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Pleochroism in thermally-treated acrylic fibres

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Acrylic fibres, coloured by inert thermal-treatments up to 573K are highly pleochroic. The preferred absorption is parallel to the fibre axis, implying that the chromophore is a molecular sequence intrinsically part of the oriented polymer chain. The biabsorption, $k_{\parallel}$-$k_{\perp}$, shows a direct correlation with amount of nitrile reacted in the polymer. Although the development of chromophore is directly related to polymerization of nitriles, the polymerized nitrile sequences themselves may not necessarily be the specific chromophore.

Compensated biabsorption, corrected essentially for chromophore concentration, is substantially constant throughout the thermal-treatment, showing that the preferred orientation of both "inert" chromophore and polymer chain is maintained. An exception arises when light oxidation in air follows inert thermal-treatment, indicating that the "oxidation" chromophore is oriented perpendicular to the "inert" chromophore and polymer chain.

1. Introduction

It is well known that acrylic fibres which are thermally-treated either in oxidizing or inert environments at temperatures above 410 K undergo a deepening colouration from pale straw yellow through deep red-brown to black [1-8]. Chromophoric groups responsible for the colouration have been described variously as aromatic naphthyridine [1], hydrogenated naphthyridine [9-13], partially hydrogenated naphthyridine [6, 7], conjugated carbon chain (pendant nitrile) [14] and random imine-nitrone [8, 15-17] sequences. A shift in absorption frequencies on the change in colour from yellow to reddish-brown has been taken to imply lengthening of the chromophoric sequences rather than duplication of chromophoric species [12].

Measurements of absorption dichroism of acrylic fibres in the visible region have been limited previously to dyed materials [18] where the dye molecule becomes oriented with respect to the polymer-chain axis. In well-stretched acrylic fibres there is a high degree of preferred orientation of the polymer chains, and thermal-treatments which cause generation of the chromophoric groups or sequences will generate absorption dichroism, or pleochroism, provided that the chromophore is suitably oriented with respect to the parent polymer chain and that the chain orientation itself is retained. In coloured minerals such as ruby, biotite, tourmaline, etc., pleochroism has been quantitatively measured in terms of the biabsorption, b [19-21],

$$b = k_{\epsilon} - k_{\omega} \tag{1}$$

where k_{ϵ} and k_{ω} are the absorption coefficients for extraordinary and ordinary rays of polarized light in a uniaxial crystal and where

$$I_{\omega}/I_{\epsilon} = \mathrm{e}^{(4\pi t/\lambda)(k_{\epsilon}-k_{\omega})} \tag{2}$$

For a pleochroic fibre the biabsorption becomes

$$b = k_{\parallel} - k_{\perp} \tag{3}$$

and Equation 2 becomes

$$I_{\perp}/I_{\parallel} = \mathrm{e}^{(4\pi t_f/\lambda)(k_{\parallel}-k_{\perp})} \tag{4}$$

where $\perp$ and $\parallel$ refer to directions perpendicular and parallel to the fibre axis.

The use of biabsorption, rather than dichroic ratios, obviates the need for introducing I_0, the intensity of the incident light and related terms such as absorbancy $(1 - I_{\perp}/I_0)$ and optical density $(\log I_0/I_{\perp})$. Provided the incident light intensity (I_0), the specimen thickness (t) and the wavelength of the transmitted light (λ) are constant, then $\log I_{\perp}/I_{\parallel}$ is directly proportional to the biabsorption. In thermally-treated acrylic fibres there are small changes in diameter (t_f) and wavelength (λ) of the transmitted light for which compensation may be made according to Equation 4.

However, the biabsorption remains dependent on the concentration of chromophore as well as its preferred orientation. A concentration term, c, is interchangeable with the thickness term, t, and implies a direct proportionality of k and $(k_{\parallel} - k_{\perp})$ with c. Compensation for the effect of chromophore concentration may be made by a determination of the individual absorption coefficients, $k_{\parallel}$ and $k_{\perp}$, which will involve a measurement of $\log I_0/I$. Alternatively, an empirical compensation factor may be derived from the term $k_{\max}/k$, where $k_{\max}$ corresponds with maximum development of the chromophore or 100% chromophoric reaction. With this correction the pleochroism reflects the degree of preferred orientation of the chromophoric group or sequence with respect to the polymer chain and fibre axis.

2. Experimental

Acrylic fibres of essentially circular cross-section, 14 µm in diameter, and containing 7% methyl acrylate as copolymer were thermally-treated as described elsewhere [23] in the temperature range 453 to 573 K in the absence and, in two cases, in the presence of air. Individual fibres from the thermally treated samples were immersed in an inert liquid whose refractive index (n_m) approximated to an average refractive index of the fibre, $(n_{\parallel} + n_{\perp})/2$, and the fibres viewed transversely at magnifications of × 1500 using plane polarized transmitted light, care being taken to remove scattered light.

The immersed fibre was rotated such that the polarized light vibrated perpendicular and then parallel to the fibre axis. A polished wedge of suitably coloured plastic, previously calibrated for thickness and absorption coefficient, was inserted into the focal plane of the microscope eyepiece for the two directions and the wedge thickness which matched the colour intensity of the fibre recorded. The intensity of the incident light was held constant throughout. Determination of $I_{\perp}/I_{\parallel}$ using this procedure was found to be more precise than the double image method of Mandarino [19] using a thin calcite plate.

The intensity ratio of the transmitted light in the two directions was calculated from the Equation:

$$\ln I_{\perp}/I_{\parallel} = 4\pi(t_{\mathrm{w}\parallel} - t_{\mathrm{w}\perp})\, k_{\mathrm{w}}/\lambda \qquad (5)$$

where t_{w} was the wedge thickness, k_{w} was the absorption coefficient for the wedge material, previously determined as 4.30×10^{-5} and λ, the mean wavelength of transmitted light, taken to be 0.60 µm in both wedge and fibre. The fibre biabsorption was then calculated from Equation 4 where t_f was the fibre diameter, 14 µm. Corrections for reflection losses [19,21] and electro-magnetic scattering [22] were found to be negligible for even the most highly birefringent ($\Delta n = 0.22$) fibres when $n_m = [(n_{\parallel} + n_{\perp})/2] \pm 0.01$.

A compensated biabsorption was calculated to take account of minor variations in fibre density and transmitted wavelength and the major variation of chromophore concentration. The fibre density variation was equivalent to an average fibre diameter change from 14.0 to 11.6 µm and the mean wavelength variation was estimated to be from 0.58 to 0.65 µm over the range of thermal-treatments. Compensation for variation in chromophore concentration was made applying the factor $t_{\mathrm{w(max)}}/t_{\mathrm{w}}$ where $t_{\mathrm{w(max)}}$ is the maximum wedge thickness for the most coloured sample, where it is known that the nitrile reaction is complete (Fig. 2), and where both $t_{\mathrm{w(max)}}$ and t_{w} refer to the parallel direction of the fibre. The compensated biabsorption therefore becomes

$$(k_{\parallel} - k_{\perp})_{\mathrm{comp}} = (t_{\mathrm{w(max)}}/t_{\mathrm{w}})(\ln I_{\perp}/I_{\parallel})(\lambda/4\pi\, t_f) \quad \ldots\ldots(6)$$

3. Results and discussion

The relative colour intensities of a series of thermally-treated fibres are illustrated in Fig. 1, reproduced from colour prints. The pleochroic nature of the fibres is readily apparent throughout the temperature and chromophore intensity range. At the higher colour intensities there was an apparent shift in wavelength from straw yellow to red underlying the brown, indicating a probable shift in average transmitted wavelength from 0.58 to 0.65 µm. In two samples partly oxidized in air (not illustrated) a more intense neutral colouration was apparently superimposed on the typical yellow-brown of the inert treated fibres. No shift in transmitted wavelength was detected between the two polarization directions for a fibre of any given thermal-treatment.

Determined values of biabsorption for variously heat-treated fibres are given in Table I; a set of compensated biabsorption values are included.

The values of biabsorption presented in

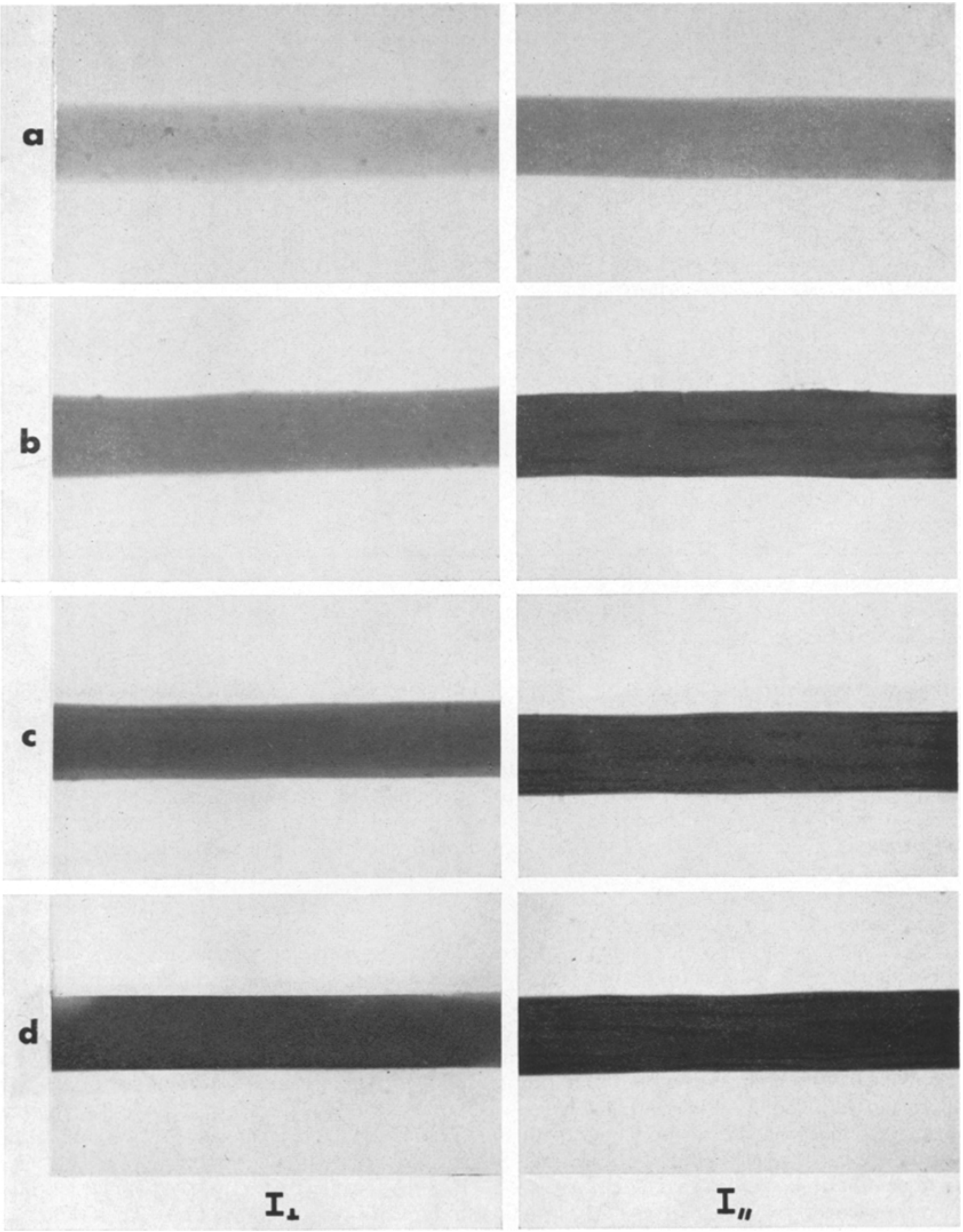

Figure 1 Pleochroism in acrylic fibres, thermally-treated in inert environment for 1.08×10^4 sec at (a) 453, (b) 493, (c) 533 and (d) 573 K. Fibres viewed in transmitted light polarized perpendicular ($\perp$) and parallel ($\parallel$) to fibre axis. Colour variation from pale yellow to deep reddish-brown.

Table I correspond with those of minerals classified by Toubeau [20] as strongly pleochroic, $b > 8$ (λ in Å, t in μm). The preferred absorption is shown to be in the direction parallel to the fibre axis ($k_{\parallel} > k_{\perp}$), corresponding to the direction of preferred orientation of the polymer

TABLE I Biabsorption of thermally-treated acrylic fibres

Heat-treatment* Time, sec	Temp., K	Atmosphere	$\ln I_{\perp}/I_{\parallel}$	Biabsorption $k_{\parallel} - k_{\perp}$	Compensated biabsorption $(k_{\parallel} - k_{\perp})$ comp
0	473	Inert	0.23	7.7×10^{-4}	67×10^{-4}
10800	473	Inert	0.50	17	70
21600	473	Inert	0.72	25	75
0	493	Inert	0.41	14	68
3600	493	Inert	0.72	25	75
10800	493	Inert	0.90	31	75
21600	493	Inert	0.81	28	81
0	513	Inert	0.72	25	61
3600	513	Inert	0.81	28	67
10800	513	Inert	1.17	40	77
21600	513	Inert	1.17	40	69
0	533	Inert	0.81	28	60
10800	533	Inert	1.21	41	68
0	573	Inert	1.80	61	78
10800	573	Inert	1.62	55	72
0	493	Air	1.26	43	66
3600/3600	513/493	Inert/air	0.72	35	43

*Includes heating to temperature at 0.1 K $\sec^{-1}$ [23].

chains in the precursor acrylic, as determined from the 100 polymer arc of X-ray diffraction [23]. It is concluded that the chromophore is composed of molecular sequences which are an intrinsic part of the polymer chain. Correlation of biabsorption with amount of nitrile removed [23] during the thermal-treatment in an inert atmosphere is shown in Fig. 2.

The correlation implies that, in the absence of oxygen, generation of the chromophore is directly related to the zipping of nitrile groups into structures such as naphthyridines [1, 6-13, 23]. In addition to nitrile polymerization, partial dehydrogenation takes place simultaneously during inert thermal-treatments [23, 24] which possibly leads to a conjugation chromophore in the carbon back-bone. While it may be concluded, therefore, that nitrile polymerization is the primary cause of the chromophore generation, it cannot be concluded that the polymerized nitrile sequences are themselves the specific chromophore.

The biabsorption values compensated for chromophore concentration, and minor changes in transmitted wavelength and fibre density, show a marked constancy and imply that, as the chromophore develops, its preferred orientation with respect to the fibre axis is substantially retained. An exception is the final sample in which inert thermal-treatment was followed by light oxidation in air. Here an oxidation chromophore is rapidly developing and the reduction in compensated biabsorption implies that the oxidation chromophore is oriented approximately normal to the inert chromophore. The intense absorption of the oxidation chromophore inhibits confirmation of this reduction and change in orientation at longer oxidation times. The observation does suggest, however, the formation of groups, such as nitrone or carbonyl which are oriented perpendicular to the polymer chain.

It has been inferred that the inert chromophore is a molecular sequence intrinsically part of the polymer chain which starts as polyacrylonitrile but transforms during the thermal-treatment to a partially zipped, partially dehydrogenated, ladder polymer. It has also been inferred that the orientation of the inert chromophore with respect to the fibre axis is substantially constant throughout the transformation. It may be further concluded that the preferred orientation of the original polymer chain is also substantially retained throughout the thermal-treatment, at least under the conditions used in this study. This confirms the qualitative evidence of birefringence measurements [23].

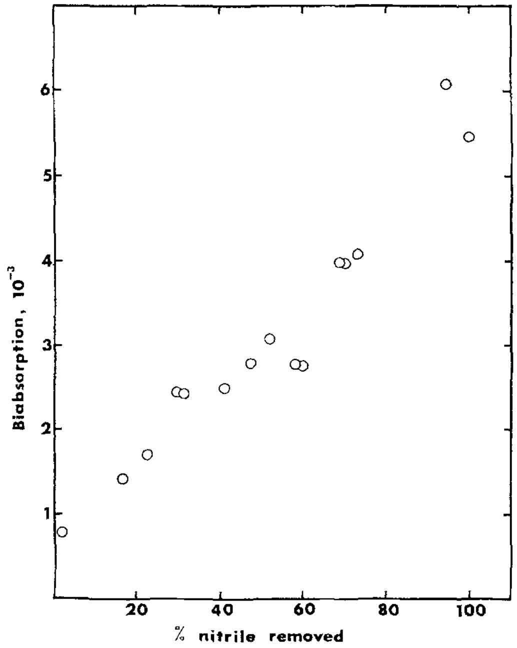

Figure 2 Biabsorption versus loss of nitrile in acrylic fibres thermally-treated in inert environment.

4. Conclusions

Acrylic fibres thermally-treated in the temperature range 453 to 573 K in inert environment have been shown to be highly pleochroic. Values of biabsorption $k_{\parallel} - k_{\perp}$, increase from 7.7 to 61 × 10^{-4} as the colour develops from straw-yellow to deep reddish-brown. The preferred absorption is parallel to the fibre axis from which it is concluded that the chromophore is composed of a molecular sequence which is an intrinsic part of the oriented polymer chain. A correlation of biabsorption with amount of nitrile groups reacted in the polymer shows that the generation of chromophore is directly related to nitrile polymerization on inert thermal treatment, although polymerized nitrile sequences are not necessarily the specific chromophore.

Compensated biabsorption, corrected for changes in chromophore concentration and minor changes in transmitted wavelength and fibre density, were substantially constant throughout the series of thermal-treatments. It is concluded that the preferred orientation of the "inert" chromophore, and polymer chain, is remaining fairly constant during inert thermal treatment, at least under the conditions [23] used in this study. An exception occurs when the inert thermal-treatment is followed by light oxidation in air from which it is tentatively concluded that the intense "oxidation" chromophore is oriented perpendicular to the "inert" chromophore and polymer chain.

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