Effect of Polymer Microstructure on Dye Diffusion in Polyamide 66 Fibers

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ABSTRACT: Our previous work showed that drawing polyamide 66 (PA 66) fibers at room temperature does not change the degree of crystallinity, but only increases the molecular orientation. We therefore have used a series PA 66 fibers with different draw ratios to establish a direct correlation between (noncrystalline) molecular orientation f_a and the dye diffusion coefficient D. For both acid and disperse dyes, the relationship $\log D \propto f_a^2$ provides reasonable fits to the data for PA 66 fibers, and a similar relationship appears to be applicable to PA 6 fibers. Heat-setting the fibers results in a continuous decrease in diffusion coefficient; unlike PA6 and PET fibers, no minimum in D was found in the region of 160°C. If this decrease in D is attributed to the increase in volume fraction crystallinity X taking place during heat-setting, it must be deduced that $\log D \propto X^6$. This dependence is surprisingly strong, but is consistent with observations we have made on PET and PA6 fibers. It is possible that some other structural rearrangement is partially or largely responsible for the decrease in diffusion coefficient, but Fourier transform infrared, density, and X-ray diffraction measurements do not indicate any other structural changes taking place. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 3803–3807, 2003

Key words: polyamides; dyes/pigments; diffusion coefficient; amorphous orientation; crystallinity; heat setting

INTRODUCTION

The dye diffusion behavior of polyamide fibers depends on microstructure properties. Most polyamide fibers are currently dyed either with acid or disperse dye. Dye diffusion is a thermally activated process and depends on segmental mobility of the amorphous phase, amorphous volume per crystallites, crystallinity, chain folding, and orientation of the amorphous phase. Acid dyes are preferred for dying of polyamides (PA) because of their excellent fastness properties.[1,2] In the case of ionic dyes, dyes are attached to the polyamide fiber by strong ionic interactions. On the other hand, dying of polyamides by disperse dyes is a nonionic process, and dyes interact with the fiber by weak interactions such as hydrogen bonding or van der Walls interactions.[3]

The determination of dye diffusion is usually carried out by measuring the dye concentration in a fiber that has been partially dyed from an infinite dye bath. This measurement has been accomplished by removing the fiber at different time intervals during the dying process, dissolving the dyed fibers in a solvent, and measuring the dye uptake by visible spectroscopy.[4] Determination of the dye diffusion coefficient using nondestructive techniques, such as microspectrophotometry and confocal microscopy,[5,6] has also been attempted.

The effect of microstructure on dye diffusion on fibers is still a controversial and challenging subject. Various structural parameters affect the dye diffusion, and it is difficult to determine the effect of each microstructure property on diffusion behavior. Our previous work revealed that drawing of polyamide 66 (PA 66) fibers does not change the crystallinity and only changes the molecular orientation.[7,8] These results provide an opportunity to develop a correlation between molecular orientation and dye diffusion for PA 66 fibers. Such information could then be used as a basis to interpret the dye diffusion data for polyamide fibers that show changes in both crystallinity and molecular orientation. In this paper we present a study of the microstructure dependence of diffusion of acid and disperse dye in PA 66 fibers.

EXPERIMENTAL

Materials

Commercially drawn PA 66 fibers with draw ratios of 1, 1.5, 2, 2.4, 2.9, and 3.5 were obtained from Solutia and were used for the dye diffusion study. Commercially drawn PA 6 and PET fibers were also obtained from BASF and ENKA. The material was conditioned at 65% relative humidity and 23°C overnight prior to dying. Heat setting was carried out in the oven at 100, 150, and 175°C for 0.5 h. Wet heat setting was carried
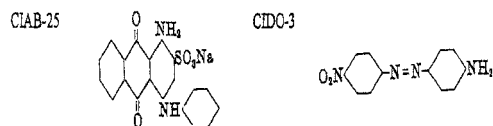
Figure 1 Chemical structures of acid dye (CIAB-25) and disperse dye (CIDO-3).

out at 60°C in water for 1 h. Acid blue dye (CIAB-25), supplied by Ciba-Geigy Inc., and disperse dye CIDO-3, supplied by AAKASH Chemical Inc., were used for dying. Structures of these dyes are shown in Figure 1.

Dying

The infinite dye bath dying was carried out in an Ahiba Texomat apparatus. The pretreated fiber was dyed in 350 mL of dye liquor containing 0.06 g of acid dye or 0.10 g of disperse dye. Acetic acid was used to adjust the pH to 5. Dyed samples were collected at various time intervals and washed in 0.01% Merphol detergent at 60°C for 15 min to remove unfixed residue dye on the surface, followed by rinsing with water at room temperature. Dye uptake was estimated by dissolving. 0.01–0.02 g of dyed fiber in 10 mL of formic acid and measuring the absorbance using the visible spectrum at a suitable wavelength (513 nm for CIAB-25 and 500 nm for CIDO-3) using a spectrometer. The diffusion coefficient was calculated by Hill's method,[9] which measures the dye uptake from the dye bath of the fiber at time intervals t. Hill's equation is as follows
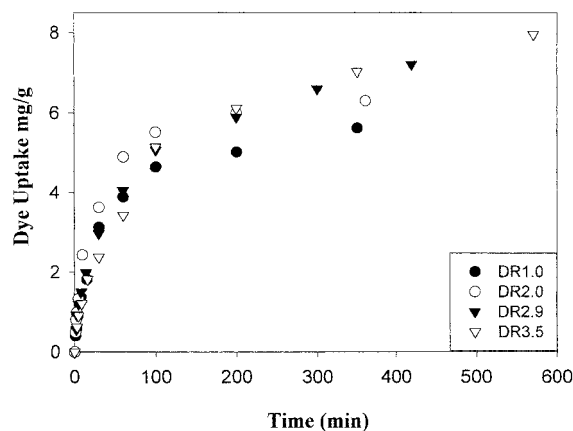
$$C_t/C_\alpha = D\ t/r^2\ \pi$$

where D = diffusion coefficient, C_t = dye uptake at time t, r = radius of the fiber, and t = dying time. Diffusion coefficients were measured in $m^2\ s^{-1}$.

RESULTS AND DISCUSSION

Effect of drawing

All the samples were pretreated at 60°C for 60 min prior to dying to eliminate shrinkage during the

Figure 2 Dye uptake of CIDO-3 versus time for PA 66 fibers drawn to different draw ratios.

dying process. Microstructure characterization was carried out for these fibers and reported elsewhere.[10] Crystallinity, crystallite size, and crystalline and amorphous orientation of these fibers is tabulated in Table I. Dye uptake for disperse dye (CIDO 3) as a function time for different draw ratios is shown in Figure 2. It is apparent that the maximum dye uptake increases slightly with increasing draw ratio. The initial slope of the curve represents the rate of diffusion, which decreases with increasing draw ratio. It is apparent from the data in Table I that crystallite size increases with increasing draw ratio. This increase will decrease the glass transition temperature due to the lower cross-linking effect. The increase in crystallite size at higher draw ratios leads to increase in dye uptake. Dye uptake for acid dye (CIAB 25) as a function of draw ratio is shown in Figure 3. As the draw ratio increases, the rate of diffusion becomes slower. However, the maximum dye uptake is approximately the same for all draw ratios.

Crystallinity measured by density stays constant as draw ratio increases, whereas the crystalline and amorphous orientation increase with increasing draw ratio.[8] Dye diffusion behavior might therefore be expected to be predominantly influenced by changes in the amorphous orientation. Therefore,

TABLE I
Microstructure Characterization of Polyamide 66 Fibers

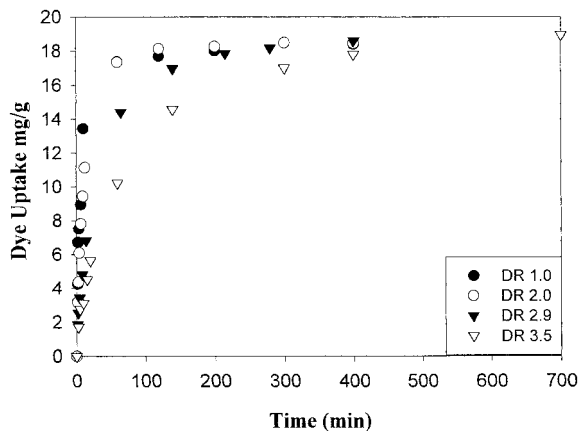| Sample	Crystallinity (X_c)	Crystal Height (^{0}A)	Crystalline Orientation (f_c)	Amorphous Orientatio (f_{am})
DR 1	0.27	18.4	0.15	0.03
DR 2	0.27	27.6	0.38	0.21
DR 2.9	0.27	31.5	0.64	0.38
DR 3.5	0.27	33.1	0.78	0.48
DR 2, Heat set at 100°C	0.28		0.38	0.21
DR 2, Heat set at 150°C	0.32		0.38	0.21
DR 2, Heat set at 175°C	0.34		0.38	0.21

Figure 3 Dye uptake of CIAB-25 versus time for PA 66 fibers drawn to different draw ratios.

we plotted the diffusion coefficient measured for acid and disperse dye against draw ratio in Figure 4, which shows D for both dyes decreasing with draw ratio.To obtain an approximate quantitative relationship between amorphous orientation (f_a) and diffusion coefficient, a plot of log D versus f_a was obtained for both acid and disperse dyes, as shown in Figure 5a. For comparison, similar plots for PET and PA 6 are shown in Figures 5b and 5c for. From these plots, the dependency of amorphous orientation on diffusion coefficient was established. The relationship of log $D \propto f_a^2$ was obtained for PA 66 and PA 6 fibers for both dyes while the relationship of log $D \propto f_a^4$ was obtained for dying of PET by disperse dye. This result suggests that diffusion of disperse dye in PET fibers is more sensitive to amorphous orientation than in PA 66 and PA 6 fibers.

Effect of heat setting

We have shown previously that heat setting of PA 66 fibers results in thermally induced crystallization and
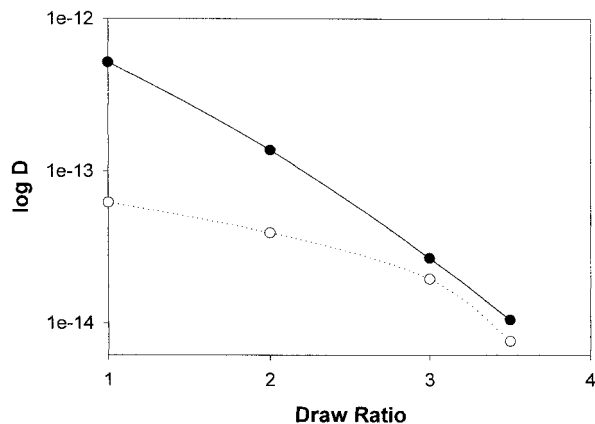

Figure 4 Diffusion coefficient (D) of CIAB-25 (●) and CIDO-3 (○) versus draw ratio for PA 66 fibers.
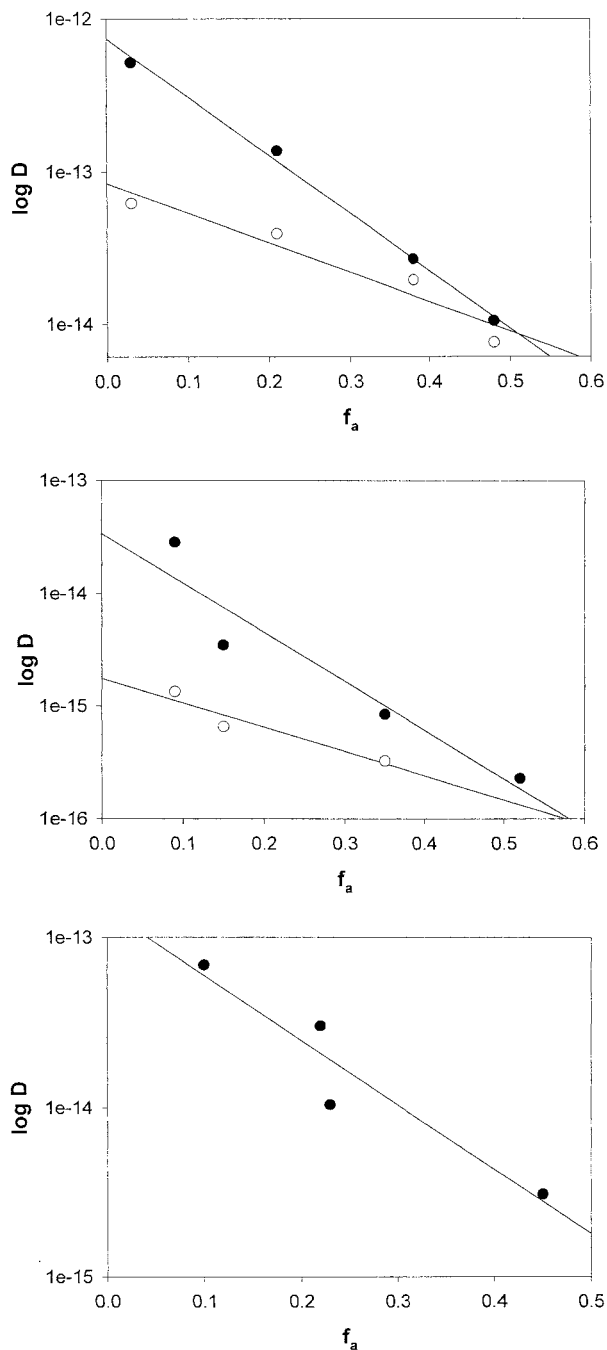

Figure 5 Log D of CIAB-25 (●) and CIDO-3 (○) versus amorphous orientation for (a)PA 66 and (b) PA6 fibers, and (c) log D of CIDO-3 versus amorphous orientation for PET fibers.
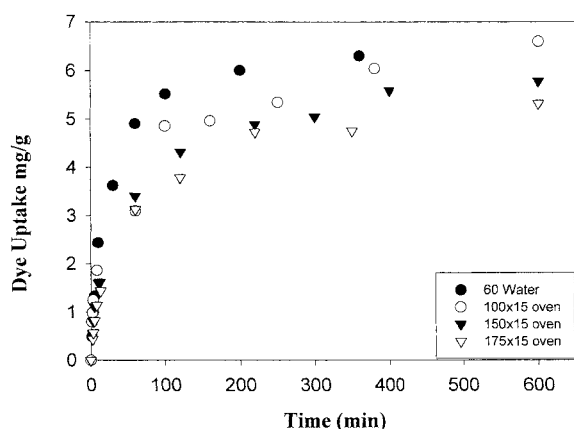
increases the crystallinity of the fiber.[7] Therefore we have heat set PA 66 fibers at 100, 150, and 175°C for 15 min in dry conditions to obtain fibers with different crystallinity. The crystallinity of these samples, measured by density gradient column, is tabulated in Table I. We have also carried out heat setting of PA 66 fibers at 60°C for 1 h under wet conditions. Dye diffusion studies were carried out for all four samples to
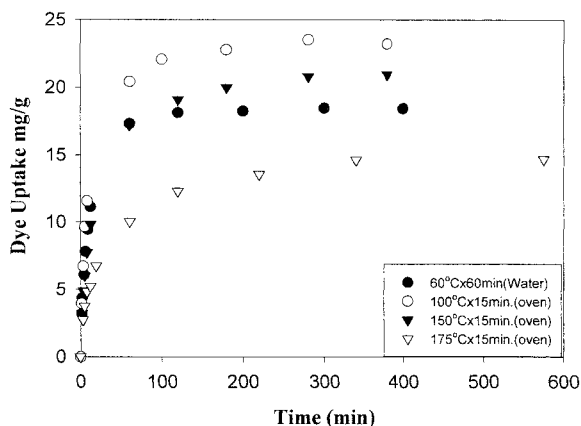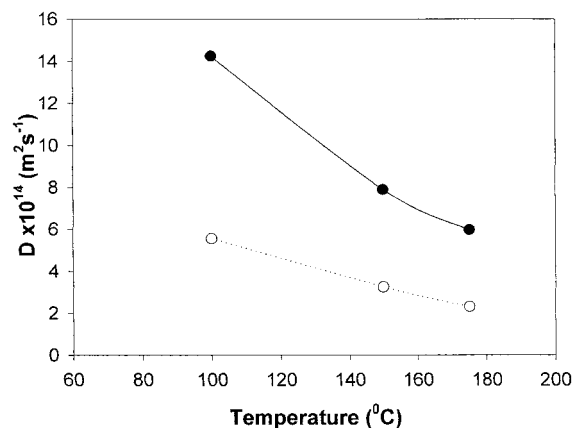
**Figure 6** Dye uptake of CIAB-25 versus time for PA 66 fibers heat set at various temperatures.

Figure 8 Diffusion coefficient (D) of CIAB-25 ($\bullet$) and CIDO-3 ($\circ$) versus heat set temperatures for PA 66 fibers.

determine the effect of crystallinity on dye diffusion behavior.

The dye uptake for acid dye as a function of different heat setting temperatures is shown in Figure 6. It is apparent from Figure 6 that the maximum dye uptake decreases with increasing heat setting temperature. The sample heat set at 60°C in water gives the maximum uptake, somewhere between the PA 66 fibers heat set at 150 and 175^7°C under dry conditions. The dye uptake of disperse dye with time for different heat set samples is shown in Figure 7. The maximum uptake also depends on heat setting temperature but this is less pronounced in the case of disperse dye than acid dye. Published data indicate that a plot of diffusion coefficient versus heat set temperatures shows a minimum at 160^0 C for PET[3]. Similar plots have also been observed for PA 6 fibers. The plot of diffusion coefficient versus heat set temperatures for PA 66 fibers is shown in Figure 8. The results shows no minimum at 160°C, only a continuous decrease in diffusion coefficient with increasing heat-setting temperature.

Inter-crystalline tie segments estimated from various microstructure properties were shown to have large impact on dye diffusion of PET fibers. It has been shown that thermal treatment of PET fibers at temperature between 200°C and melting point causes a substantial increase in the fraction of adjacent crystal chain folds.[11] Chain folding may therefore play a major role in the reduction of tie segments and resulting increase in D at high temperatures. Competition between reduction of tie segments and increase in crystallinity is responsible for the minimum at 160°C for PET and PA 6 fibers. We have recently shown that the band at 1224 cm^{-1} in the infrared spectrum could be used to quantify the chain folding in PA 66 fibers. Because chain folding was not detected in the heat-treated PA 66 fibers, we can conclude that crystallinity may the only factor controlling the dye diffusion in PA 66 fibers.

The diffusion coefficients measured for both acid and disperse dyes are plotted against crystallinity in Figure 9a. Both coefficients show a linear decrease with increasing crystallinity. The relationship of log D $\propto X^6$ was obtained for PA 66 fibers for both dyes. For comparison, a similar plot was obtained for PET (see Figure 9b). This plot provided the relationship of log D α X.[9] This observation suggests that crystallinity affects the dye diffusion of PET fibers much more than that of PA 66 fibers. In both cases, the apparent effects of crystallinity on diffusion coefficient are surprisingly high, and we cannot discount the possibility that some other structural rearrangement, possibly involving the entanglement density and void structural changes, is partially or largely responsible for the decrease in diffusion coefficient.

Figure 7 Dye uptake of CIDO-3 versus time for PA 66 fibers heat set at various temperatures.

CONCLUSIONS

Dye diffusion of PA 66 fibers drawn to different draw ratios and heat set at different temperatures
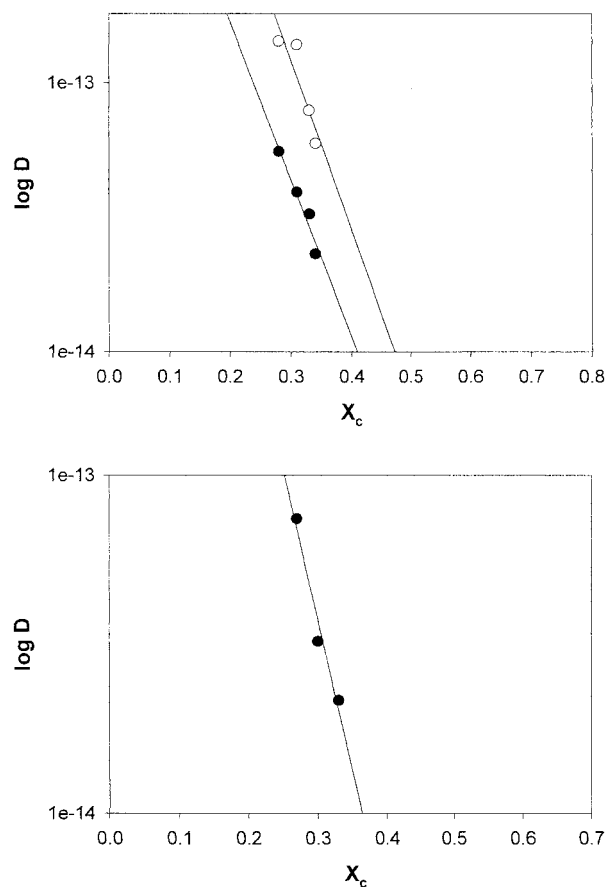
Figure 9 (a) Log *D* of CIAB-25 (○) and CIDO-3 (●) versus crystallinity for PA 66 fibers. (b) Log *D* of CIDO-3 versus crystallinity for PET fibers.

were investigated using acid and disperse dyes. A rigorous correlation between microstructure and diffusion coefficient was established for the first time for PA 66 fibers. We found a sharp decrease in diffusion coefficient with increasing draw ratio that was attributed to increasing amorphous orientation, f_a. Heat setting of PA 66 fibers showed increase in crystallinity and no change in amorphous orientation. We found that the influence of thermally induced crystallinity on diffusion coefficient was exceptionally strong. We concluded that in addition to crystallinity changes something else may be contributing to the reduction of diffusion coefficient.

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