −1), leads to a value of the coefficient B_{FC} differing greatly from that characterizing known textile fibres which produce the optical path differences δ not greater than, say, 10 μm and their birefringence B is low or moderate. Otherwise, if $\delta > 10$ μm or B and $B(\lambda)$ are high, as in the case of aramid fibres, the value of B_{FC} becomes improbable when m_1 differs from its true value by ±2 or more. This defect is reduced if the VAWI-1 technique is used[3], due to the fact that m_1 can also be calculated from a formula which is similar to (4), but λ_1 and λ_s are replaced by the interfringe spacings. It is also important to note that the wavelengths λ_1 and λ_s must be known or measured as accurately as possible, say, with an error of $\leqslant \pm 0.1$ nm.

The above approach to the spectrophotometric method appears to be more accurate than the procedure used to date based on the derivation of the interference orders from the slope of a plot of m as a function of $1/\lambda$. Moreover, it is worth noting that the fibre thickness (or diameter d if the fibre is cylindrical) must be measured more accurately than the optical path difference δ to achieve the same inaccuracies of ΔB, due to Δd and $\Delta\delta$, in determining the fibre birefringence B. This problem is discussed at length in references 7 or 8.

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