Relation Between Nylon Fiber Mechanical Properties and Dye Diffusion Behavior

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Synopsis

The mobility of polymer chain segments is shown to play a major role in the diffusion of dyes in nylon 66. The rate of dye diffusion has been related to the time-dependent mechanical properties, such as creep and stress relaxation, which are controlled by the mobility of the chain segments. The theoretical relations derived by Fujita et al. relating the diffusion of small molecules in amorphous polymers to other properties are shown to be applicable for the dyeing of semicrystalline nylon. Data showing the effects of surface area, temperature, and the amount of dye absorbed at saturation on the dyeing rate are presented and discussed.

INTRODUCTION

For many years it has been known that nylon fibers from various sources dye at vastly different rates. No quantitative explanation of this in terms of fiber structure has been given. The present paper attempts to show that dye diffusion in semicrystalline nylon is controlled by the same structural parameters as the diffusion of small molecules in amorphous polymers. Since the same structural parameters control dye diffusion and the dynamic mechanical properties, creep, and stress relaxation, these properties are quantitatively interrelated.

Fujita et al.[1] have presented data for the concentration and temperature dependence of diffusion coefficients for n-alkyl acetates diffusing in poly-(methyl acrylate). The data were explained by using the free volume–segmental motion concepts developed by Williams, Landel, and Ferry.[2] Fujita et al. derived an equation for the temperature and concentration dependence of diffusion analogous to the Williams-Landel-Ferry (WLF) equation[2] for the temperature dependence of the viscoelastic properties of polymeric materials. The assumption was made that the degree of motion of polymer chain segments and the free volume available for this motion should govern the rate of diffusion, as well as the rate of creep and stress relaxation. Using this assumption and the other assumptions used in the original derivation of the WLF equation,[2] Fujita et al. arrived at the relations:

$$\ln (D_T/D_0) = B_d \ln (\eta_0/\eta_T) = B_d \ln (1/A_T) \tag{1}$$

and

$$\ln (D_T/RT) = C - B_d \ln \eta_T \qquad (2)$$

where D_T, D_0 are diffusion coefficients at temperature T and at the reference temperature T_0, respectively, η_T and η_0 are polymer viscosity at temperature T and at the reference temperature T^0, respectively; C is a constant characteristic of the particular polymer–dye system used; A_T is the "shift factor" for time–temperature superposition which is obtained from the WLF equation; B_d is a constant, taken equal to unity in the WLF equation derivation. No particular value of the constant B_d is assumed in the derivation of Fujita et al., although in the derivation it is assumed to be independent of temperature and penetrant concentration.[1] Fujita found the value of B_d to be slightly less than unity for several polymer–penetrant systems.[3]

The equations as presented above are slightly modified from the form presented by Fujita et al. because the original equations took into account both a variation in temperature and a variation in the volume fraction of the diffusate. Since the volume fraction of dye in the polymer is always very low, the effect of diffusate volume fraction has been omitted.

The shift factor A_T provides a direct link between the diffusion constants in eq. (1) and the temperature dependence of creep and stress relaxation. For A_T to be applicable, the temperature of investigation must be at or above the glass transition temperature. For nylon in water this transition appears from dynamic mechanical measurements to be in the vicinity of $0°C$.

Fujita et al. found the constant B_d to be slightly less than unity, in reasonable agreement with the assumption made in the derivation of the WLF equation. The experimental data of Fujita et al. for n-alkyl acetates in poly(methyl acrylate) agree with eqs. (1) and (2).

Rosenbaum[4] has shown that a relation exists between the diffusion constant and the polymer tensile compliance or viscosity, for the case of diffusion of Malachite Green in polyacrylonitrile. Rosenbaum proposed that the amount of motion of the polymer chain segments is the controlling factor on dye diffusion as well as in creep and similar relaxation processes. While quantitative theory was not used, the correlation of diffusion with tensile compliance and viscosity was a significant contribution to dyeing technology.

EXPERIMENTAL

The two dyes used in this work were Kiton Red 2G (C. I. Acid Red 1) and Edicol Supra Geranine 2GS (C. I. Food Red 10). The purity of the Kiton Red 2G was found to be 79% by comparison with the extinction coefficient of the pure dye. C. I. Food Red 10 is essentially pure dyestuff. C. I. Food Red 10 has the same chemical structure as Acid Red 1, and gave the same dyeing rate when dyebath solutions containing equivalent amounts of pure dye were used. Since the impurity in Acid Red 1 had no effect on the dyeing rate (on a pure dye basis) the Acid Red 1 was used to obtain the data

shown in the figures in this paper. The pH of the dyebath was adjusted to 3.2 with formic acid, and the Acid Red 1 concentration was 0.75 g./l.

The two principal fibers used were commercial samples of nylon 66 and nylon 6. Both samples were textile multifilament yarns having a yarn denier of 40. The nylon 66 yarn consisted of 13 filaments and the nylon 6 yarn 12 filaments. Before dyeing the yarns were scoured to remove finish as follows: The samples were extracted twice for 10 min. with CCl₄ at room temperature. The sample was boiled for 30 min. at 100°C. in an aqueous solution containing 1 g./l. sodium carbonate and 0.5 g./l. Igepal CTA639 (registered Trade Mark of General Aniline and Film Corporation). The liquor ratio was 65 g. of solution to 1 g. fiber. The sample was rinsed in warm tap water with frequent agitation for approximately 10 min. The sample was next blotted with paper towels and air was circulated through it without heat until it was judged dry. Specimens used for dynamic mechanical measurements were about 9 in. long; the remainder of the sample was cut into pieces ∼2 in. long to facilitate separation and weighing of samples before dyeing. The sample was conditioned at 65% R.H. and 70°F. before use.

Dyeing rate measurements were made using 1-oz. capacity screw-cap bottles, which were rotated in a constant temperature oil bath. The rotation was in a vertical plane, so that the bottles were completely inverted once per revolution. The speed of rotation was 36 rpm.

After weighing, 0.375 g. of the yarn to be tested were placed in a sample bottle, and 13 cc. of water adjusted to pH 3.2 with formic acid were added to the bottle, which was then rotated in the bath for 8 min. or more to bring the solution to the bath temperature. The bottle was then opened, with the bottom half of the bottle remaining in the bath. A spatula was used to lift the yarn up on the side of the bottle, out of the dilute acid solution. Next, 2 ml. dye solution was added, and the top was replaced. The dye solution was prepared in a typical case by dissolving 5.625 g./l. of Kiton Red 2G in distilled water and adjusting the pH to 3.2 with formic acid. The bottles were then lowered completely into the dye bath and rotation was started. After the desired dyeing time the sample bottle was quickly removed from the oil bath and opened. The yarn sample was rinsed in distilled water, blotted, and retained for future measurements. A 5-ml. portion of the dye bath was diluted to 100 cc. for optical density measurement. The amount of dye absorbed by the fiber was obtained from the change in optical density of the dye bath.

The dynamic mechanical properties of the fibers were determined by using a Vibron dynamic viscoelastomer (Model DDV-II) (manufactured by Toyo Measuring Instruments Co., Ltd.), which has been previously described by Takayanagi.[5] The Vibron imposes a sinusoidal tensile stress on the specimen, and a transducer at the other end of the specimen measures the sinusoidal strain response to the stress. The phase angle δ between the stress and strain permits direct readout of tan δ, the loss tangent. The dynamic modulus $|E^*|$ is obtained from another transducer which measures

the ratio of the maximum stress amplitude to the maximum strain ampli-
tude.   The elastic component E' of the dynamic modulus $|E^*|$ is given by
$|E^*|$ cos δ, and the viscous component or loss modulus E'' is given by
$|E^*|$ sin δ.

The dynamic measurements were made at a frequency of 11 cps, at an
initial strain level of 1%.   A relative humidity of 100% was used, since one
is interested in the dynamic properties under dyeing conditions.   It was
found that the 100°C. treatment during the scouring pretreatment was
adequate to stabilize the structure against further structural changes during
the E'' measurement.   A repeat measurement of E'' at 100% R.H. on the
same sample gave the same result as the initial measurement.

RESULTS AND DISCUSSION

Diffusion Equation

The original diffusion equation used in this work was based on a model
developed by Hermans[6] for cases of diffusion with simultaneous irreversible
reaction.   A study of the variables in the original equation revealed a
correct dependence of the diffusion constant upon all variables except C_∞.
The form of the equation with the experimentally determined dependence
on C_∞ is shown in eq. (3).

$$D = (K/C_\infty{}^2)(M/S)^2(1/t) \tag{3}$$

where D is the diffusion constant (in square centimeters/second), K is a con-
stant of proportionality, taken as 22.2 in this work, C_∞ is grams dye per
cubic centimeter polymer absorbed at saturation, M is grams dye on the
fiber at time t, S is surface area of the fiber (in square centimeters), and
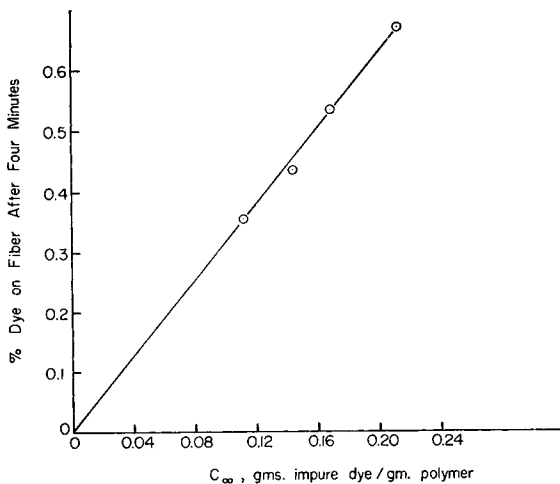t is time (in seconds).

Fig. 1. Effect of C_∞ on dyeing rate at 70°C.

Although the improper dependence on C_∞ makes the original model questionable, the value of the constant K was retained as 22.2 for lack of a better value. The diffusion constant calculated from the equation is proportional to the true integral diffusion coefficient, but the constant of proportionality is not yet known.
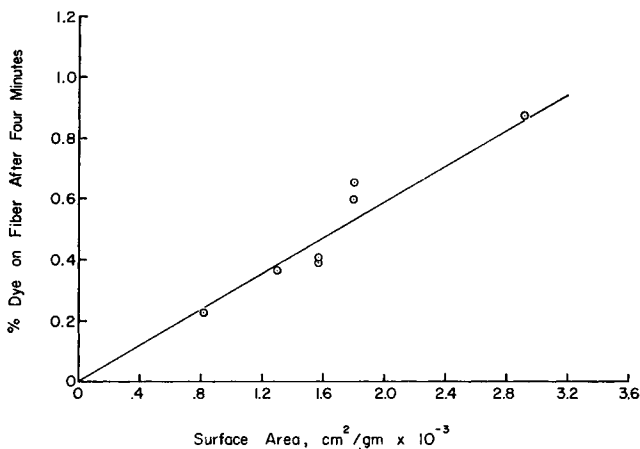

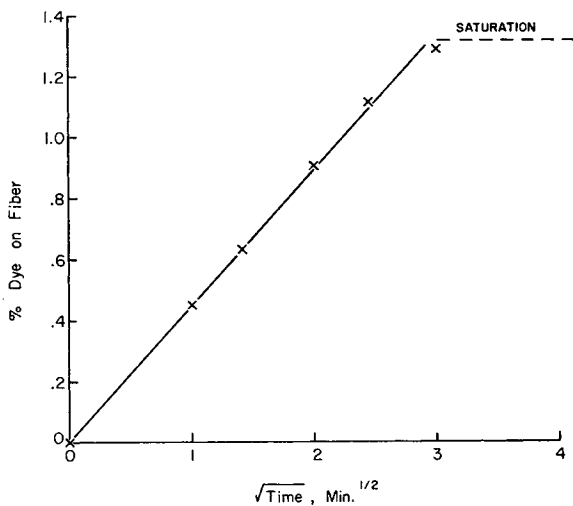Fig. 2. Effect of fiber surface area on dyeing rate at 70°C.

Fig. 3. Dye absorbed vs. time at 100°C.

After development of this equation it was found to be essentially the same as the solution of Fick's equation for semi-infinite media used by Rosenbaum in his studies of dye diffusion in polyacrylonitrile fibers.[4] The equation holds quite well to about 70% saturation of the fiber. Data showing the relations between M, t, C_∞, and S are shown in Figures 1–3.

Figure 1 shows that as the number of dye sites is increased the per cent dye on the fiber increases linearly and passes through the origin, as expected from the equation.

Figure 2 indicates that almost all the fiber surface area is available to the diffusing dye molecules, since a major intercept on the surface area axis is not observed. The scatter in the data is caused by the different processing conditions required for the different filament sizes. The dye absorption results have been normalized to bring all samples to the same number of dye sites (see Fig. 1). The data support a linear relation between the surface area S and the dye absorbed M, as predicted by the diffusivity equation.

The relation between M and $\sqrt{t}$ is linear and passes through the origin as expected (Fig. 3).

Note that no effect of dye bath concentration has been included in the equation, other than through the effect on C_∞; in the case of acid dyes this effect of dye bath concentration on C_∞ is very small. It has been experimentally shown that for the acid dyeing of nylon the dye bath concentration has little effect on the dye diffusion rate.[7]

Applicability of the Equations of Fujita et al. to the Dyeing of Nylon

The equations of Fujita et al. were derived in a manner similar to the WLF[2] equation from the Doolittle[8] viscosity–free volume relationship, so that for the equations to be applicable the polymer should obey the Doolittle equation under the conditions of diffusion, i.e., the diffusion should be governed by the free volume and segmental motion concepts associated with the Doolittle equation.

A second point to consider in application of the equations is that nylon is partially crystalline. It is well known that dyeing occurs primarily in the "amorphous" or less-ordered regions of the polymer. To apply the equations then one should either hold the degree of order constant or use a viscosity value which represents the product of the activation energy for motion per chain segment and the number of segments moving. The loss modulus E'' divided by the frequency ω fits this description. At low frequencies the value of E''/ω approaches the steady-state viscosity[9] and has been substituted for it in the equations.

A last point to consider is that ions and ionic linkages are involved in the acid dyeing of nylon, whereas small uncharged molecules and van der Waals interactions were involved in the work of Fujita et al. Whether or not this affects the applicability of the equations is best determined experimentally.

Dependence of the Diffusion Constant and the Loss of Modulus upon Dye Bath Temperature

Data showing the temperature dependence of the diffusion constant are shown in Figure 4. Note that the activation energy for diffusion, as taken from the slope at various temperatures on Figure 4 and replotted on Figure 5, is not at all constant with temperature. The activation energy for diffusion as a function of temperature has the same qualitative shape as the
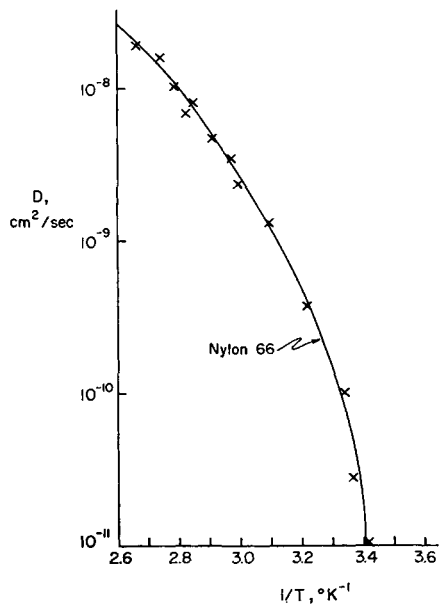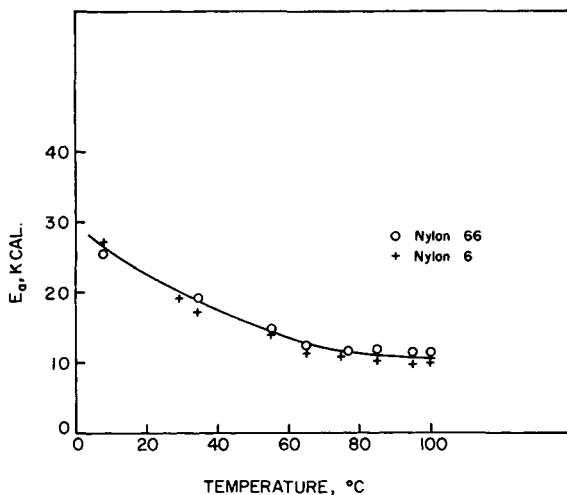
Fig. 4. Diffusivity of Acid Red 1 in nylon 66.

Fig. 5. Activation energy for diffusion of Acid Red 1 in nylon 6 and nylon 66.

curve for the activation energy of rubbery flow versus temperature. Further, the absolute values of the activation energy for the two processes are similar. The shape of the log D versus $1/T$ curve is qualitatively the same as found by Rosenbaum for the temperature dependence of dye diffusion in poly-acrylonitrile.[10]

The dynamic mechanical properties show the behavior one expects just above a major transition (Figs. 6 and 7). The transition temperature

(at 11 cps) appears to be 0°C. to −10°C.   The region of 20–100°C. can be characterized as a "rubbery flow" region.   The loss modulus E'' decreases rapidly with temperature.
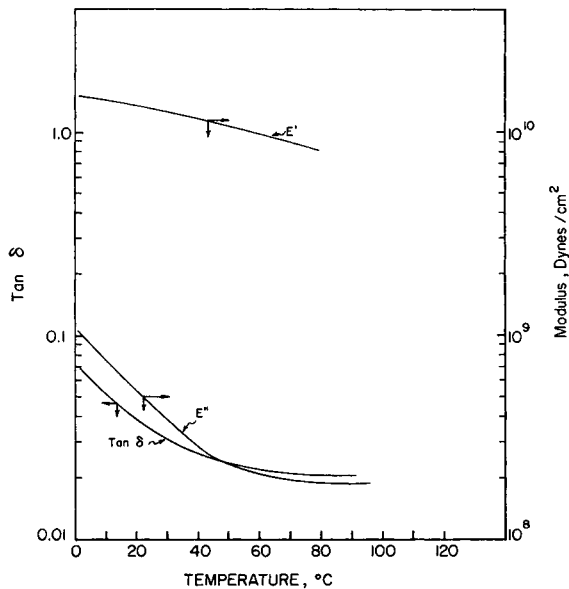

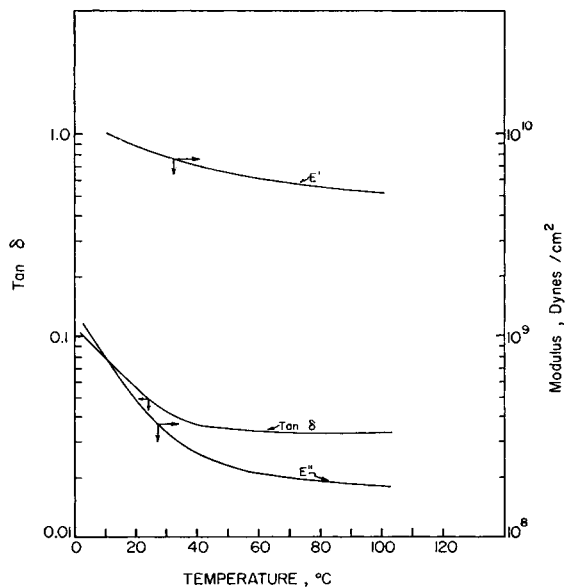Fig. 6. Dynamic mechanical properties of nylon 66 at 100% R.H.

Fig. 7. Dynamic mechanical properties of nylon 6 at 100% R.H.

Experimental Application of the Equations of Fujita et al.

A plot of $\log (D_T/D_0)$ versus $\log (E''_0/E''_T)$ is shown in Figure 8.   The plot is linear, as expected from the equation, giving a value of $B_d = 4.5$.   The curves for nylon 6 and nylon 66 may or may not be significantly different. The data were obtained from the measurements of D and E'' as a function of temperature (Figs. 4, 6, and 7).

Plot of:

$$\ln (D_T/D_0) = B_d \ \ln \left(\frac{E''_0}{E''_T}\right)$$

O Nylon 66
× Nylon 6

Dye: Acid Red I
        0.75 g/l, 3°–100°C

pH 3.2

$B_d = 4.5$

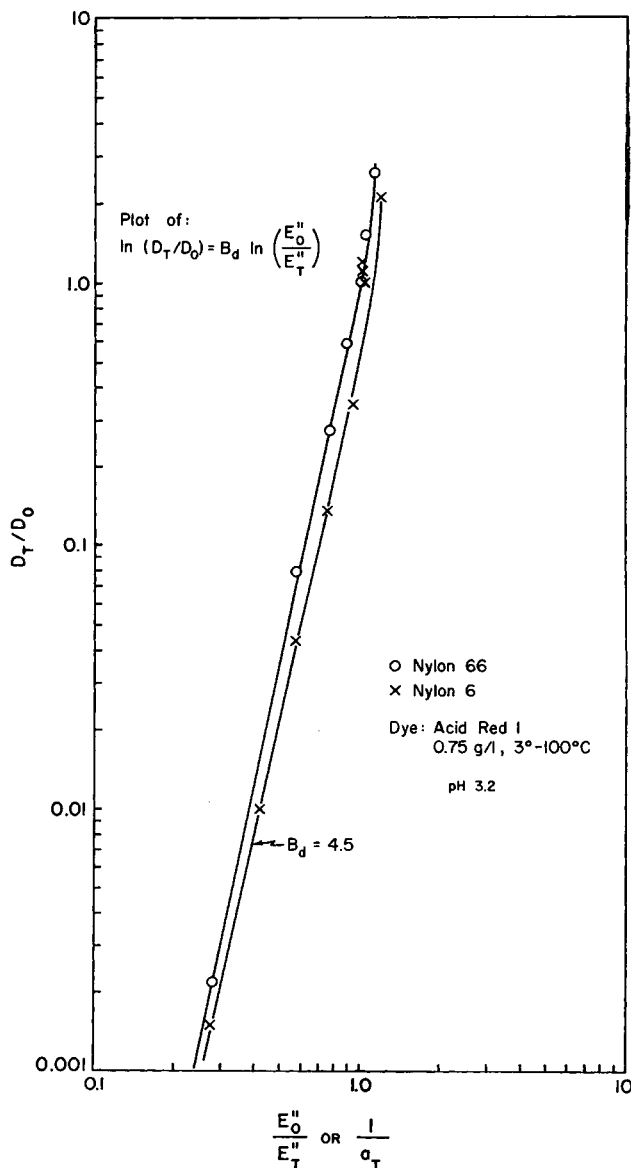$\dfrac{E''_0}{E''_T}$ OR $\dfrac{1}{a_T}$

Fig. 8. Relation between dynamic loss modulus and diffusion of an acid dye in nylon.
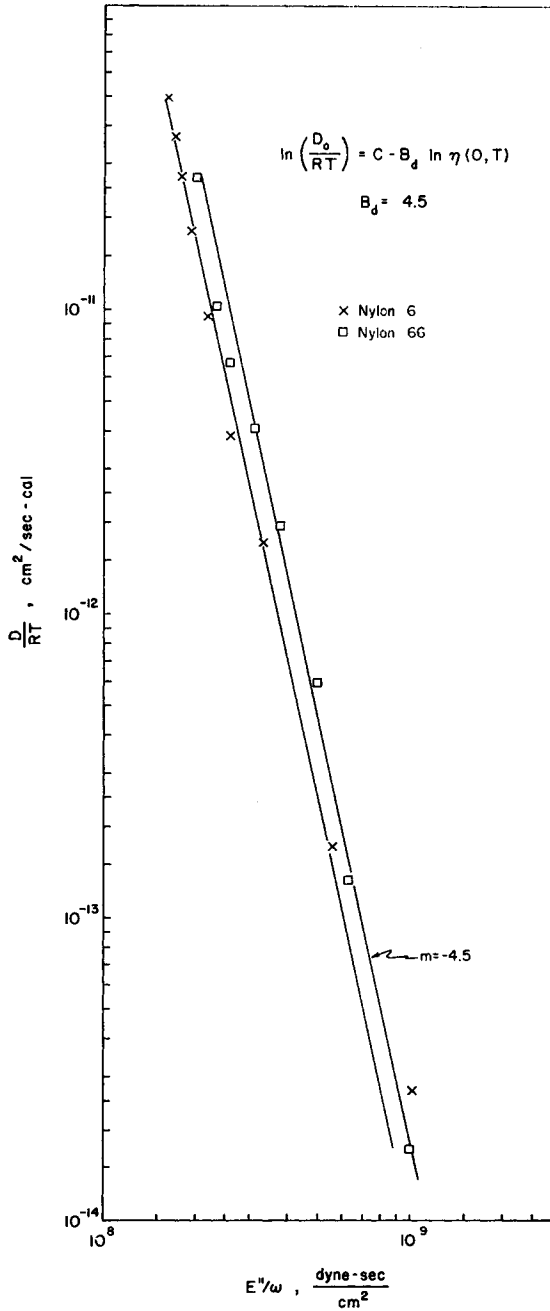
Fig. 9. Relation between dynamic loss modulus and diffusion.

The data have been replotted in the form of eq. (2) in Figure 9. The data were plotted, and then lines with slope -4.5 were drawn. The fit of the data is apparent.

The constant C describes the interaction between the polymer and the dye. As one might expect from their similarity in chemical structure, nylon 6 and nylon 66 have similar values of C. The difference between the two curves may or may not be real.

The constant $B_d = 4.5$ is considerably greater than the value of unity assumed for the WLF equation or the value of slightly less than unity found by Fujita et al. There are several factors which could account for the difference.

(a) Dye motion takes place primarily perpendicular to the fiber axis, whereas the loss modulus is measured from stress and response values parallel to the fiber axis. The polymer chains were oriented parallel to the fiber axis.

(b) The electrostatic interaction of the dye and the amine ends could influence B_d.

(c) The loss modulus E'' is equal to the steady-state viscosity only at zero frequency, whereas our measurements were carried out at 11 cps. It may be that the ratio of the loss moduli E''_0/E''_T is not strictly equal to the ratio of the viscosities η_0/η_T, differing by some constant of proportionality. A plot of $\log E''_0$, versus $\log (D_0/D_T)$ would therefore have a different slope than a plot of $\log (\eta_0/\eta_T)$ versus $\log (D_0/D_T)$. This could be tested by repeating some of the measurements at a different frequency, but this has not yet been done.

CONCLUSION

The theoretical relations derived by Fujita et al.[1] relating the diffusion of small molecules in amorphous polymers to other properties are shown to be applicable for the dyeing of semicrystalline nylon. The diffusion constant for acid dye diffusion has been related to the time-dependent mechanical properties, such as creep and stress relaxation, which are controlled by the mobility of the chain segments. While the fit of the data to the theoretical equation is good, the slope of 4.5 is higher than the values near unity that are usually encountered.

References

1. H. Fujita, A. Kishimoto, and K. Matsumoto, *Trans. Faraday Soc.*, **56**, 424 (1960).
2. M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.*, **77**, 3701 (1955).
3. H. Fujita, *Fortschr. Hochpolymer-Forsch.*, **3**, 1 (1961).
4. S. Rosenbaum, *J. Appl. Polymer Sci.*, **7**, 1225 (1963).
5. M. Takayanagi, *Mem. Fac. Eng. Kyushu Univ.*, **23**, 1 (1963).

6. J. J. Hermans, *J. Colloid Sci.*, **2,** 387 (1947).

7. J. P. Bell, W. C. Carter, and D. C. Felty, *Textile Res. J.*, **37,** 512 (1967).

8. A. K. Doolittle and D. B. Doolittle, *J. Appl. Phys.*, **28,** 901 (1957).

9. J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 1961, p. 33.

10. S. Rosenbaum, *J. Polymer Sci. A*, **3,** 1949 (1965).