Dependence of disperse dye diffusion on the structure and morphology of oriented heat-set polyester fibres

J Radhakrishnan†, U P Kanitkar and V B Gupta*

Dept of Textile Technology, Indian Institute of Technology, New Delhi 110 016, India

†*Dept of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1 O-Okayama, Meguro-ku, Tokyo 152, Japan*

The structural parameters that predominantly influence dye diffusion behaviour in heat-set polyester fibres have been identified. Dye diffusion has been shown to depend on two factors: the volume of the accessible region (amorphous region) and the tortuosity of the dye diffusion path. The accessible region can be represented in terms of the amorphous volume per crystal, and the tortuosity can be expressed quantitatively by combining the orientation of the amorphous phase and the nature of coupling between the amorphous and the crystalline regions. An integrated model has been proposed by combining these parameters, and has been shown to correlate well with dye uptake in polyester fibres heat-set under slack and taut conditions.

INTRODUCTION

The role played by the structure and morphology of polyester on its dye diffusion behaviour has been well documented. Several attempts have been made to establish qualitative and quantitative correlations between dye diffusion on the one hand, and the structure and morphology of polyester on the other. A common feature observed for annealed polyester in these works is that the dye uptake decreases initially as the annealing temperature increases and shows a minimum at a temperature range of 180–200°C and then increases with rising annealing temperature, which is in accordance with the observation made by Marvin [1].

Dumbleton and Murayama suggested that the dye uptake in polyester is controlled by the number of crystals present and the orientation of the amorphous phase [2]. This is based on the fact that the dye diffusion depends on the segmental mobility of the amorphous region, which in turn depends on the order in this region and the number, size and size distribution of the crystallites. Huisman and Heuvel proposed a qualitative description of the dye uptake behaviour of polyester by suggesting that the dye uptake of a yarn is controlled by two structural parameters: the total amount of amorphous material and volumes of the individual amorphous regions [3].

A quantitative correlation was attempted by Vassilatos *et al.* to explain dye uptake behaviour of structurally varying high-speed-spun polyester fibres [4]. They suggested that dye uptake is controlled by the combined effect of the free volume of the amorphous regions per crystallite and the tortuosity of the diffusional path suggested by Peterlin [5]. The free volume was represented by the amorphous volume per crystal V_a (Eqn 1):

$$V_a = \frac{V(1-X_c)}{X_c} \quad (1)$$

where V is the mean volume of a crystal and X_c the degree of crystallinity, suggested by Dumbleton and Murayama [6]. Tortuosity T is was represented by Eqn 2:

$$T = \frac{1-f_a}{f_a} \quad (2)$$

where f_a is the Hermans orientation factor of the amorphous region.

The modified free volume obtained by multiplying free volume and tortuosity was found to correlate with the relative dye uptake.

Previous studies carried out in this laboratory on polyester fibres heat set at different temperatures have provided support to the Williams–Landel–Ferry (WLF) model of the temperature-dependence of diffusion, which indicates that dye diffusion may be related to the segmental mobility in the non-crystalline regions of the fibre [7]. The porosity of the fibre, i.e. the number, size and size distribution of the holes existing in the matrix, can also affect dye uptake [8].

In the present study an attempt has been made to identify the free volume and degree of accessibility (tortuosity) from various structural parameters, and to propose a more comprehensive model which quanti-

*To whom any correspondence should be addressed

tatively correlates the dye diffusion in heat-set polyester yarns with fibre structure. Extensive structural characterisations have been carried out in this laboratory over the years on polyester fibres heat set under taut and slack conditions, which allowed very accurate data to be used in this study. We selected two heat-setting conditions and a wide range of heat-setting temperatures to represent the lower and upper regions of the temperatures used in industrial operations. This gave samples with a wide spectrum of structure and morphology so that a generalised correlation could be obtained.

EXPERIMENTAL

Sample preparation

The starting material was a drawn commercial multifilament polyester yarn, 84.3 dtex, 36 filaments, zero twist. It was produced on an industrial unit by melt spinning of fibre-grade polyester chips at 290°C at a take-up speed of 800 m/min. The as-spun yarns were stretched to a draw ratio of 3.92 on a draw twister with a top godet temperature of 140°C and a winding speed of 642 m/min. This sample will be referred to as the control. Heat setting of this yarn was done in a silicone oil bath at temperatures of 100, 180, 195, 210, 230 and 250°C for 5 min under two conditions, i.e. when the sample was held at a constant length (designated as TA or taut annealed) and when the sample was allowed to shrink during the heat setting (designated as FA or free annealed). After heat setting the samples were allowed to reach the ambient temperature and then washed thoroughly with carbon tetrachloride to remove the silicone oil. They were then dried and stored in a conditioned laboratory.

Dyeing experiments

The control and various heat-set samples were dyed with CI Disperse Red 11 under infinite dye bath conditions (for 5, 20, 30, 45, 75, 150 min and 24 h at 130°C and liquor ratio 1000:1). The amount of dye on the fibre was measured spectrophotometrically. The relative dyeing rate was determined using a method described by Frankfort and Knox [9]. This involved taking the initial slope of the plot of percentage of dye present in the filament versus the square root of the dyeing time, as a measure of the dye diffusion coefficient. The relative dyeing rate R was then obtained by normalising the dyeing rate in respect to a commercially drawn yarn of 2.34 dtex per filament and having a density of 1.38 g/cm^3 (Eqn 3):

$$R = \frac{R_d d}{2.34} \times \frac{1.38}{\rho} \times \frac{100}{100 - B} \qquad (3)$$

where R_d is the measured disperse dyieng rate, d = filament linear density (dtex) per filament, ρ is the sample density and B the yarn boil-off shrinkage. The relative dyeing rate is for practical purposes independent of the surface-to-volume ratio of the dyed filaments and reflects differences in filamentary structure affecting the diffusion.

Boil-off shrinkage

The boil-off shrinkage B of different samples was measured by immersing the samples in boiling water (100°C) for 5 min, after which they were removed and allowed to come to room temperature under ambient conditions (Eqn 4):

$$B = \frac{L_0 - L_S}{L_0} \qquad (4)$$

where L_0 is the initial length and L_S is the length after shrinkage.

X-ray diffraction studies

X-ray diffraction studies were made to measure the crystallinity and crystal size of the samples. The half-widths β of the (010), (100) and ($\bar{1}$05) scans were used to obtain the crystal size (t_{hkl}) from Eqn 5:

$$t_{hkl} = \frac{0.89\lambda}{\beta \cos\theta_{hkl}} \qquad (5)$$

where λ is the wavelength of the X-rays, t_{hkl} is the crystal dimension perpendicular to the (hkl) plane and θ_{hkl} is the Bragg angle for this plane. Corrections due to instrumental broadening were estimated and found to be negligible. Crystal volume was estimated by taking $t_{(010)}$ and $t_{(100)}$ as the two sides of the crystal and $t_{(\bar{1}05)}$ as its length.

Amorphous orientation factor

To obtain accurate values of amorphous orientation factor f_a, the attenuated total reflection (ATR) infra-red technique was used. Details of the method used are given elsewhere [10].

Coupling between amorphous and crystalline regions

The coupling parameters (series and parallel) were estimated using an indirect method based on Takayanagi's model [11]. Details of the method used are given elsewhere [12].

RESULTS AND DISCUSSION

Dye uptake behaviour

Figure 1 describes the relative dyeing rate as a function of heat-setting temperature for FA and TA samples. In both the cases the relative dyeing rate showed the usual trend of passing through a minimum at a heat-setting temperature of 180°C. FA samples exhibited higher relative dyeing rates.

Physical and structural characteristics

Table 1 summarises the physical and structural characteristics of the various samples investigated. These

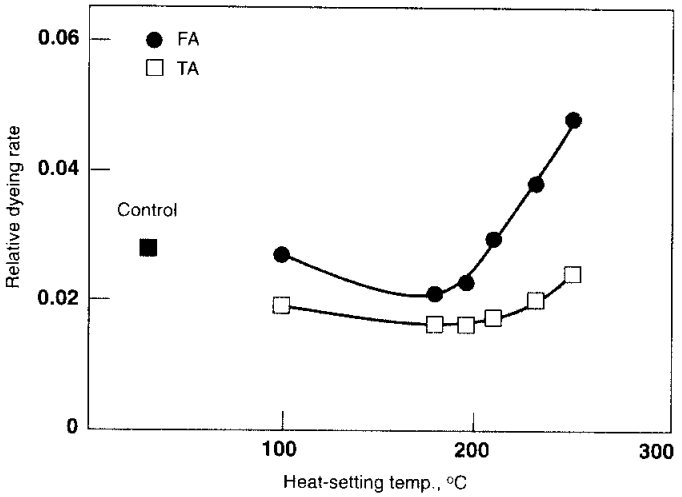

Figure 1 Relative dyeing rate as a function of heat-setting temperature for FA and TA samples

Table 1 Physical and structural characteristics of samples studied

Sample	B (%)	X_c	$t_{(100)}$ (Å)	$t_{(010)}$ (Å)	$t_{(\bar{1}05)}$ (Å)	f_a	σ^a	ϕ^b
Control	7.2	0.34	30.4	41.2	68.9	0.582	0.41	0.83
100FA	3.3	0.42	31.0	42.3	69.3	0.522	0.48	0.87
140FA	1.2	0.45	31.6	44.6		0.505	0.78	0.57
180FA		0.47	35.1	53.2	77.1	0.430	0.91	0.52
195FA		0.49	38.5	56.0	81.0	0.365	1.00	0.49
210FA		0.51	41.0	60.0	84.0	0.300	1.00	0.51
220FA		0.52	43.6	63.4	85.5	0.258	1.00	0.52
230FA		0.55	50.4	71.7	87.5	0.200	1.00	0.55
240FA		0.57	53.8	74.9	89.1	0.156	1.00	0.57
250FA		0.59	57.6	82.4	90.2	0.039	1.00	0.59
100TA	7.2	0.39	31.0	43.4	72.0	0.519	0.38	0.87
140TA	4.5	0.42	32.3	47.1	71.0	0.494	0.53	0.83
180TA	2.1	0.47	33.6	50.0	78.0	0.470	0.61	0.79
195TA	1.6	0.49	37.5	54.0	82.5	0.455	0.64	0.77
210TA	1.1	0.51	40.0	59.0	89.5	0.440	0.68	0.76
220TA	1.0	0.52	42.4	63.4	90.0	0.433	0.70	0.75
230TA	0.6	0.52	44.8	65.0	92.0	0.416	0.81	0.74
240TA	0.5	0.57	46.1	68.7	93.7	0.369	0.83	0.74
250TA	0.2	0.58	47.4	71.7	97.0	0.318	0.85	0.74

a σ – series coupling parameter
b ϕ – parallel coupling parameter

samples represent a wide range of structures and morphologies. Some noteworthy features include:

(a) There were no significant differences in the crystallinities of FA and corresponding TA samples
(b) Crystal size increased linearly with increase in heat-setting temperature
(c) The amorphous orientation factor of FA samples decreased drastically at higher heat-setting temperatures, whereas the TA samples showed relatively little reduction as the heat-setting temperature was increased.

The series and parallel coupling parameters, which provide a measure of the mode of arrangement of the crystalline and amorphous phases in the fibres, were also estimated indirectly and are included in Table 1. The boil-off shrinkage of FA samples was lower than that of the corresponding TA samples. At higher heat-setting temperatures the values of B of TA and FA samples were low, indicating that the residual stress in these samples was relaxed to a significant extent.

The effect of heat setting on the structure of polyester fibres has already been discussed in detail elsewhere [10,12–16], and only those structural changes that are relevant to the present study will be discussed in this article

Amorphous volume per crystal

As mentioned earlier, the volume of the amorphous region is an important factor in controlling the dyeing behaviour. In the present study the amorphous volume per crystal was estimated using the method suggested by Dumbleton and Murayama [6] (Eqn 1). They observed an initial decrease in amorphous volume with increase in annealing temperature. In order to check the correlation between amorphous volume per crystal and dye uptake, the former was plotted against the relative dye uptake for both FA and TA samples (Figure 2). Most of the points lie on a straight line indicating a correlation, in that the dye uptake increases with the increase in the volume of the accessible region. The control sample and the samples annealed at low temperatures (FA 100 and TA 100), however, did not follow this trend. This was apparently because they could undergo significant structural changes in the dyebath, and hence it was considered advisable not to include the data on these samples. A least-square fit of the data when considered individually for FA and TA samples showed a correlation coefficient of about 0.94, whereas when considered together the correlation coefficient was 0.78.

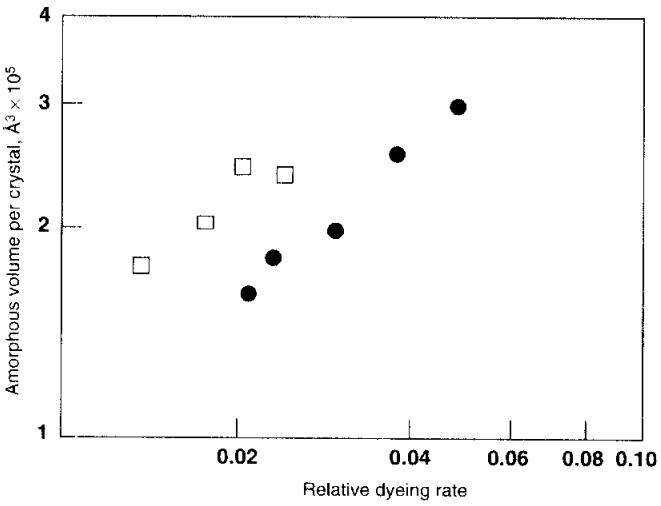

Figure 2 Relationship between relative dyeing rate and amorphous volume per crystal for TA and FA samples (for key see Figure 1)

There are two noteworthy points about this data. Firstly the amorphous volumes per crystal of TA and FA samples did not differ significantly, whereas the dye uptake values showed considerable differences. Secondly the two sets of samples stand out as different populations. These observations indicate that though amorphous volume per crystal is a major factor in controlling the dye uptake, it alone does not explain the dye uptake behaviour of structurally different annealed polyester samples. This suggests that some additional structural parameters need to be considered.

Modified amorphous free volume

The role of the tortuosity of the dye diffusion path in controlling dye uptake has been recognised by many authors [2,5,17,18]. Peterlin has suggested that as the orientation in the amorphous region increases, the dye diffusion path becomes tortuous [5]. This is because the direction of all diffusional paths in the amorphous region is not radial but more circuitous, owing to amorphous orientation. Huisman and Heuvel have stated that the amorphous orientation has a second-order effect on dye diffusion behaviour [8]. According to them the molecules in the amorphous region are likely to relax towards an equilibrium value instantaneously in the dyebath. In other words, only in those cases where amorphous orientation in the fibre is lower than the equilibrium value corresponding to the dyeing conditions applied can the amorphous orientation have an effect on the dye uptake of a fibre. In the case of fibres heat set at higher temperatures, the molecules in the amorphous region are likely to relax to the equilibrium value before entering into the dyebath. Recently Toda *et al.* related dye diffusion in polyester to amorphous density, and showed that the state of the amorphous phase has an important role in controlling dye uptake [19].

Vassilatos *et al.* quantified the tortuosity factor by using Eqn 2 [4]. They suggested a modified free volume that was obtained as a product of amorphous volume per crystal multiplied by the tortuosity factor [5]. The modified accessibility factor so obtained correlated well with the relative dye uptake in high-speed-spun fibres. In the present case such an analysis was attempted for the samples investigated. The modified accessibility factor data for both TA and FA samples are plotted against relative dye uptake in Figure 3. With the introduction of the tortuosity factor, the results for the TA and FA samples showed greater similarity. Here also, taken individually, a linear relationship with a correlation coefficient of 0.96 was observed, but when considered together the correlation coefficient dropped to 0.91.

In order to improve the correlation further, we examined the influence of other structural and morphological parameters that might influence dye diffusion. We have so far considered the amorphous orientation as the major factor in determining the tortuosity of the dye diffusion path. In a semi-crystalline material the location of the amorphous region with respect to the crystalline phase can also play an important role in determining the tortuosity of the dye diffusion path. This aspect is considered below.

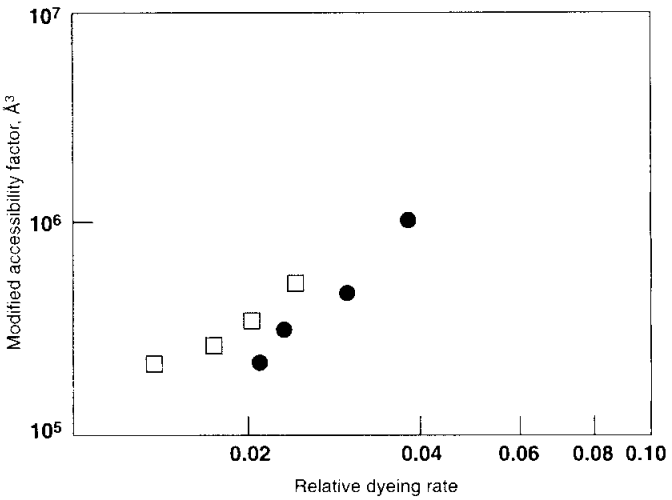

Figure 3 Relationship between relative dyeing rate and modified accessibility factor (MAF) for TA and FA samples (for key see Figure 1)

Effect of morphology on tortuosity

It has been shown that the two-phase model, with the amorphous and crystalline regions arranged vertically in series along the fibril, does not represent the morphology of polyester fibres heat set at high temperatures under slack and taut conditions [20]. It had also been shown that considerable amounts (30%) of the amorphous material may be located outside the fibril [3,20]. Hence the coupling of the two phases is more appropriately described in terms of a series/parallel model rather than a series model. In this scenario the dye molecules have to pass through a more tortuous path to reach the interfibrillar amorphous materials. The path will be more tortuous if the coupling is predominantly parallel.

Coupling parameters for the present samples were determined using an indirect method and are given in Table 1. It can be seen that in the samples which had been annealed in the slack state at higher temperatures, series coupling predominated, while the corresponding TA samples had a significant degree of parallel coupling superimposed on the series coupling.

Since these arrangements can influence dye diffusion in FA and TA samples, the modified accessibility factor was corrected to take account of this factor by multiplying it by the ratio of the series/parallel coupling parameter, leading to the new proposed accessibility factor, which has been plotted for the FA and the TA samples against the relative dye uptake in Figure 4. Now the points fall on a straight line, indicating a linear relationship between dye diffusion and the structural factors considered. The correlation coefficient was 0.98. This indicates that the tortuosity of the dye diffusion path is more appropriately represented by the combination of amorphous orientation and the type of coupling between the amorphous and crystalline regions.

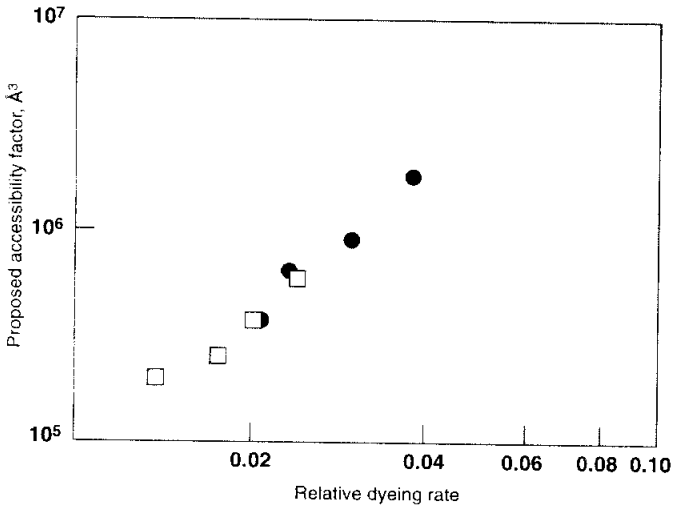

Figure 4 Relationship between relative dyeing rate and proposed accessibility factor (PAF) for TA and FA samples (for key see Figure 1)

CONCLUSIONS

Some structural parameters affecting dye diffusion behaviour in polyester fibres heat set under slack and taut conditions have been identified. It was found that dye diffusion in heat-set polyester fibres is controlled by two factors: the volume of the accessible region (amorphous region) and the tortuosity of the dye diffusion path. While the accessible region was well represented by the amorphous volume per crystal, tortuosity could be expressed quantitatively by combining the orientation of the amorphous phase and the type of coupling between the amorphous and the crystalline regions. An integrated model is proposed in which these parameters are combined. This was found to correlate well with dye uptake in polyester fibres heat set under slack and taut conditions.

* * *

The authors are extremely grateful to Dr C J M van den Heuvel of Akzo Nobel Central Research BV at Arnhem for the data on t_{105}.

REFERENCES

1. D N Marvin, *J.S.D.C.*, **70** (1954) 16.
2. J H Dumbleton, J P Bell and T Murayama, *J. Appl. Polymer Sci.*, **12** (1968) 2491.
3. R Huisman and H M Heuvel, *J. Appl. Polymer Sci.*, **22** (1978) 943.
4. G Vassilatos, B H Knox and H R E Franfort in *High speed fiber spinning: science and engineering aspects*, Ed. A Ziabicki and H Kawai (New York: John Wiley, 1985) 389.
5. A Peterlin, *J. Macromol. Sci.–Phys.*, **B11** (1) (1987) 57.
6. J H Dumbleton and T Murayama, *Kolloid Z. fur Polymere*, **220** (1967) 41.
7. V B Gupta, A K Gupta, V V P Rajan and N Kasturia, *Text. Res. J.*, **54** (1984) 54.
8. A K Kulshreshta, M V S Rao and N E Dweltz, *J. Appl. Polymer Sci.*, **30** (1985) 3423.
9. H R E Frankfort and B H Knox, USP 4 134 882 (1979).
10. A K Jain and V B Gupta, *J. Appl. Polymer Sci.*, **42** (1990) 2931.
11. M Takayanagi, K Ikeda and T Kajiyama, *J. Polymer Sci.*, **C15** (1966) 263.
12. V B Gupta, C Ramesh and A K Gupta, *J. Appl. Polymer Sci.*, **29** (1984) 3115.
13. V B Gupta and Satish Kumar, *J. Appl. Polymer Sci.*, **26** (1981) 1865.
14. V B Gupta and Satish Kumar, *J. Appl. Polymer Sci.*, **26** (1981) 1877.
15. V B Gupta and Satish Kumar, *J. Appl. Polymer Sci.*, **26** (1981) 1885.
16. V B Gupta and Satish Kumar, *J. Appl. Polymer Sci.*, **26** (1981) 1897.
17. J Andriessen and J van Soest, *Textilveredlung*, **3** (1968) 618.
18. V B Gupta, M Kumar and M Gulrajni, *Text. Res. J.*, **45** (1975) 463.
19. T Toda, H Yoshida and K Fukunishi, *Sen-i Gakkaishi*, **12** (1994) 599.
20. C Ramesh, V B Gupta, J Radhakrishnan and C J M van den Heuvel, Unpublished work.