

RELATION BETWEEN DYNAMIC LOSS MODULUS AND DIFFUSION COEFFICIENT IN A MODIFIED PET FIBER*

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ABSTRACT

The mobility of polymer chain segments is shown to play a major role in the diffusion of disperse dyes in a copolymerization modified PET system, monoepoxy compound

$\text{CH}_3(\text{CH}_2)_3\text{OCH}_2\text{CH}-\text{CH}_2$ modified PET. The rate of dye diffusion (diffusion coefficient D) has been related to the time-dependent mechanical property, dynamic loss modulus E'' , which is controlled by the mobility of chain segments. In this modified copolyester system, the variance of amount of modifier in the copolyester fibers causes the change in disperse dye diffusion coefficient to fiber, and in the dynamic loss modulus of the fibers, but the relationship between the diffusion and the dynamic loss modulus is in agreement with the theoretical relation derived by Bell and Dumbleton. The relation obtained in this paper is:

$$\ln D = -2.28 \ln E'' + 26.81$$

INTRODUCTION

The dynamic parameters (E' , E'' and $\tan \delta$) of polymers in liquids give useful information not only on mechanical properties of polymer but also on diffusion. Fujita, Kishimoto, and Matsumoto^[1] have shown that above the glass transition the diffusion coefficient D of organic liquids in an amorphous polymer, polymethyl acrylate, is related to the steady-state viscosity η by the equation

$$\ln (D/D_0) = B \ln (\eta_0/\eta) \quad (1)$$

where D_0 and η_0 are the value when volume fraction of the penetrant reaching zero. Based on equation (1), through replacement of η by E''/ω , Bell^[2] and Dumbleton^[3] had deduced the equation

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

where E'' is the dynamic loss modulus measured at frequency ω and

temperature T under dyeing condition, R is the gas constant, B and C are constants too. The relationship between dye diffusion coefficient D and the dynamic loss modulus E'' under the dyeing condition has been observed in polyester^[3,4], acrylic fiber^[5], and polypropylene film^[6]. These indicate that the diffusion is controlled by the mobility of the polymer chain segments.

Bell^[2] had applied the equation (2) to the system of diffusion of acid dyes in drawn nylon 66 fiber, the relationship was found:

$$\ln(D/RT) = -4.5 \ln(E''/\omega) + C \quad (3)$$

where E'' was measured under dyeing condition. Also, Dumbleton et al.^[3] had found the relationship between E'' and D to polyester fiber following the equation (2). Of them, for undrawn PET fiber, $B=1$; and for the drawn PET fiber, B is greater than 1.

The author of this paper had studied a copolymerization PET system^[7],

monoepoxy compound $\text{CH}_3(\text{CH}_2)_3\text{OCH}_2\text{CH}-\text{CH}_2$ modified PET, and investigated the change of dyeing ability of this modified PET fibers (drawn ratios 3.75) with the amount of modifier. In this work, we are interested in the relationship between the dynamic mechanical property (E'') and dye diffusion behavior in this modified PET fiber system, and their relation has been studied.

EXPERIMENTAL

The monoepoxy compound $\text{CH}_3(\text{CH}_2)_3\text{OCH}_2\text{CH}-\text{CH}_2$ modified PET^[7] was prepared from polycondensation of dimethyl terephthalate, ethylene glycol, and the monoepoxy modifier. The modified PET was melted and extruded in conventional melt-spinning device to be made into fiber. The disperse dye used in dyeing was a commercial grade disperse dye Foron—E—BLN (made in Switzerland), the dyeing condition were: dyeing temperature 100°C, liquid/fiber ratio 200 : 1, and dye concentration 200 mg/L. Dyeing rate of all modified PET fiber samples were measured by techniques previously described^[7,3]. All data of dyeing diffusion coefficient D for modified PET fiber samples are listed in Table 1.

The dynamic mechanical properties were measured at a constant frequency of 11 CPS with a Vidron Dynamic Viscoelastometer (Model DDV-II -EA, Toyo Instrument Co., Tokyo, Japan). The rate of heating 2°C/min,

Table 1 Dyeing diffusion coefficients for modified PET fibers

Sample No.	1	2	3	4
The amount of modifier (mol % based on DMT*)	0	4	6	9
D (cm ² /s)	6.35×10^{-13}	7.57×10^{-13}	11.47×10^{-13}	14.58×10^{-13}
$\ln D$	-28.09	-27.91	-27.49	-27.25

* DMT:dimethyl terephthalate which is the main monomer for polymerization of modified PET.

temperature rangs 25—180°C were adopted. The instrument automatically printed the figures of $|E^*|$, E'' , $\tan \delta$ at the interval of 2°C, and pointed the plots of $|E^*| - T$, $E'' - T$, and $\tan \delta - T$. In the previous research work^[2,5], all the measurements were made with the samples in a 100% relative humidity environment, since one was interested in the dynamic properties under dyeing condition. In this paper, limited by the experiment device, the E'' was measured under dry air environment. The value of E'' at 125°C was approximately chosen as the value of E'' at 100°C in water (dyeing condition) based on the following experimental facts: ① many results of the investigation^[8] have shown that the immersion in water appears to be equivalent to increase temperature of 25°C for as-spun PET fiber; ② though the presence of water decrease the glass transition by some 20°C to PET fiber, the height of the E'' maximum is not appreciably altered due to its dependence on the extent of crystallinity^[3]; ③ the result of investigation^[9] shows that the curve shape of dynamic loss modulus versus temperature does not change with content of water (0—1.2%) for PET fiber, only moving in parallel to the low temperature direction.

Table 2 Dynamic loss modulus for modified PET fibers at dyeing temperature 100°C

Sample No.	1	2	3	4
The amount of modifier (mol % based on DMT*)	0	4	6	9
E'' (dyn/cm ²)	4.82×10^9	4.66×10^9	3.70×10^9	3.46×10^9
$\ln E''$	22.30	22.26	22.03	21.96

RESULTS AND DISCUSSION

From equation (2) listed above, we know that there is a linear relation between $\ln(D/RT)$ and $\ln(E''/\omega)$ for amorphous or semicrystalline

polymers diffusion by small organic molecules. However, in this work, all the diffusion coefficients of disperse dye to modified PET fibers were measured under the condition of 100°C dyeing, so we can regard the temperature as a constant, the frequency used in measuring E'' was 11 Hz, a constant too. So equation (2) could change its form into the following:

$$\ln D = -B \ln E'' + (B \ln \omega + \ln(RT) + C)$$

command: $(B \ln \omega + \ln(RT) + C) = C'$ (another constant), then the equation

$$\ln D = -B \ln E'' + C' \quad (4)$$

was found.

Equation (4) indicates the relationship between diffusion coefficient of small molecules to polymers and their dynamic loss modulus while the test temperature do not change, and the variance of the mobility of polymer chain segments is caused by other structural factors.

In order to investigate the effect of copolymerization modifier on the mobility of polymer chain segments in the modified PET fibers, we made the plot of $\ln D$ versus $\ln E''$ in Fig. 1, and found the points fitted the line well.

By the least square regression of data for $\ln D$ and $\ln E''$, the equation

$$\ln D = -2.28 \ln E'' + 26.81 \quad (5)$$

was found. (regressive coefficient $r=0.99$)

From the curve in Fig. 1 and equation (5), we know that dyeing diffusion coefficient D and loss modulus E'' of monoepoxy compound modified PET fibers measured at 100°C dyeing condition can meet equation (4) well. It shows that equation (2) derived by Bell and Dumbleton can be used in this modified PET fiber system. Comparing equation (5) with equation (4), the constant B in the modified PET fiber system is 2.28, more than 1. This result is in agreement with that reported by Dumbleton et al. to the drawn PET yarn^[3]. In Dumbleton's work, it was

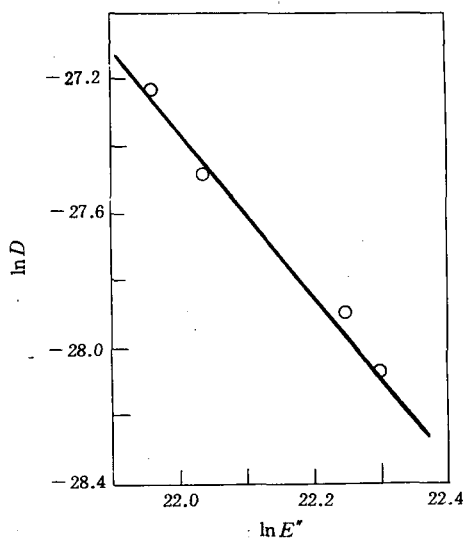
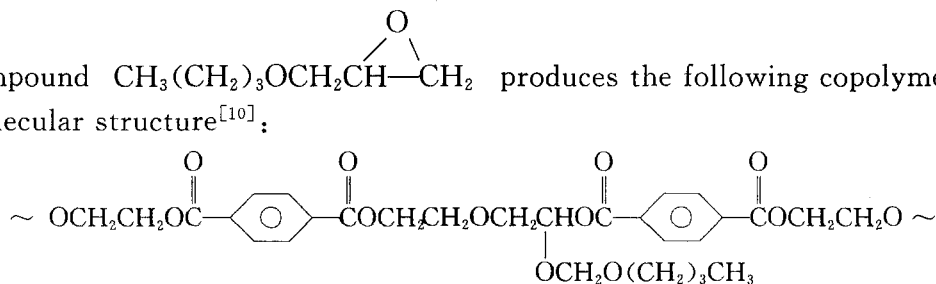


Fig. 1 Relationship between $\ln D$ and $\ln E''$ for monoepoxy modified PET fibers.

found that constant $B=1$ for undrawn, semicrystalline PET fibers, and for the drawn PET samples, B is greater than 1, with a larger value of B for the 4.25X yarn than for the 3X yarn. So it appears that the reason $B>1$ in drawn PET fibers is due to the molecular orientation. From the equation (1) and equation (2), we know that $\ln(D/RT)$ represents the mobility of polymer chain segments and $\ln(E''/\omega)$ represents the steady-state viscosity of polymer. Therefore, we may regard that the constant B is the changing rate of decreasing of the mobility of polymer chain segments with the increasing of the steady-state viscosity of polymer. The molecular orientation in polymer will decrease the mobility of amorphous polymer chains and increase the macromolecular steady-state viscosity due to polymer chain's close and order arrangement and its advantageous effect on increasing secondary force of polymer chains. Consequently, the more the molecular orientation is, the greater the constant B is.

In view of molecular structure, the PET modified with monoepoxy compound $\text{CH}_3(\text{CH}_2)_3\text{OCH}_2\text{CH}-\text{CH}_2$ produces the following copolymer molecular structure^[10]:



It means that the epoxy compound joins the PET main chain by opening epoxy group and introduces an ether bond and a long flexible side chain in PET main chain. Both the ether bond and the side chain are helpful to increase the mobility of copolyester chain segments. It is advantageous to the disperse dye diffusion to the copolyester fibers.

It has to be pointed out that previous investigation about the relation between D and E'' mainly involved the polymer constructional variance caused by the change of test temperature. It means, for the same kind polymer sample, its E'' and D were measured under the different dyeing temperature condition, then the $\ln(D/RT)$ was related to $\ln(E''/\omega)$, as a function of temperature, in order to investigate if these two parameters met the equation (2). The aim of this research was to investigate how the polymer construction and mobility of polymer chain segments were affected by temperature to the same kind polymer material. However, in this work, we have studied the relationship between D and E'' among the modified PET

fibers which contained the same kind, but different amount of modifier, so that we can investigate how the amount of modifier contained in copolyester fibers affects their dyeing diffusion coefficient.

The result of this work shows that dyeing diffusion coefficient D is related to E'' in the way of meeting equation(2) whenever the change of E'' and D was caused by the change of temperature or by the degree of modification in the modified PET fiber system.

Keywords:

Dynamic loss modulus E'' ; Dyeing diffusion coefficient D ; Modified PET fiber

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