

Relation Between Dynamic Mechanical Properties and Dye Diffusion Behavior in Acrylic Fibers from Polymer Blends

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Synopsis

The extension of the relation between the dynamic viscoelastic parameters (E'' and $\tan \delta$) and diffusion coefficient (D) to modified acrylic blend fibers indicates that the dependence of dye diffusion on polymer chain mobility is a general phenomenon not limited to a single component system. The relationship of D to mechanical properties permits one to "tailor" fibers with good mechanical properties while maintaining adequate dye-diffusion behavior.

INTRODUCTION

In previous studies¹ on the diffusion of a disperse dye, 1-amino-4-hydroxy-antraquinone (C.I. Disperse Red 15), into poly(ethylene terephthalate) (PET) fibers as a function of heat-setting temperature and draw ratio, it was found that the dynamic loss modulus E'' , measured at the dyeing temperature in aqueous medium (100% relative humidity), was related to dye diffusivity. More recently, a linear relationship was found between the diffusion coefficients of a disperse dye and loss modulus for PET fiber in tetrachloroethylene.²

Rosenbaum³ reasoned that dye diffusion should be related to the mobility of the polymer chain segments and 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). Theoretically, these relationships should also apply to polymer blends. It was of interest to study the dynamic mechanical properties and dye diffusion in acrylic fibers from polymer blends.

EXPERIMENTAL

A number of fibers were prepared that were blends of acrylonitrile/vinyl bromide (AN/VBr) plus other modified AN polymers. The composition of these fibers is listed in Table I. The dye used was C.I. Basic Blue 22, Sevron Blue 2G (du Pont). The dyeing temperature and the liquor/fiber ratio were 100°C and 40:1, respectively. A dye concentration of 5 g/l. was used and the pH adjusted to 5.2 with acetic acid. The dyeing rates were measured using the Cary II spectrophotometer.

The dynamic mechanical properties were measured at a constant frequency of 11 Hz with a Vibron viscoelastometer. This instrument applies a sinusoidal tensile strain to one end of the sample and measures the stress output at the other end. The instrument uses two transducers to read directly the absolute dynamic

TABLE I
Dynamic Loss Moduli (E'') of Acrylonitrile/Vinyl Bromide (AN/VBr) Blend Fibers^a in Aqueous Medium (Extrapolated to 100°C)

Sample no.	Description		% Polymer B in blend	E'' , dynes/cm ²
	Polymer A	Polymer B ^b		
1	AN/VBr (5% VBr)	—	0	1.25×10^9
2	AN/VBr	10% MA	20	8.09×10^8
3	AN/VBr	20% MA	20	6.20×10^8
4	AN/VBr	45% MA	20	7.00×10^8
5	AN/VBr	75% MA	20	6.90×10^8
6	AN/VBr	AN polymer containing just sulfonated monomer	20	9.10×10^8
7	same as 2, DMAc/PEG spin bath coagulant	—	—	7.10×10^8
8	same as 3, DMAc/PEG spin bath coagulant	—	—	5.60×10^8
9	AN/VBr	AN polymer containing 22% vinylidene chloride and a sulfonated monomer	20	1.24×10^9

^a Coagulated in DMAc/H₂O spin bath.

^b Samples 2-5 are acrylonitrile polymers containing various levels of methacrylate (MA) and a sulfonated monomer.

modulus E^* (the ratio of maximum stress amplitude to maximum strain amplitude) and the phase angle δ between stress and strain. From these two quantities, the real part E' (dynamic modulus) and the imaginary part E'' (loss modulus) can be calculated. The principles of this direct method and instrument are described in detail by Takayanagi.⁴ To measure the dynamic properties in a liquid medium, it was necessary to devise an apparatus to keep the sample immersed in the medium and the transducers outside, and yet aligned with the sample. This apparatus and procedure is described in detail by Murayama and Armstrong.^{5,6} Dynamic measurements were carried out in water; samples were heated at a rate of 1°C/min, and measurements of the tensile modulus E and loss tangent ($\tan \delta$) were made at 5°C or 10°C increments. Samples were allowed to equilibrate at each temperature for 20 min before measurements were made.

RESULTS AND DISCUSSION

The dyeing rate data are shown in Figure 1 for fibers coagulated in dimethylacetamide (DMAc)/water, and in Figure 2 for fibers coagulated in DMAc/polyethylene glycol (PEG). The dye uptake (C_t) was found to be linear as a function of time ($t^{1/2}$), except for those samples approaching saturation. From the data given in Table II it was possible to calculate diffusion constants using the diffusion equation modified for the fiber dimension:

$$D = 6.95 \times 10^{-8} \left[\frac{C_t}{C_\infty} \right]^2 \frac{d}{\rho t} \quad (1)$$

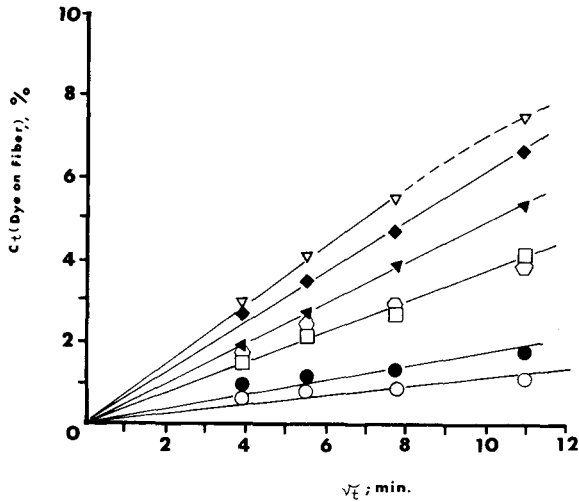


Fig. 1. Relationship of dye uptake (C_t) to dyeing time (\sqrt{t}) for acrylonitrile fibers from polymer blends (DMAc/H₂O spin bath coagulant). See Table I for sample description: (O) 1; (□) 2; (▽) 3; (◆) 4; (○) 5; (▼) 6; (●) 9.

where D = diffusion constant (cm²/sec), C_∞ = dye uptake at saturation (g dye per g fiber), C_t = dye uptake at time t (g dye per g fiber), d = denier (g fiber per 9×10^5 cm length of fiber), and ρ = fiber density (g/cm³).

The relationship between the dynamic loss modulus E'' and dye diffusion constant D is shown in Figure 3 plotted in the modified form of the equations of Fujita et al.,⁸ eq. (2), reported previously for the diffusion of acid dyes into drawn nylon 66 fiber,⁹ basic dyes into acrylic fiber,¹⁰ and disperse dyes into polyester fiber¹:

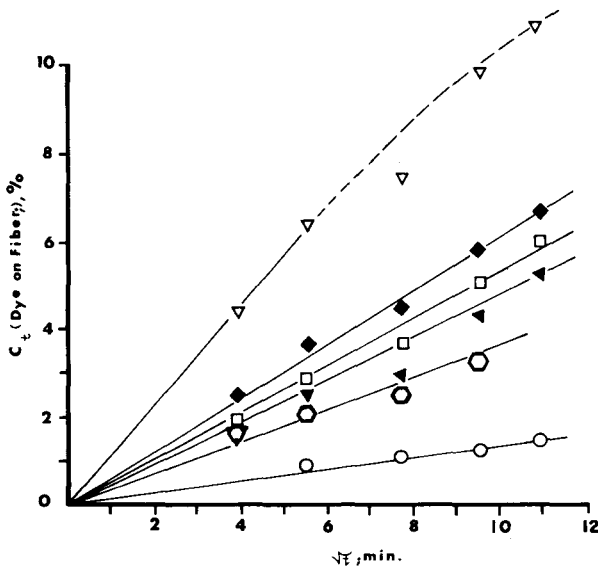


Fig. 2. Relationship of dye uptake (C_t) to dyeing time (\sqrt{t}) for acrylonitrile fibers from polymer blends (DMAc/PEG spin bath coagulant). Samples: (O) 1; (□) 7; (▽) 8; (◆) 4; (○) 5; (▼) 6.

TABLE II
Diffusion Coefficients of Modified Acrylic Fibers from Polymer Blends^a

Sample no.	C_{∞} , g/g	C_t , g/g	t , sec	d	ρ , g/cm ³	$D \times 10^{12}$, cm ² /sec
1	0.051	0.007	2160	2.8	1.20	1.39
2	0.141	0.022	2160	2.9	1.19	1.90
3	0.152	0.042	2160	3.0	1.19	6.40
4	0.125	0.037	2160	3.0	1.20	7.24
5	0.107	0.023	2160	2.9	1.20	3.55
6	0.178	0.030	2160	2.8	1.19	2.15
7	0.143	0.032	2160	2.7	1.19	3.65
8	0.154	0.060	1500	3.1	1.19	15.42
9	0.074	0.010	2160	2.6	1.21	1.27

^a Where C_{∞} = dye uptake at saturation (g dye/g fiber), C_t = dye uptake at time t (g dye/g fiber), t = time (sec), ρ = fiber density (g/cm³), d = fiber denier (g fiber/9 \times 10⁶ cm length of fiber), and D = diffusion constant (cm²/sec).

$$\ln (D/RT) = C - B_d \ln (E''/\omega) \quad (2)$$

where D = diffusion coefficients, R = gas constant, T = temperature, C and B_d = constants, E'' = the tensile dynamic loss modulus, and ω = frequency. The data fit the equation quite well. The value of B_d was 1.1. A value of B_d was previously reported as 2 for draw oriented acrylic fibers¹⁰ and 4.5 for oriented nylon.⁹

The value of $B_d = 1$ was found by Fujita et al. in their studies of the diffusion of organic liquids in amorphous polymers above the T_g . One possible cause of the deviation from unity in earlier nylon and acrylic data 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 are probably different for E'' and D . That B_d is indeed influenced by orientation was shown by Dumbleton et al., who found that $B_d = 1$ for undrawn semicrystalline PET and was >1 for yarn drawn 3–4.25 \times (orientation). All of these modified acrylic fiber samples had been annealed, thereby diminishing the effect of draw orientation on dye diffusion. The dyeing rate data in Figures 1 and 2 clearly show that the diffusivity of the AN/VBr matrix is influenced by blend

TABLE III
Relative Ratios of Diffusion Coefficients (D/D_0) and Dynamic Loss Moduli (E''/E_0'') for Acrylonitrile Fibers from Polymer Blends

Sample no.	D/D_0	E''/E_0''	% Residual PEG-400
1	1.00	1.00	—
2	1.37	0.71	—
7	2.63	0.57	1.81
3	4.60	0.49	—
8	11.09	0.45	2.52
4	5.21	0.56	0.53
5	2.55	0.55	0.35
6	1.55	0.73	0.73
9	0.91	0.99	—

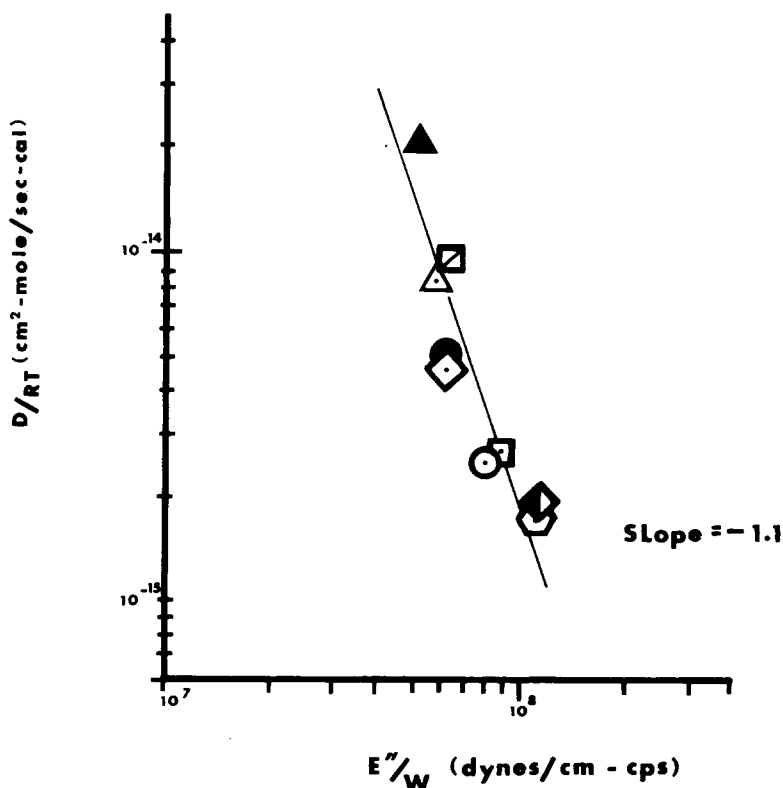


Fig. 3. Relationship of dye diffusion coefficient (D) to dynamic loss modulus (E'') for acrylonitrile fibers from polymer blends. Samples: (\blacklozenge) 1; (\circ) 2; (\triangle) 3; (\boxplus) 4; (\diamond) 5; (\square) 6; (\bullet) 7; (\blacktriangle) 8; (\circ) 9.

composition. Regardless of coagulant (DMAc/H₂O or DMAc/PEG), dye uptake versus \sqrt{t} remains essentially constant for all fibers except samples 2 and 3. When coagulated in DMAc/PEG, these two fibers had higher basic dye acceptance (BDA) and larger diffusion coefficients. The relative ratios of the diffusion coefficients (D) and loss moduli (E'') of the blends to those of AN/VBr (D_0 and E_0'' , respectively) are listed in Table III. Sample 8 (DMAc/PEG coagulant) has a diffusion coefficient one order of magnitude larger than unblended AN/VBr (sample 1), whereas when coagulated in DMAc/H₂O, sample 3, D is only 4.6 times larger than that of sample 1. The same is true for sample 2, but less dramatically so, with just a 2.6-fold increase in D when the sample was coagulated in DMAc/PEG. Analysis for residual PEG-400 revealed a fair amount of PEG in these two samples compared to the others, as shown in Table III. The correlation between the relative ratios of diffusion coefficients and loss moduli is shown in Figure 4. The relative ratio of diffusion coefficients for the AN/VBr blend fibers increases as the relative ratio of loss moduli decreases. These parameters are useful for defining the effect of blend composition in multicomponent systems.

When the hot-wet moduli of acrylic fibers from polymer blends are plotted versus the diffusion coefficients (Fig. 5), a relationship very similar to that obtained with E'' values shown in Figure 3 is observed. The diffusion coefficient

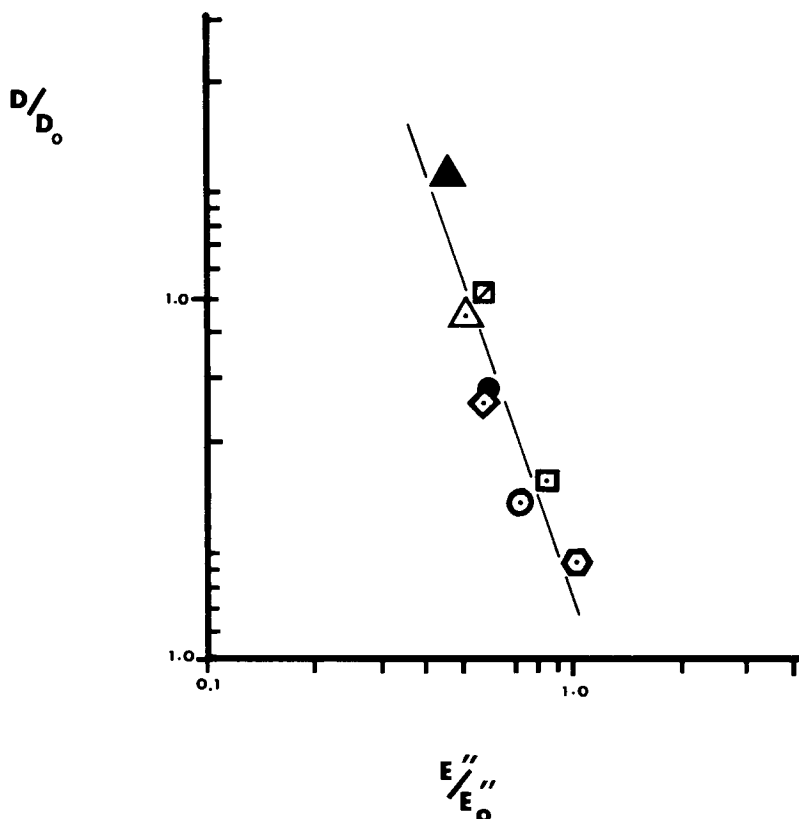


Fig. 4. Relationship of relative ratio of diffusion coefficients (D/D_0) to relative ratio of loss moduli (E''/E''_0) for acrylonitrile fibers from polymer blends. Symbols the same as in Fig. 3.

increases as the hot-wet modulus decreases. One possible explanation for this observation might lie in the fact that the hot-wet modulus is related to the response of the elastic component in viscoelastic systems above T_g ; the loss modulus at 100°C in water is a damping term occurring above T_g . At temperatures above this transition region (rubbery region), molecular segments in these blend fibers are not frozen in but are very free to move, so the modulus (E'') is low. With the low internal friction among segments after T_g , the damping also is low. For this reason, similar relationships are observed using either the hot-wet modulus or loss modulus. These viscoelastic properties (E'' , hot-wet modulus) in liquid medium are important controlling parameters for the dyeability of the blend fibers.

Relationship Between $\tan \delta$ and Increased Dyeability

Table IV lists $\tan \delta$ temperature and intensities at 0% and 100% relative humidity (R.H.) for most of the unannealed and annealed fibers reported in this study. For all annealed fibers at 100% R.H., the intensities of $\tan \delta$ are greater than at 0% R.H. but, with the exception of sample 1 (AN/VBr), have almost the same magnitude, although the maxima occur at different temperatures. How-

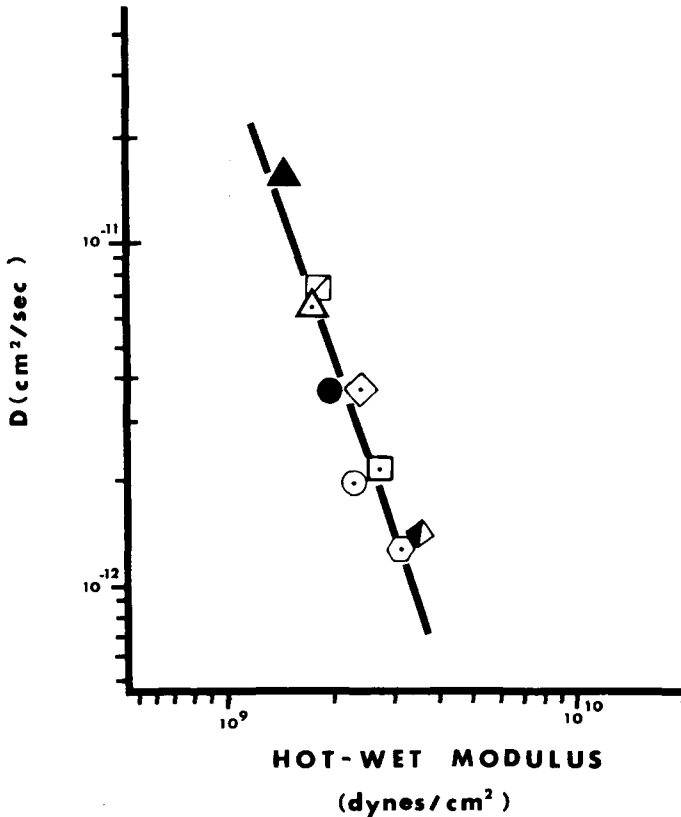


Fig. 5. Relationship of dye diffusion coefficient (D) to hot-wet modulus for acrylonitrile fibers from polymer blends. Symbols the same as in Fig. 3.

ever, at 0% R.H., as one compares the data for the blend fiber to that of AN/VBr alone, the two-stage transition observed in AN/VBr (Fig. 6) is either broad and unresolvable with a higher $\tan \delta$ intensity or, if resolved, the intensities of the two peaks will either increase or decrease relative to AN/VBr depending on the nature of the additive. For every increase or decrease in these intensities, a corresponding response was observed in dyeing.

From a study of the plasticization and swelling of Acrilan* acrylic fiber under dye bath conditions, Gur-Arieh and Ingamells¹¹ concluded that there is no predictable connection between fiber swelling and plasticization; it is the segmental mobility of the fiber molecular chains that controls diffusion of dyes into the fiber. Ingamells and co-workers support this with a study of carrier dyeing of Acrilan with disperse dyes.¹² In dynamic mechanical testing, segmental mobility is reflected in $\tan \delta$ intensity. If $\tan \delta$ is a measure of the internal friction of a system and passes through a maximum close to T_g , the greater the mobility, the greater the internal friction, the greater the amount of heat dissipated, and consequently the higher the intensity of $\tan \delta$ observed. On the other hand, in the case of restricted segmental mobility, a less intense $\tan \delta$ is observed due to less internal friction, which is reflected in lower heat dissipation.

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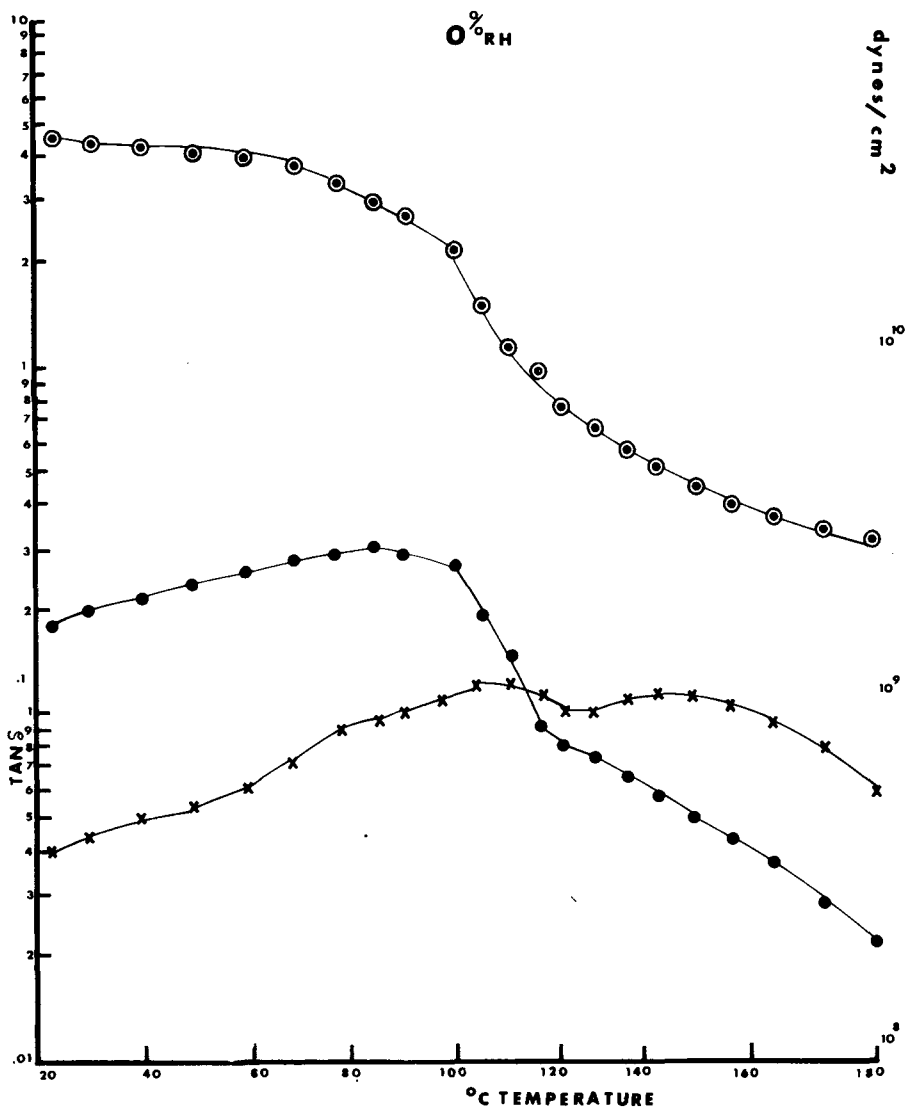


Fig. 6. Dynamic mechanical data (0% R.H.) for annealed acrylonitrile fiber containing vinyl bromide (5% VBr): (○) E' ; (●) E'' ; (×) $\tan \delta$.

TABLE IV
Tan δ Temperature and Maxima for Multicomponent Fibers at 0% and 100% Relative Humidity (R.H.)

Fiber no.	0% R.H.				100% R.H.	
	Unannealed		Annealed		Annealed	
	Tan δ , °C	Tan δ , Max	Tan δ , °C	Tan δ , Max	Tan δ , °C	Tan δ , Max
1	114	0.140	106, 140	0.125, 0.115	>90	0.195
2	120	0.170	130 ^a	0.170	86	0.225
3	120	0.185	130 ^a	0.195	84	0.240
4	116	0.200	116, 150	0.170, 0.130	85	0.235
5	110	0.150	100, 140	0.165, 0.130	86	0.220
6	106, 150	0.120, 0.090	100, 145	0.110, 0.140	90	0.215
9	—	—	108, 144	0.140, 0.120	90	0.210

^a Broad transition centered at respective temperature.

The extension of the relation between the dynamic viscoelastic parameters (E'' and $\tan \delta$) and diffusion coefficient (D) to modified acrylic blend fibers indicates that the dependence of dye diffusion on polymer chain mobility is a general phenomenon, not limited to a single component system. The relationship of D to mechanical properties permits one to "tailor" fibers with good mechanical properties while maintaining adequate dye diffusion behavior.

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