polymer reports

The adsorption of a synthetic tanning agent and a sulphonated phenol-formaldehyde novolac by nylon-6

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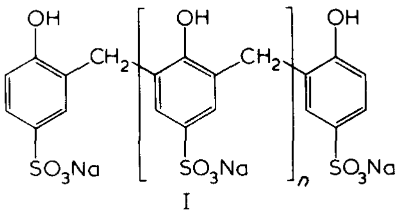
INTRODUCTION

It is well known that the wet-fastness properties of acid dyes on nylon-6 are inferior to those obtained for nylon-6,6. This is presumed to be due to the more open structure of the former[1]. The traditional method of improving the wash-fastness of these dyes has been the application of tannic acid followed by a treatment with potassium antimonyl tartrate. This system has been studied by Shore[2] and the efficacy of such treatments has been attributed to the formation of an insoluble complex. More recently synthetic tanning agents have been developed to achieve improvements in wet-fastness. Little attention has been paid to these materials[3] and it is the aim of this work to study the interaction of these compounds with nylon-6 fibres. These materials are described by their manufacturers as 'high molecular weight condensation products of phenol sulphonic acids and formaldehyde'. Details of chemical structure are not generally known. A possible structure could be represented by (I). Examples of such materials are: Cibatex PA, FB, (Ciba-Geigy), Mesitol PNP, NBS (Bayer) and Matexil FA-SN (I.C.I.).


I

EXPERIMENTAL

Materials

Nylon-6: The nylon-6 filament (Celon) used throughout this work was supplied by Courtaulds Ltd.

Synthetic tanning agent (Syntan): A commercial sample of Cibatex PA was obtained from Ciba-Geigy Ltd.

All other materials were of general reagent grade.

Pretreatment of nylon fibre

Samples of fibre were treated at 85°C for 20 min in a solution containing 0.25 g l^{-1} Calgon T (I.C.I.) and 0.50 g l^{-1} Lissapol NX (Albright & Wilson). The fibre was removed and rinsed thoroughly in distilled water and allowed to dry naturally in the atmosphere.

Purification of sulphonated novolac and synthetic tanning agent

Aqueous solutions (5.0 g l^{-1}) of the compound to be purified were repeatedly passed down a cation exchange column (Zeo Karb 225, 14–52 mesh acid form) and an anion exchange column (De-Acidite E, 14–52 mesh) until no sodium ions could be detected by a flame test. The solutions free of sodium and inorganic anions were evaporated to dryness under vacuum at 40°C. The solid material obtained was stored in a dessicator over phosphorus pentoxide.

Synthesis of sulphonated novolac

(i) Preparation of 4,methyl-2,6-dimethylol phenol.

p-Cresol (10.8 g 0.1 mol) was dissolved in dilute sodium hydroxide (200 ml 2 M). To this solution was added formaldehyde (7.5 ml, 40%, 0.2 mol) and the mixture obtained was refluxed at the boil for 12 h. On cooling an oily, viscous liquid settled out. This was removed from the mother liquour using a separating funnel and washed three times with distilled water.

(ii) The reaction of 4,methyl-2,6,-dimethylol phenol with phenol.

The dimethylol *p*-cresol was added to water (200 ml) with stirring. Phenol (18.8 g 0.2 mol) was added over a period of 20 min. The temperature was raised to 80°C and the reaction allowed to continue for 8 h. On cooling and evaporation under vacuum a brittle resin was formed.

(iii) Sulphonation of resin.

The above resin (50 g) was added to chlorosulphonic acid (50 ml) in carbon tetrachloride (100 ml), the temperature being maintained at 10°C during the addition. The temperature was raised to 40°C and the reaction left for 12 h with gentle agitation. At this point the reaction product was found to be completely soluble in boiling water and the reaction was judged to be complete.

The mixture was carefully poured into water (2 l) and boiled for 30 min, cooled and neutralised with sodium hydroxide. After purification by ion exchange as described above a brittle red resin was obtained (26 g).

Rate of adsorption of synthetic tanning agents and sulphonated novolacs by nylon-6

Adsorption rates were measured by continuously monitoring the absorbance of a solution of the compound under investigation at 260 nm in the apparatus illustrated

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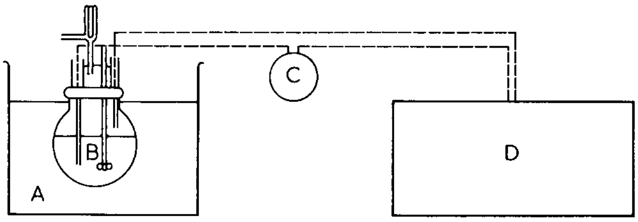


Figure 1 Apparatus for measurement of rates of adsorption. A, thermostatically controlled water bath; B, treatment vessel with agitator; C, peristaltic pump; D, Unicam SP700 spectrophotometer with 'flow through' cuvette

in *Figure 1*. A solution of the syntan or sulphonated novolac (200 ml, c.a. 0.05 g l^{-1}) adjusted to pH 4 was placed in the reaction vessel and with the pump and agitator in action was left to reach thermal equilibrium at 80°C. A sample of the nylon fibre (0.5 g) was placed in the solution and the absorbance of the solution monitored over a period of 24 h. The final concentration of compound in solution was obtained from calibration curves and the uptake by the fibre estimated by difference.

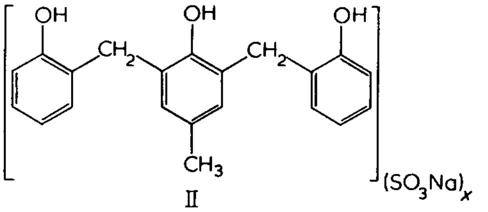
Equilibrium adsorption isotherms

A range of concentrations of each compound varying from 0.05 g l^{-1} to 0.25 g l^{-1} were prepared and adjusted to pH 4.0 with formic acid. Samples of nylon fibre (0.2 g) were placed in these solutions (50 ml) and treated at 80°C for 48 h. The solutions were then analysed spectrophotometrically, making dilutions where necessary. Graphs of compound adsorbed *versus* concentration were thus obtained.

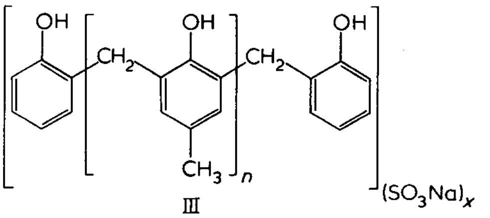
RESULTS AND DISCUSSION

Sulphonated novolac

It was hoped to produce the essentially trimeric compound (II), however because of the well established complexity of the reaction between phenol and formaldehyde it is more than likely that the compound obtained could be better represented by (III). In addition the extent or position of sulphonation is unclear. Work recently carried out[4] has shown that sulphonation would appear to occur preferentially at terminal phenyl groups.



II



III

Rates of adsorption of Cibatex PA and the sulphonated novolac

Rates of uptake curves are shown in *Figure 2*. They are very similar to those obtained for the uptake of anionic dyes by nylon-6. From these curves it is possible, assuming that diffusion within the fibre is the rate controlling process, to calculate an apparent diffusion coefficient for the compounds within the nylon. This can be achieved by the use of one of the many approximate solutions to Fick's second law of diffusion for a finite 'dyebath'[5]. The method chosen was the very simple approach proposed by Militky and Rais[6]. The results obtained were, 4.5×10^{-15} m^2 s^{-1} and 10.5×10^{-15} m^2 s^{-1} for the sulphonated novolac and Cibatex PA respectively.

Equilibrium adsorption isotherms of sulphonated novolac and Cibatex PA

The isotherms are shown in *Figure 3* and *Figure 4*. The similarity between the shapes of the isotherms is striking, presumably indicating the closely related structure of the compounds. The isotherms obtained are those associated with classical 'Freundlich Adsorption' which suggests that the forces of interaction between the adsorbate and the nylon are non-specific, in the sense that a maximum or saturation value is not reached. This is a characteristic of the adsorption of relatively hydrophobic but water soluble solutes such as high affinity dyes by nylon. This type of isotherm has been predicted for polyamides and anionic solutes by McGregor and Harris[7]. Such a model can be expressed by equation (1):

$$C^f = K\lambda^z C^s \qquad (1)$$

where C^f and C^s are the concentrations of solute in the fibre phase and solution phase respectively. K is the equilibrium adsorption coefficient, λ is the Donnan distribution coefficient and z the charge on the solute. Such a model makes no assumption as to the nature of the forces involved in binding the solute to the polymer. The most probable forces of interaction involve hydrogen bonding and hydrophobic bonding between the phenyl nuclei of the novolacs and hydrophobic regions of the fibre. The shape of the isotherms also suggests the formation of multilayers of the species adsorbed as is postulated for the adsorption of direct dyes by cellulose[8]. This is difficult to envisage if one considers the non-planar nature of novolac molecules, however during this work it was noticed that even relatively dilute solutions of the syntan and sulphonated novolac were very prone to aggregate even at very low electrolyte concentrations.

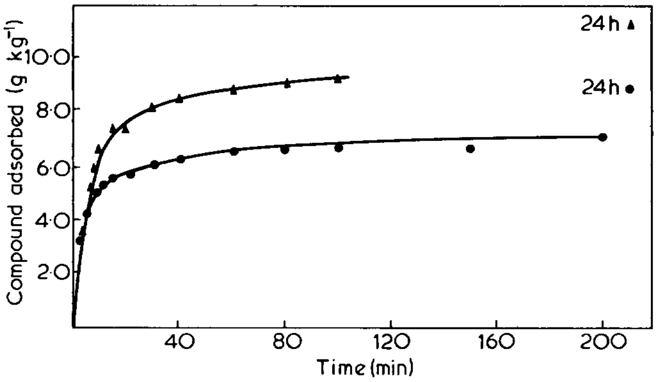


Figure 2 Rates of adsorbance curves for sulphonated novolac and Cibatex PA. ▲, sulphonated novolac; ●, Cibatex PA

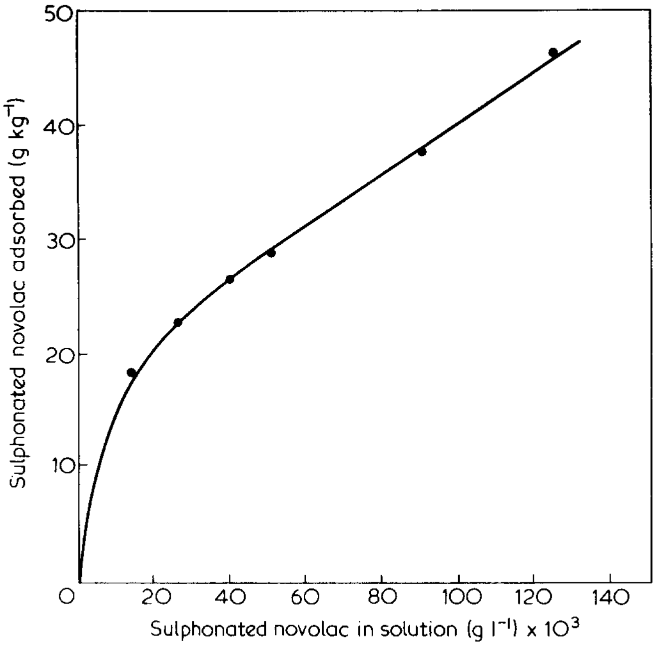


Figure 3 Equilibrium adsorption isotherm for sulphonated novolac

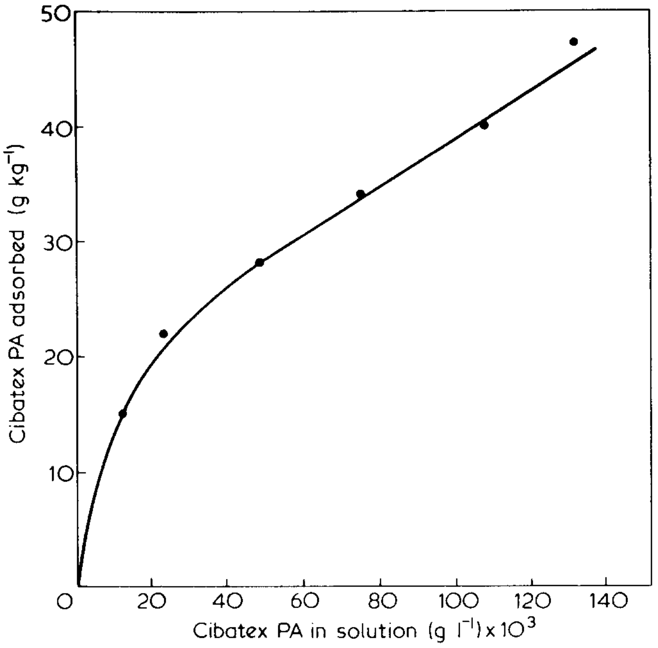


Figure 4 Equilibrium adsorption isotherm for Cibatex PA

CONCLUSIONS

The synthetic tanning agent, Cibatex PA, is readily adsorbed by nylon-6 polymer. It shows a type of behaviour very similar to that obtained for a sulphonated novolac. The equilibrium isotherms indicate that the compounds are taken up by a mechanism similar to that for a relatively hydrophobic anionic dye. The hydrophobicity of these materials (degree of sulphonation) is at present under investigation.

Some estimation has been made of the diffusion coefficients of these materials in nylon, although the measurement of diffusion coefficients from rate of adsorption curves can often be misleading, it would appear that the apparent diffusion coefficients are about ten times smaller than those found for anionic dyes[9].

REFERENCES

1 Ashworth, J. L. and Blackburn, D. *J.S.D.C.* 1965, **81**, 569
2 Shore, J. *J.S.D.C.* 1971, **87**, 3
3 Herbert, C. G. *Ph.D. Thesis*, Salford University, 1975
4 Lo, K. W. *M.Sc. Thesis*, Queen's University, Belfast, 1980
5 Crank, J. 'The Mathematics of Diffusion', Oxford, Clarendon Press, 1956
6 Militky,J. and Rais, J. *J.S.D.C.* 1977, **93**, 346
7 McGregor, R. and Harris, P. W. *J. Appl. Polym. Sci.* 1970, **14**, 513
8 Baddi, N. T. *et al.*, *Text. Res. J.* 1964, **34**, 807
9 Shimizu, T. and Ohya, S. *Sen-i Gakkaishi* 1967, **23**, 550, 602

The effect of hydrodynamic interaction on the intrinsic flow birefringence of a rigid rod

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A few years ago Svetlov[1] proposed a solution to the Krikwood–Riseman diffusion equation without preaveraging of the Oseen tensor of hydrodynamic interaction. Using this solution, he derived a general relation for the intrinsic flow birefringence, $[n]$. Since this expression is rather complicated, Svetlov suggested an approximative relation in a later paper[2]. In this note we try to compare expressions for $[n]$ and the ratio of intrinsic birefringence with intrinsic viscosity, $[n]/[\eta]$, of a rigid long rod obtained from the exact[1] and approximative[2] Svetlov's theory, and from the theory of Shimada and Yamakawa[3].

For the intrinsic flow birefringence, equation[1] (in ref. 1, G is inadvertently used instead of η_s)

$$[n]=\frac{\pi}{135}\cdot\frac{(n_s^2+2)^2}{\eta_s n_s}\cdot\frac{N_A}{M}\langle Tr\,\underset{\sim}{X}\;Tr\,\underset{\sim}{\gamma}-3Tr(\underset{\sim}{\gamma}\cdot\underset{\sim}{X})\rangle \quad (1)$$

is valid; n_s, η_s denote the refractive index and viscosity of the solvent respectively, M is the molecular mass of the particle, γ is its polarizability tensor, N_A is the Avogadro number, $\langle\ \rangle$ denotes averaging over conformations of the particle, Tr is the trace of the tensor, and the tensor $\underset{\sim}{X}$ is the solution to equation[1]

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