

Relation between Dynamic Mechanical Properties and Dye Diffusion Behavior in Acrylic Fibers

INTRODUCTION

In a previous study¹ of the relation between the mechanical properties of nylon fiber and dye diffusion behavior it was found that the theoretical relations derived by Fujita et al.,² relating the diffusion of small molecules in amorphous polymers to the mechanical properties, are applicable to the dyeing of semicrystalline nylon. A relationship exists between the dynamic loss modulus and the dye diffusion constant in nylon, both experimentally and theoretically.

Since theoretically these relations should also apply to other polymers, the dynamic mechanical properties and dye diffusion behavior in acrylic fibers were studied.

Rosenbaum³ also reasoned that dye diffusion should be related to the mobility of the polymer chain segments, and he plotted the diffusion constant in acrylic polymers as a function of the tensile compliance (reciprocal of the initial modulus) and as a function of the fluidity (the reciprocal of the steady-state viscosity from creep measurements). The data appeared to follow a linear relationship in both cases, within the range of diffusion constants investigated.

EXPERIMENTAL

The dye used in this work was a commercial grade of C. I. Basic Blue 22, Sevron Blue 2G (du Pont). The dyeing temperature was 100°C., and the liquor/fiber ratio was 40:1. A dye concentration of 5 g./l. was used, and the pH of the dye bath was adjusted to 5.2 with acetic acid. Dyeing rates of four acrylic fiber samples were measured by techniques previously described.¹

The fibers were as follows: No. 1, acrylonitrile-vinyl acetate copolymer containing 10.8% vinyl acetate; No. 2, acrylonitrile-vinyl acetate copolymer containing 7.5% vinyl acetate, stretched 300%; No. 3, acrylonitrile-vinyl acetate copolymer containing 9.2% vinyl acetate, stretched 300%; No. 4, same as No. 3 but stretched 400%.

The dynamic mechanical properties were measured at a constant frequency of 11 cps with a Vibron Dynamic Viscoelastometer (Toyo Instrument Co., Tokyo, Japan). This instrument has been described in detail by Takayanagi.⁴ Briefly, a sinusoidal tensile strain is imposed on a sample, producing a sinusoidal tensile stress. The instrument uses two transducers for direct reading of the absolute dynamic modulus $|E^*|$, or ratio of maximum stress amplitude to maximum strain amplitude, and the phase angle δ between the stress and strain. From these two quantities the real part E' and imaginary part E'' of the complex dynamic tensile modulus E^* can be calculated. The elastic component E' of the dynamic modulus $|E^*|$ is given by $|E^*| \cos \delta$, and the viscous component, or loss modulus E'' , is given by $|E^*| \sin \delta$. All measurements were made with the sample in a 100% relative-humidity environment, since one was interested in the dynamic properties under dyeing conditions.

RESULTS AND DISCUSSION

Dynamic Mechanical Properties

Figure 1 shows the dynamic modulus E' , the loss modulus E'' , and the loss tangent at 0 and 100% r.h. as a function of temperature for sample 1. At 0% r.h. the temperature of the maximum of the $\tan \delta$ peak for this sample occurs at 128°C. at a maximum $\tan \delta$ value of 0.380. This α dispersion is due to the amorphous regions in the structure and occurs in many semicrystalline polymers.⁴ At 100% r.h. the peak temperature of $\tan \delta$ is shifted approximately 48°C. lower than it is at 0% r.h., but the maximum height

TABLE I
Dynamic Loss Modulus of Acrylic Fibers

	E'' , dynes/cm. ²
No. 1, acrylonitrile-vinyl acetate copolymer containing 10.8% vinyl acetate	1.70×10^8
No. 2, acrylonitrile-vinyl acetate copolymer containing 7.5% vinyl acetate stretched 300%	1.30×10^9
No. 3, acrylonitrile-vinyl acetate copolymer containing 9.2% vinyl acetate stretched 300%	2.40×10^8
No. 4, same as No. 3 but stretched 400%	3.20×10^8

of the $\tan \delta$ peak is unchanged. A larger shift is found for nylon 66 through dynamic data^{1,5} and creep.⁶ The shift for nylon is 15°C. per 1% of moisture. Since the water absorption of acrylic fibers at 90°C. and 100% r.h. is about 3%,⁷ the shift is 16°C. per 1% of moisture. This suggests that the effect of moisture on the α dispersion is due to a similar mechanism in these semicrystalline polymers.

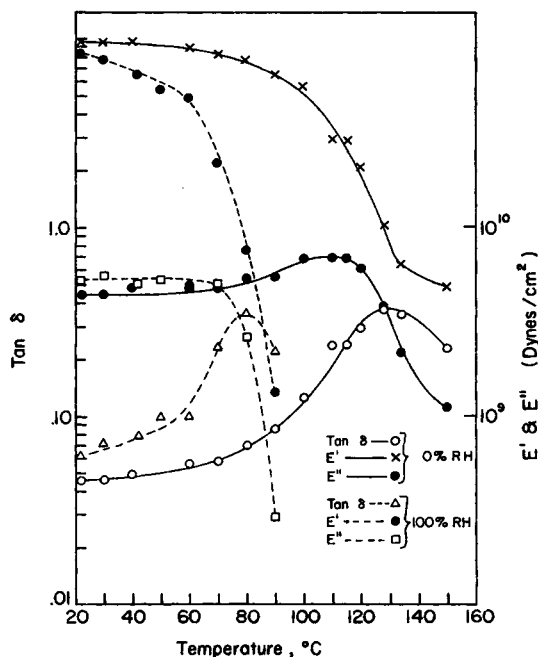


Fig. 1. Dynamic mechanical properties of acrylonitrile-vinyl acetate copolymer containing 10.8% vinyl acetate, as a function of temperature at 0 and 100% R.H.

The values of E'' at 100% r.h. and 100°C. that were used with the dyeing data are listed in Table I. They were obtained by extrapolating the $\tan \delta$ and E' values to 100°C. and then using the relation $E'' = (\tan \delta)(E')$.

TABLE II
Calculation of Diffusion Constants

Sample No.	C_{∞} , g./cm. ³	C_{∞}^2	25 min. = 1500 sec. C_{15} , g./g.	C_{15}^2 ($\times 10^{-4}$)	A_w , cm. ²	A_w^2 ($\times 10^{-6}$)	t , sec.	$\frac{C_{15}^2}{2\pi^{1/2}C_{\infty}^2A_w^2t}$
1	0.135	0.0180	0.057	32.5	1860	3.46	1500	9.76×10^{-12}
2	0.126	0.0158	0.008	0.65	1760	3.10	1500	2.44×10^{-13}
3	0.1245	0.0152	0.0345	11.9	1745	3.05	1500	4.80×10^{-12}
4	0.104	0.0111	0.0315	9.95	1790	3.20	1500	2.78×10^{-12}

Dye Diffusion Constant

The dye diffusion constant was calculated by the method used by Rosenbaum,³ which gives numerical results proportional to values obtained by the method used in the work on nylon.¹ The equation is

$$D = \frac{C_t^2}{2\pi^{1/2}C_\infty^2 A_w^2 t}$$

where D = diffusion constant ($\text{cm.}^2/\text{sec.}$), C_∞ = dye uptake at saturation (g. of dye per cm.^3 of fiber), C_t = dye uptake at time t (g. of dye per g. of fiber), A_w = fiber surface area ($\text{cm.}^2/\text{g.}$ of fiber), and t = time (sec.).

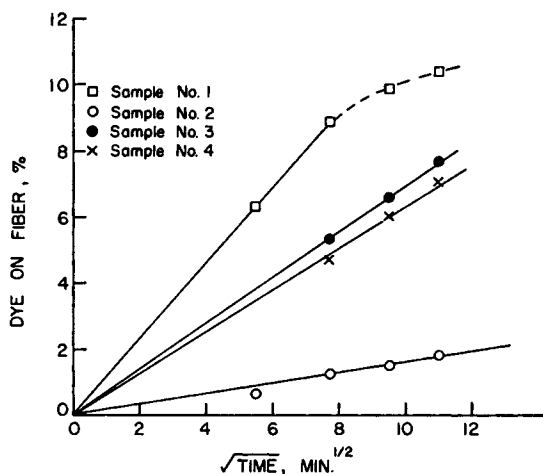


Fig. 2. Dye absorption as a function of time.

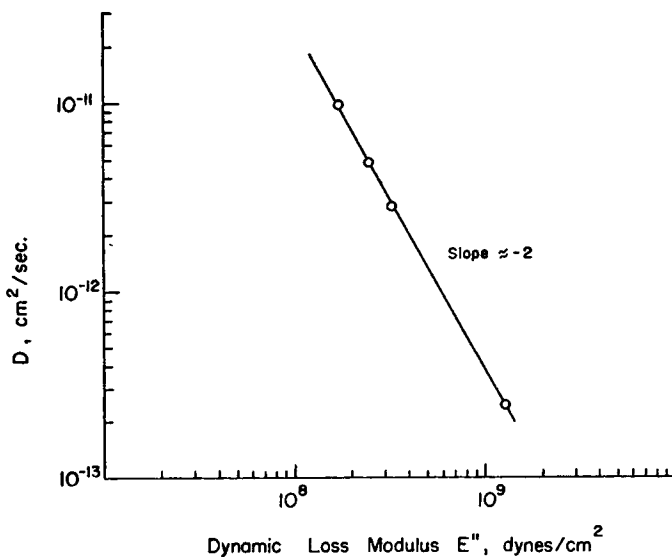


Fig. 3. Relation between diffusion constant and dynamic loss modulus.

The dyeing rate data are shown in Figure 2. The dye uptake C_t is linear as a function of $t^{1/2}$, as predicted by the equation, and the data pass through the origin. The deviation from linearity in the top curve is caused by the approach to saturation.

The diffusion constants calculated from the data of Figure 2 are shown in Table II.

The relationship between E'' and D is shown in Figure 3, plotted in the modified form of the equations of Fujita et al. used for nylon:¹

$$\ln (D/RT) = C - B_d \ln E''$$

where D = diffusion coefficient, R = gas constant, T = temperature, C = constant, B_d = constant similar to the B used in the WLF equation,¹ and E'' = dynamic loss modulus.

As for nylon, the data appear to fit the equation. In the acrylic case $B_d = -2$, whereas for nylon $B_d = -4.5$. The value of $B_d = 1$ was found by Fujita et al. in their studies of the diffusion of organic liquids in amorphous polymers. The deviation from unity in the nylon data has been discussed,¹ and the same factors are applicable to acrylics. One possible cause is that E'' measurements are made parallel to the fiber axis, whereas dye diffusion takes place primarily perpendicular to it. The effects of orientation parallel to the fiber axis is probably different for E'' and D .

The extension of the relation between E'' and D to acrylic fibers indicates that the dependence of dye diffusion on polymer chain mobility is a general phenomenon, not limited to nylon. A relation of D to mechanical properties permits one to "tailor" fibers with good mechanical properties while maintaining adequate dye diffusion behavior.

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