The Effect of Phenol and Biphenyl on the Properties of Poly(ethylene Terephthalate) Film

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Synopsis

Evidence is presented which justifies the use of the dyeing transition temperature (T_D) instead of the glass transition temperature (T_g) as a reference temperature when using the WLF equation to describe the carrier dyeing of polyester film. Changes in the properties of the substrate caused by the effect of "carriers" on the molecular structure of the polymer have also been detected and a connection between the location of T_D and chain folding is suggested from IR measurements.

INTRODUCTION

The use of special dyebath assistants or "carriers" which increase the rate of diffusion of dyes into hydrophobic fibers is well established. The mechanism by which "carriers" act involves plasticization of the fiber, and the increased rate of diffusion of dye resulting from their use conforms to the Williams, Landells, and Ferry (WLF) equation for the variation of the viscoelastic properties of amorphous polymers with temperature.[1] Using this equation, it has been demonstrated that the reduction of the glass transition temperature (T_g) of the fibers caused by the carrier is equivalent to the effect of a corresponding rise in the temperature of a similar dyebath without the carrier. The equation was used in the form

$$-\ln a_T = \ln \frac{D_T}{D_{T_g}} = \frac{A(T - T_g)}{B + (T - T_g)} \tag{1}$$

where a_T is the shift factor for the viscoelastic properties of the fiber, A and B are constants, and D is the diffusion coefficient at the temperature indicated by the subscript.

Results from the dyeing of both acrylic and polyester substrates have been treated in this way, but there were difficulties in locating the T_g of the polyester films when they were immersed in solutions of carrier.

The very small change in dimensions of the polyester film with temperature precluded the use of the mechanical method employed for the determination of the T_g of acrylic filaments,[1] and consequently, an alternative reference temperature had to be used.

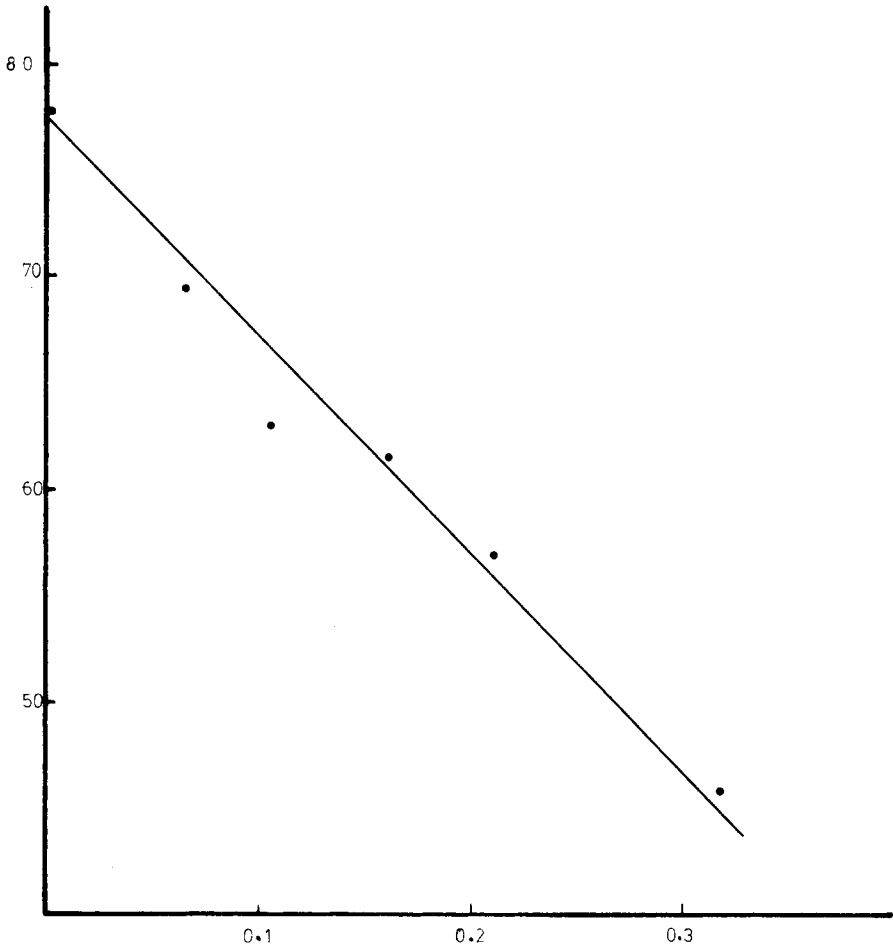If the rate of diffusion of dye into the substrate is controlled by the seg-

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Fig. 1. Effect of phenol concentration on dyeing transition temperature T_D of C.I. Disperse Orange 3, dyed on poly(ethylene terephthalate) film: x-axis, Phenol Concentration used in the pretreatment (mole/l.); y-axis, dyeing transition temperature T_D (°C).

mental mobility of the polymer chains, a marked increase in the rate of diffusion of dye into the fiber is to be expected as the temperature passes through the T_g. Such an increase in dyeability can be located for both acrylic fibers and poly(ethylene terephthalate) substrates; for the acrylic fibers, it occurs at a temperature close to the experimentally determined T_g.[1,2] The temperature at which the dyeing properties change is referred to as the "dyeing transition temperature," and it is this temperature which was tentatively assumed to be a satisfactory replacement for the T_g as a reference temperature in eq. (1). However, the dyeing temperature range covered and the number of results obtained for poly(ethylene terephthalate) films was small in the previous investigations. Therefore, the first aim of the work described here is to justify the use of T_D as an alternative to T_g in eq. (1) when proving that the enhanced dyeing of poly(ethylene terephthalate) in the presence of carriers is governed by the fluid-like mobility of the polymer chains.
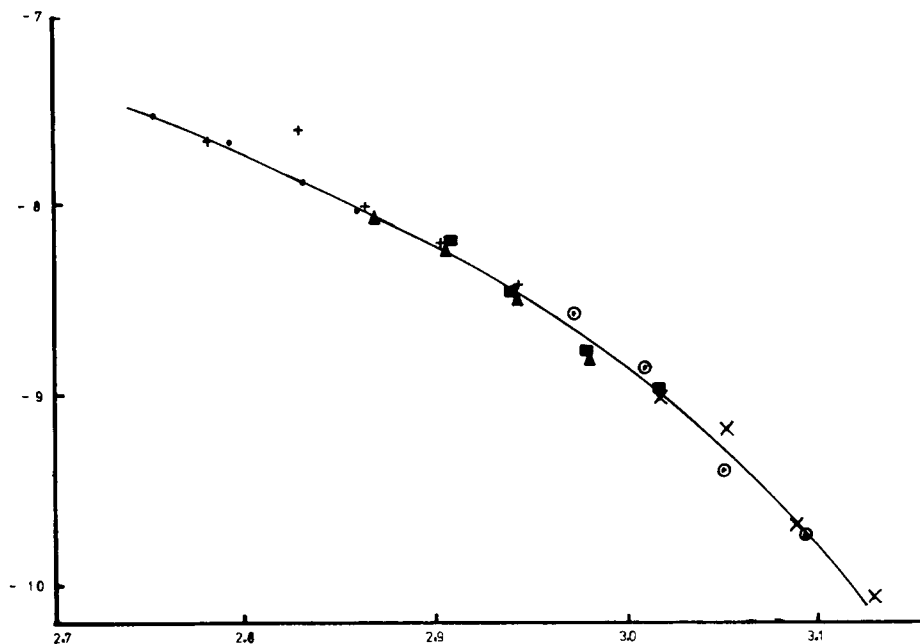
Fig. 2. Superimposition of $\log_{10}D$ for C.I. Disperse Orange 3, onto a common curve: x-axis, $\log_{10}(D_T)$ (cm^2/min); y-axis $(1/T) \times 10^3$ (°K^{-1}); (×) dyeings in water; (⊙) dyeings in water 0.05 mole/l. phenol; (■) dyeings in water 0.10 mole/l. phenol; (▲) dyeings in water 0.16 mole/l. phenol; (+) dyeings in water 0.21 mole/l. phenol; (●) dyeings in water 0.32 mole/l. phenol.

The Influence of Carriers on the Molecular Structure of the Substrate

One of the essential steps in the application of eq. (1) to carrier dyeing was to condition the substrate in an aqueous solution of the carrier before dyeing. This provided a uniform distribution of the carrier in the substrate at the outset and ensured that the results were not influenced by the relative rates of diffusion of carrier and dye, respectively. Previous workers[3,4] have demonstrated that the carrier may diffuse ahead of the dye or that the diffusion front of the dye may move simultaneously with that of the carrier. If the former situation exists, then the rate-controlling step of the dyeing process will be the diffusion of the dye through the substrate, so long as the plasticization of the substrate by the carrier rapidly reaches an equilibrium state. If the alternative situation exists, then the rate of diffusion of dye will be influenced by the changing situation in the substrate at the diffusion front. Consequently, when making quantitative measurements of dye diffusion, conditioning the substrate in the carrier solution before dyeing is the best which can be done to ensure that the dye is moving through a physically stable environment. Unfortunately, by adopting this procedure, other associated and important aspects of carrier action may be overlooked. Molecular relaxation processes and crystallization are likely to be encountered in any treatment which enhances the segmental mobility of the polymer chains. It is well known that significant changes in the morphology and dyeing properties of poly(ethylene terephthalate) substrates can occur when they are subjected to
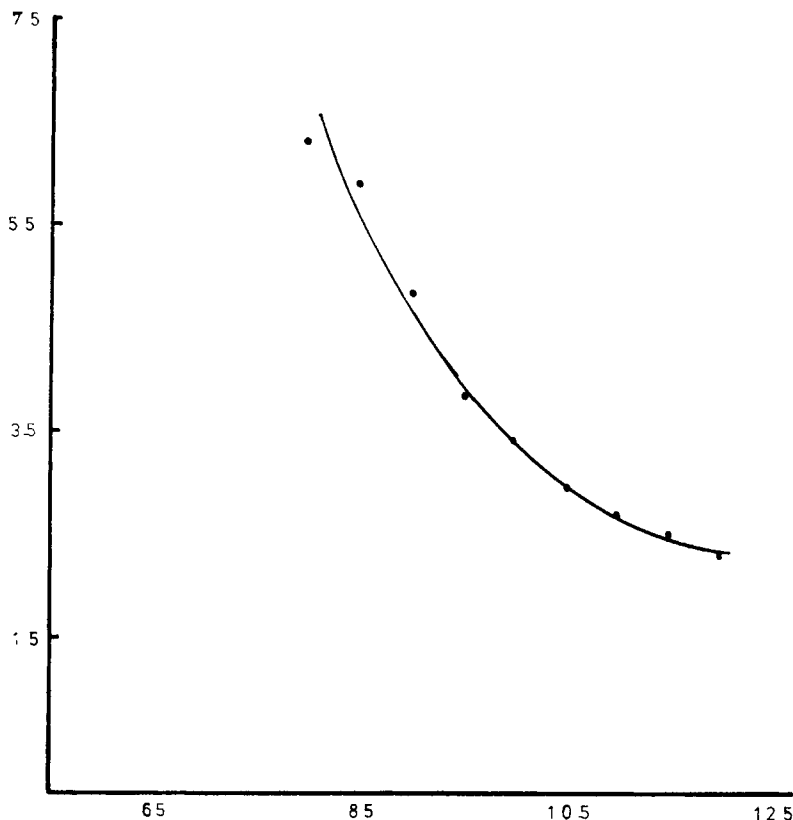
Fig. 3. Variation of activation enthalpy of diffusion of C.I. Disperse Orange 3 into poly(ethylene terephthalate) film with temperature (derived from Fig. 2): x-axis, ΔH (k cal/mole); y-axis, temperature (°C).

heat treatments or immersed in some solvents. Plasticizing agents are also known which induce crystallisation.[5]

The Effect of Carriers on the Molecular Structure of Poly(ethylene Terephthalate)

Attempts have been made to determine whether or not the effects of carriers on the dyeing and physical properties are reversible. The results favor the conclusion that the properties never revert back completely to their former state on removal of the carrier. The extraction of the carrier has been carried out using hot water,[6] ice-cold acetone,[6,7] and refluxing under acetone[8] for a few hours. Total extraction of o-phenylphenol from poly(ethylene terephthalate) requires up to 40 hr immersion in hot acetone.[9] There are, therefore, two difficulties inherent in these experiments. If the temperature of the extraction process has been below the T_g of the polymer, it is not certain whether all the carrier has been completely removed within the extraction times used. On the other hand, if the temperature of the extraction process is raised above the T_g, there is a danger that the extraction process itself may have caused additional changes in the substrate.
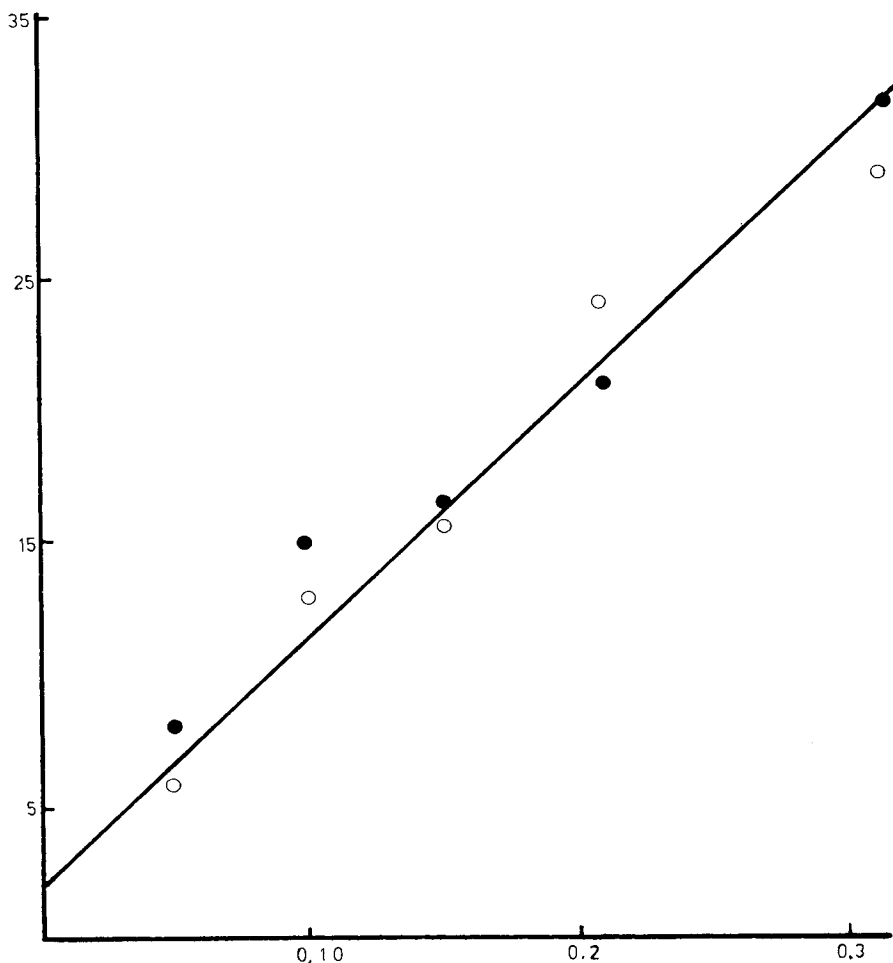
Fig. 4. Variation of T_D (ΔT_D) for C.I. Disperse Orange 3 and T_g (ΔT_g) with concentration of phenol used: x-axis, concentration of phenol (mole/l.); y-axis, ΔT_g and ΔT_D; (●) ΔT_D; (○) ΔT_g.

It is, therefore, clear that the study of pretreated samples[1] can demonstrate only how variations in the glass transition temperature affect the dyeing behavior.   It cannot show if changes in dyeing properties occurr due to simultaneous morphological alterations under the commercial conditions of carrier dyeing where carrier and dye are applied simultaneously.

The second aim of this publication is, therefore, to produce evidence showing that structural changes in the polyester substrate take place during the action of carriers which influence the dyeing properties.

EXPERIMENTAL

Substrate.   Polyester films (Melinex Type 442, I.C.I.) were used.   They contained no additives and were approximately 12 μ thick.

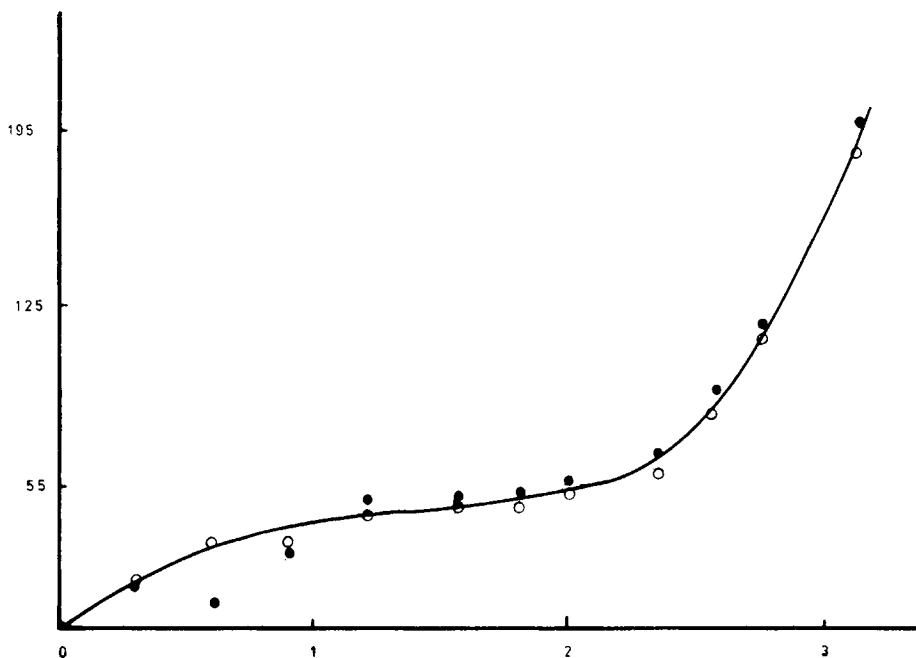**Carriers.**   Phenol (AR Grade) and Diphenyl (Tumescal D, I.C.I.) were used.

Fig. 5. Rate of dyeing of C.I. Disperse Orange 3 on poly(ethylene terephthalate) film at 95°C: x-axis, dye on film (mg dye/g film); y-axis, $\log_{10}t$ (min).

Dyes. CI Disperse Orange 3 was used after purification by hot-water extraction of the commercial powder and by successive crystallizations from toluene until a constant melting point of the product was obtained (218°C).

Examination of the Effect of Carriers on the Dyeing Properties of Poly(ethylene Terephthalate) Film. The pretreatments of the poly(ethylene terephthalate) film in aqueous solutions of carrier, the subsequent dyeing experiments from an infinite dyebath, calculation of the diffusion coefficients of the dye, and determination of the dyeing transition temperatures were carried out in exactly the same manner as described elsewhere.[1] The thickness of the film was determined by a published method[10] and did not change by more than 5% in the strongest solution of phenol used. The diphenyl was used in an emulsified form.

Dynamic Mechanical Measurement on the Pretreated Poly(ethylene Terephthalate) Film. The mechanical loss of the pretreated films, in a sinusoidal tensile deformation, was measured in air on a Rheovibron Dynamic Viscelastometer, Model DDV-II. The frequency used was 3.5 Hz, and the temperature of the sample was raised at the rate of 2°C/min. The mechanical loss was expressed as tan δ.

Measurement of the Infrared Spectra of Poly(ethylene Terephthalate) Film. The infrared spectrometer used was a Grub Parsons Spectomajor, fitted with a wire grid polarizer (KRS-5, Spectroscopic Accessory Company). Poly(ethylene terephthalate) films were sandwiched between two cardboard frames with coinciding windows. The frames held the films in the radiation beam. No sample was placed in the reference beam. Films were always mounted with the roll direction vertical.
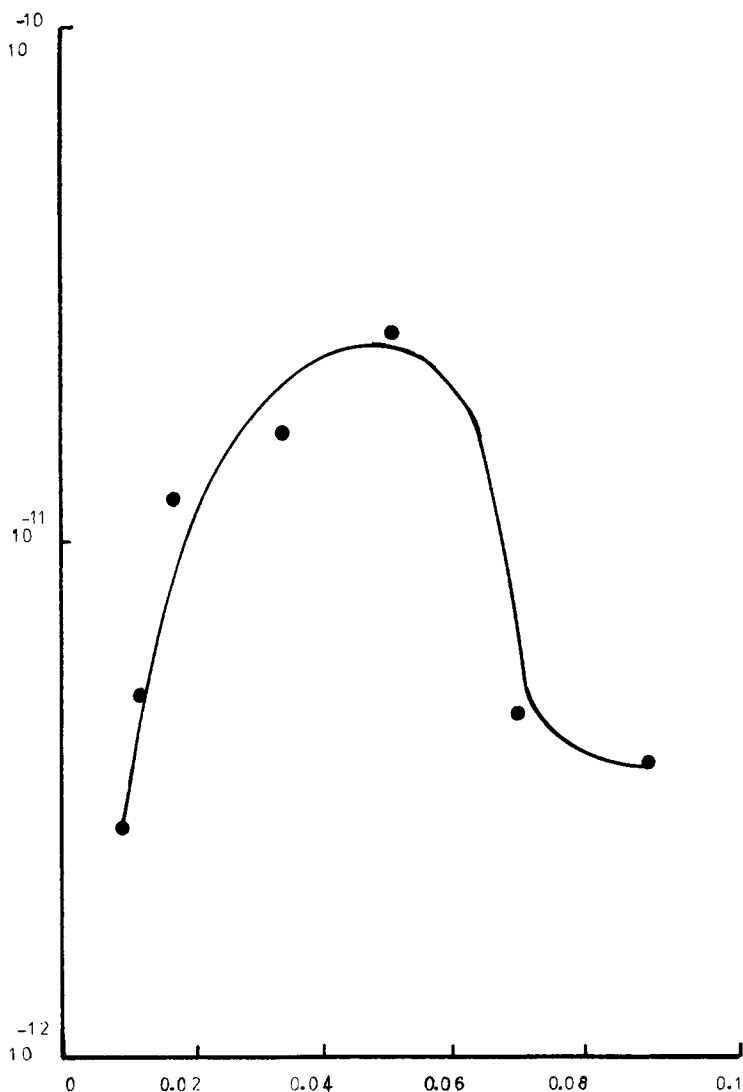
Fig. 6. Variation of diffusion coefficient D_T of C.I. Disperse Orange 3 into poly(ethylene ter-ephthalate) film at 65°C with concentration of diphenyl used in the pretreatment: x-axis, con-centration of diphenyl (mole/l.); y-axis, D_T (cm²/min).

A small peak at 988 cm⁻¹ corresponded to the chain-fold band.[11] The variation in the absorbance of this peak for films treated with different concentrations of phenol was determined by the Hill and Valley method.[12] The results are represented graphically in Figure 10 as a ratio of the absorbance at 988 cm⁻¹ to the absorbance at 795 cm⁻¹, the latter being taken as an internal reference band.[11]

DISCUSSION OF RESULTS

When the diffusion coefficients of a disperse dye into a hydrophobic fiber can be related to the segmental mobility of the polymer chains through eq.
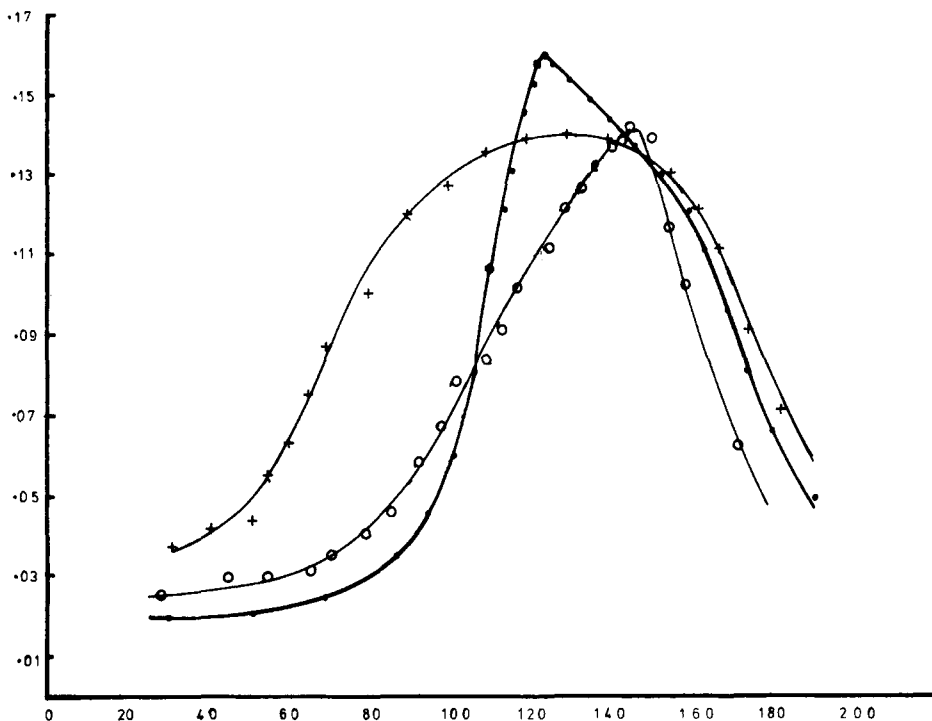
Fig. 7. Effect of phenol on mechanical damping of poly(ethylene terephthalate) film: x-axis, temperature (°C); y-axis, tan δ; (●) film pretreated 2 hr at 95°C in water; (O) film pretreated 2 hr at 95°C in water 0.05 mole/l. phenol; (X) film pretreated 2 hr at 95°C in water 0.32 mole/l. phenol.

(1), two associated relationships are to be expected. Firstly, the reduction in T_g caused by the incorporation of a plasticizing agent into the fiber should be directly proportional to the concentration of agent present. Secondly, the activation energy for the diffusion process varies with temperature, the corresponding Arrhenius plots having a pronounced curvature.

The results for the dyeing of poly(ethylene terephthalate) films appear to conform to eq. (1), but since the T_g cannot be determined directly under the conditions of dyeing, it becomes necessary to use another reference temperature as an alternative to the T_g. The use of the dyeing transition temperature for this purpose appears to be justifiable. It is reduced by an amount which is directly proportional to the carrier concentration used in the dyebath (Fig. 1), thus conforming to the first relationship mentioned above. Furthermore, the Arrhenius plots for the diffusion coefficient of C.I. Disperse Orange 3, obtained over a range of temperatures for each concentration of carrier, were found to be superimposible onto a common curve, by making a suitable vertical shift along the $1/T$ axis (Fig. 2), in accordance with the time–temperature superposition principle. The values of activation enthalpy obtained from the slope of the tangents drawn to appropriate points on the curvature show that the activation enthalpy decreases with increasing temperature, as for other properties dependent upon segmental mobility (Fig. 3).
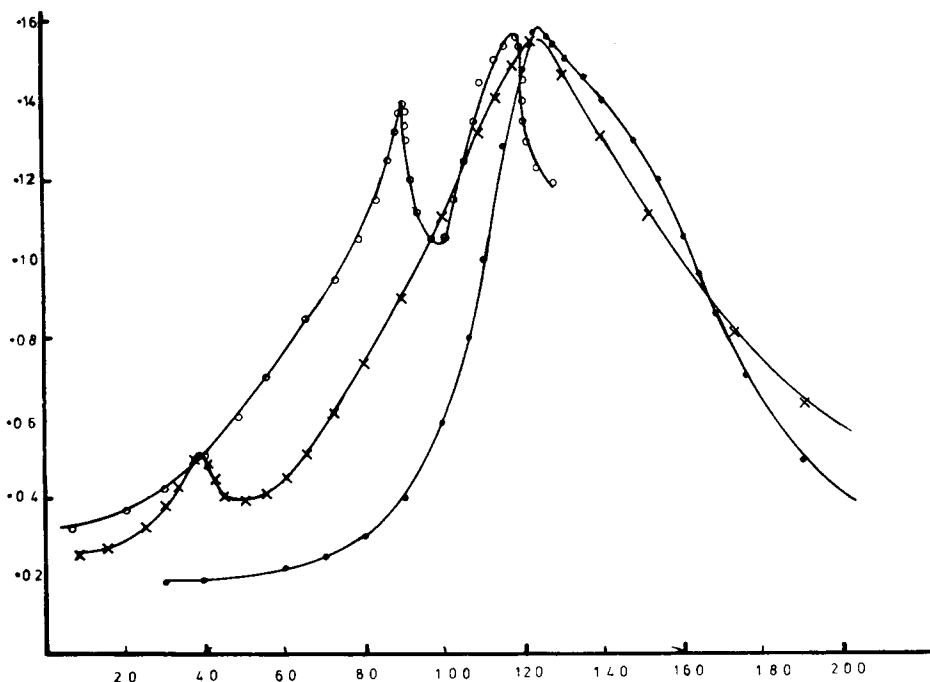
Fig. 8. Effect of diphenyl on mechanical damping of poly(ethylene terephthalate) film: x-axis, temperature (°C); y-axis, tan δ; (●) film pretreated 2 hr at 95°C in water; (O) film pretreated 2 hr at 95°C in water 0.004 mole/l. diphenyl; (×) film pretreated 2 hr at 95°C in water 0.13 mole/l. diphenyl. (Selected concentrations only are shown, to avoid confusion.)

The application of the time–temperature superposition principle to the plasticization of polymers demands that the shift required to superimpose the Arrhenius data for different plasticizer concentrations should represent the change in the T_g of the substrate. If follows, therefore, that if T_D is an appropriate reference temperature to use to replace T_g in eq. (1), then the temperature shift made for each carrier concentration in Figure 2 should also correspond to the change in T_D. This is found to be so and is represented in Figure 4, where the variation of T_D with carrier concentration (ΔT_D), and the change in T_g (ΔT_g), as calculated from the shift along the temperature axis, are plotted against the concentration of phenol used in the pretreatment. It is, therefore, reasonable to consider the dyeing transition temperature as a satisfactory replacement for the T_g when the latter cannot be determined directly.

The Effect of Carriers on the Structure of Poly(ethylene Terephthalate) Film

The foregoing discussion is relevant to films which have been pretreated in carrier before dyeing, and some consideration has, therefore, been given to changes in the substrate which may be of importance to the dyeing properties.

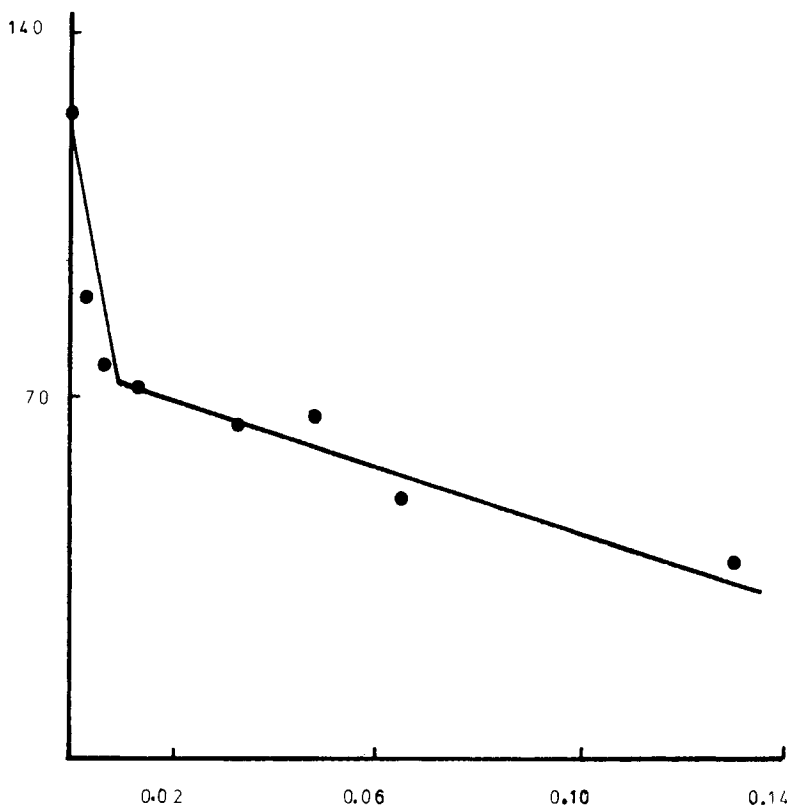Carriers recommended for use in commercial dyeing are inconvenient to

Fig. 9. Variation of α_2-peak with carrier concentration (from Fig. 8): x-axis, concentration of diephenyl (mole/l.); y-axis, temperature (°C).

use in qualitative dyeing experiments, because they have to be applied as emulsions owing to their low solubility in water. Nevertheless, an attempt is made to examine the effect of the dispersion concentration of diphenyl on the dyeing properties of polyester film.

The rate of dyeing curve obtained after pretreatment in diphenyl is very unusual. Equilibrium appears to have been reached, but when the dyeing is prolonged in an attempt to establish equilibrium, the rate of dyeing begins to increase rapidly (Fig. 5). This behavior was not observed when dyeing at 65°C. Consequently, the effect of carrier concentration on the deying properties was assessed by measuring the diffusion coefficient of CI Disperse Orange 3 at 65°C, in order to avoid the effect which takes place on prolonged dyeing at 95°C.

The amount of biphenyl present in the pretreatment bath was in excess of the published values[17] for water solubility (0.164 g/l. at 95°C) and ranged from approximately 0.01–0.1 mole/l. to 1.5–15.0 g/l., and so solid carrier was present in the bath at all times. Subsequently, the pretreated film was dyed in a bath without carrier. Since the solubility of the carrier is very low even at 95°C, it is unlikely that significant redistribution of the carrier could take place during dyeing, and, in any case, it could not exceed the even lower solubility of diphenyl at 65°C.
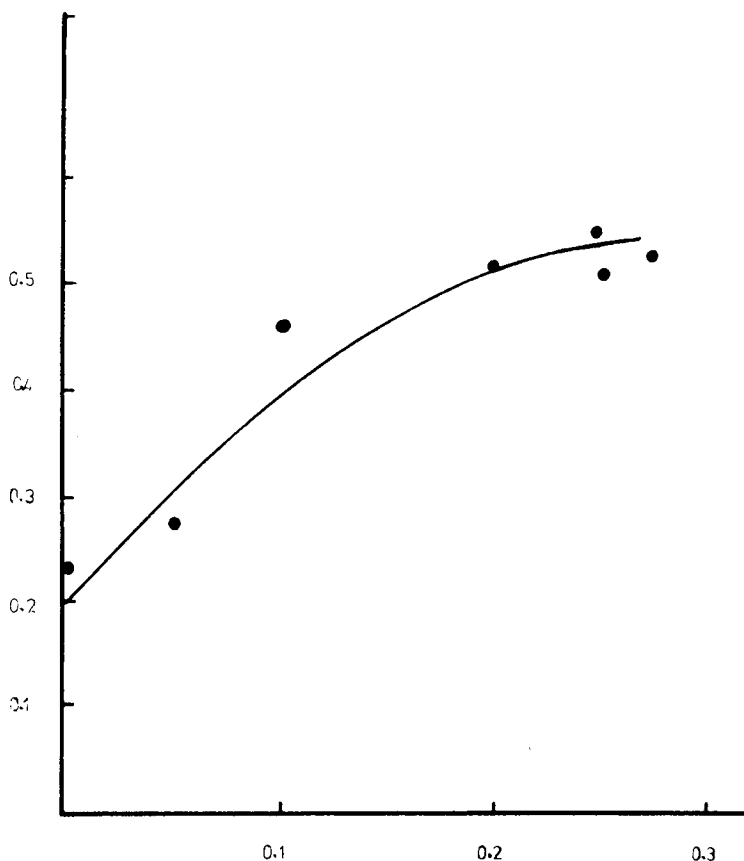
Fig. 10. Variation in the chain-fold band intensity of poly(ethylene terephthalate) film with phenol concentration used in the pretreatment: x-axis, concentration of phenol used in the pretreatment (mole/l.); y-axis, A988/A795.

Consequently, the carrier will remain almost entirely in the substrate during dyeing. It is, therefore, unlikely that the rate of diffusion of dye will be influenced by the presence of carrier in the dyebath. The results, therefore, represent an effect of the change in the substrate due to carrier action. At the lower concentrations of carrier, the rate of diffusion increases with increasing carrier content, as expected; but at the higher concentrations, the plasticization has been more vigorous, and changes in the substrate have made diffusion more difficult (Fig. 6).

The limitations of the above deduction, made entirely on the basis of dyeing experiments, are obvious. An attempt was made, therefore, to obtain measurements of the dynamic mechanical properties and the infrared spectra of carrier-treated polyester films.

The Effect of Carriers on the Dynamic Loss (tan δ) of Poly(ethylene Terephthalate) Films

The Effect of Phenol on Poly(ethylene Terephthalate). The response of the substrate to a sinusoidally oscillating stress is represented in Figures 7
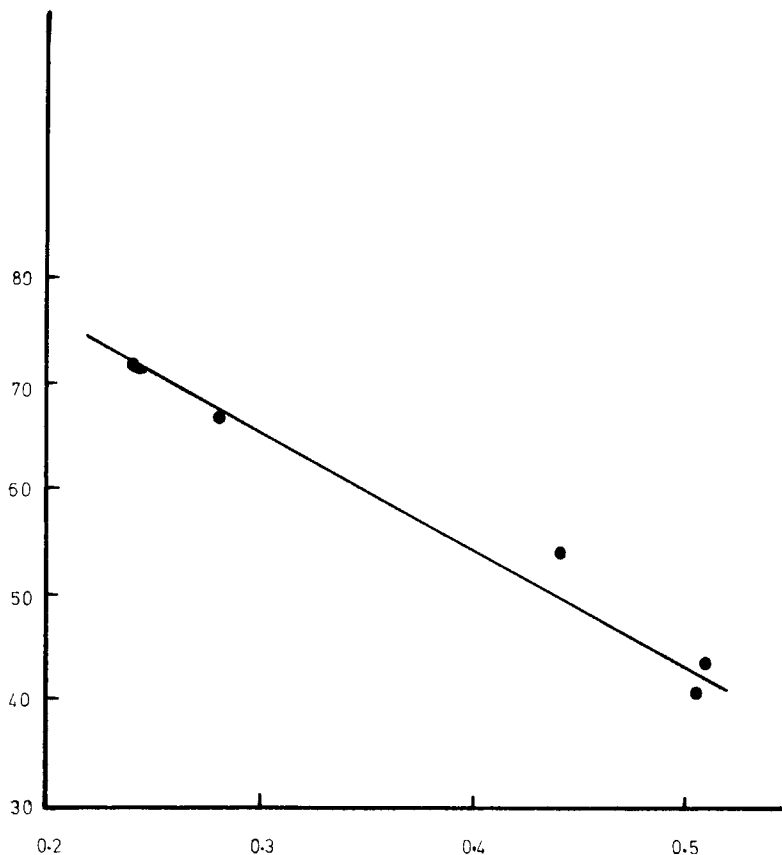
Fig. 11. Variation in dyeing transition temperature T_D with intensity of chain fold band: x-axis, A988/A795; y-axis, T_D (°C).

and 8. The reduction in the height and pronounced broadening of the peak designated as the α-peak for the film pretreated with the highest concentration of phenol are consistent with plasticizing action,[13] but the effects of the lower concentrations of phenol resemble the changes described by other workers for samples of poly(ethylene terephthalate) of increasing crystallinity.[13-15] The α-peak is moved to higher temperatures,[13,14,16] is reduced in height,[13,15] and tends to be broadened. There is, therefore, evidence of an increase in both crystallinity and plasticization.

The Effect of Diphenyl on Poly(ethylene Terephthalate) Film. The changes produced by diphenyl are more drastic than those for phenol. The α-peak is shifted from 120°C to 110°C after pretreatment in very low concentrations of carrier, and there is a considerable broadening on the low-temperature side of the α-peak due to the appearance of a new and sharp peak at 80°C (Fig. 8), referred to here as the α_2-peak. The variation of the temperature at which this peak occurs with carrier concentration is shown in Figure 9. A marked reduction in the height of the α_2-peak is also obtained as it moves to lower temperatures (Fig. 8). The α_2-peak disappears completely when the pretreatment time is prolonged from 2 to 5 hr, and very little further change is detected when the carrier treatment is increased to 18 hr. Nevertheless,

structural rearrangements must still be taking place, because the diffusion coefficient for the dye at 95°C into film pretreated with 0.065 mole/l. carrier for 5 hr (1.04×10^{-8} cm²/min) is significantly smaller than the value obtained for diffusion into the substrate after 18 hr of treatment (3.7×10^{-8} cm²/min).

The differences between the effect of phenol and diphenyl may be due to the amount of carrier absorbed by the substrate. The partition coefficient of phenol[1] (2.5) is much lower than that reported[17] for diphenyl (1310), and, therefore, other conditions being equal, a larger proportion of diphenyl will be absorbed by the substrate. In addition, there may be differences on a molecular level which affect the efficiency of plasticization by the two carriers.

The Infrared Spectra of Poly(ethylene Terephthalate) Film

Chain folding is one aspect of polymer behavior which is believed to lead to an energetically favorable conformation, and evidence for chain folding in poly(ethylene terephthalate) is already available.[11,18]

An increase in chain folding caused by the carrier treatment was detected in this work from the infrared spectra of the carrier-treated films. The effect of carrier concentration on the intensity of the chain-fold band is shown in Figure 10, where the increase in intensity with increasing carrier concentration can be observed.

Chain folding is believed to make a major contribution to the fluid-like mobility of the polymer chains; and since the diffusion of dye into the substrate is believed to be governed by this mobility, a relationship between chain folding and dyeing properties is to be expected.

Such a relationship is obtained between the intensity of the 988 cm^{-1} band and the dyeing transition temperature, the dyeing transition temperature decreasing with increasing intensity of the chain fold band (Fig. 11).

CONCLUSIONS

The use of the dyeing transition temperature as an alternative to the glass transition temperature in studies of dyeing mechanisms has been justified.

The action of "carriers" on poly(ethylene terephthalate) substrates causes changes in the molecular structure. Chain folding is involved, and this has been associated with the increased dyeability of the substrate.

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