The Dyeability and Properties of Some Structurally Modified Poly(ethylene Terephthalate) Filaments

S. C. O. UGBOLUE and O. E. EKPENYON, *Polymer & Textile Science and Technology Programme, School of Natural and Applied Sciences, Federal University of Technology, P.M.B. 1526, Owerri, Nigeria*

Synopsis

The effect of solvent treatment on the dyeability and mechanical properties of drawn poly(ethylene terephthalate) (PET) filaments has been studied. It is observed that strongly interacting solvents such as N,N-dimethyl formamide (DMF) improved the dyeability of PET which has been treated with these solvents at 74°C for 15 min before dyeing with disperse dyes at 100°C. Pretreatment in N,N-dimethyl formamide and acetonitrile also resulted in a lowering of tensile strength and initial modulus, whereas subsequent dyeing caused further reduction in extensibility but initial modulus results are less consistent.

INTRODUCTION

It is recognized that dye-fiber-specific bonds exist and are believed to hold the dye molecules onto some fibers.[1-6] The speed at which migration can occur will depend, on the one hand, on the strength of the dye-fiber bond and, on the other hand, on the size of the dye molecule. The dyeing of polyesters, however, presents some problems to the dyer since the fibers are not easily swollen in water and no specific dye-fiber bonds exist within the fibers. Dyeing can, therefore, be enhanced either by the use of dyeing auxilliaries, dyeing aids or carriers at lower temperature, or by high temperature dyeing methods. It is accepted that carriers act to counteract steric hindrance to dye mobility by causing increased chain segmental motion or a decrease in the glass transition temperature, T_g of the fiber.[7] High temperature dyeing is also usually carried out to increase segmental mobility and not necessarily to increase the kinetic energy of the dye molecules.

Marvin[8] has shown that the dye uptake relates in a complicated manner to the setting temperature of poly(ethylene terephthalate) (PET) fibers. Thermal pretreatment of PET yarns leads to changes in properties and molecular arrangements of the fibers and is used to provide a balance of properties which will remain stable in subsequent heat treatment at lower temperature. Various heat-treatment methods and their effect on dyeability have been extensively investigated and documented.[8-14, 22, 23]

Pretreatment of polyester yarns[2, 12, 15, 16] with strong interacting solvents has also been shown to lead to modifications of fiber structure which would permit rapid diffusion of "high energy" disperse dyes under atmospheric conditions without additional use of carriers. This work highlights the solvent treatment

of poly(ethylene terephthalate) filaments at 74°C with N,N-dimethyl formamide and acetonitrile and the subsequent dyeing of the treated filaments with disperse dyes at 100°C.

EXPERIMENTAL

Materials

The poly(ethylene terephthalate) filaments used in this work were supplied by the Nigerian Chemical & Textile Industries Ltd., (NICHEMTEX), Ikorodu, Lagos. The filaments were semicrystalline materials having a draw ratio of 3.5 and a yarn number of 3 tex.

The disperse dyestuffs were supplied by Chemical and Allied Products Nigeria Ltd., Lagos.

Purification of the Disperse Dyes

Dispersol Red B-2B (C.I. Disperse Red II) and Dispersol Yellow B-GR (C.I. Disperse Yellow 39) (2 g each) were extracted using the soxhlet apparatus. The process lasted until the filtrate coming out of the thimble was clear. The solvent used for extraction was sulfur-free toluene. The filtrate was transferred into a 25 cm³ conical flask and concentrated to about one-third of its original volume by evaporating on a hot plate. The flask was allowed to cool to room temperature and was then further cooled at 0°C for 24 h. The characteristics of the purified Dispersol Red B-2B dyestuff were:

Yield: 0.586 (i.e., 29.3%)

Melting point: 182°C

Peak of maximum absorption occurred at wave length of 512 nm and extinction coefficient of 35.67.

Solvent Treatment of PET Filaments

N,N-dimethyl formamide (DMF), solubility parameter 12.14 $(cal/cm^3)^{1/2}$ and acetonitrile (solubility parameter 11.75 $(cal/cm^3)^{1/2}$ were used to swell the filaments (9 cm long) which were suspended in turn from a rod placed across the top of a 50-cm measuring cylinder containing the solvents. A small force (not greater than 0.045 gf/tex) acting on the suspended filament served to keep the filaments parallel to one another, thereby minimizing entanglement. For each determination the measuring cylinder containing the solvent was kept in a thermostatically controlled water bath. Solvent treatments were given at 74°C for varying times.

In companion experiments, the effect of solvent treatment on the shrinkage property of the filaments was also studied using DMF and acetonitrile as the solvents. The first sample in each of the solvents was treated for 2 min, while subsequent samples were treated at 5 min intervals within a period of 1 h at a temperature of 74°C. A cathetometer was used afterwards to measure the changes in the length of the filaments. These solvent-treated filaments were

subsequently dried to remove traces of solvent before dyeing the selected filaments.

Dyeing of Untreated and Solvent-Treated PET Filaments

Two dyebaths were prepared, each containing the same amount of 1 g dyestuff dispersed in 1000 cm^3 of distilled water contained in a 2-liter culture flask. One bath was used for the dyeing of DMF-treated filaments while the other was used for dyeing of acetonitrile-treated yarns. About 3 g each of the yarn which had been previously treated with the relevant solvent for 15 min at 74°C were dyed in the baths. A high, uniform stirring speed was maintained throughout the period of dyeing. Samples were introduced into the dyeing flasks at 50°C and were removed after 4, 16, 36, 100, and 144 min when the dyeing temperature of 100°C had been attained. In addition, each dyebath contained about 0.5 g of the original, untreated yarn which was dyed to maximum time. All the dyed samples were rinsed in hot and then in cold water after dyeing. They were air-dried at room temperature.

Quantitative Determination of Fixed Dye on Poly(ethylene Terephthalate) Fibers

The procedure of extracting disperse dyes from dyed poly(ethylene terephthalate) fibers had previously been describeed in detail.[17,18] The procedure was adopted in this experiment. First, 0.01 g of the dyed yarn was placed in a 5-cm^3 conical flask and covered with 1 cm^3 of the extraction solvent. The flask was loosely stoppered to avoid possible air oxidation of the discharged dye. The extraction solvent was DMF with a pH which had previously been adjusted to 4.2 with the aid of p-toluene sulfonic acid solution in DMF. The flask was placed in a thermostatted oil-bath maintained at 140°C. Extraction time was 3 min. Two to three extractions were carried out depending on the concentration of the dye in the fiber. The extracts were diluted to mark with DMF in a 50-cm^3 volumetric flask. Extraction was carried out on all dyed samples.

Measurement of Absorbance of Dye Solutions

The absorbance of each dye solution was measured using the Pye UNICAM SP6-200 spectrophotometer, which had been previously calibrated using standard dye solutions. In the very dilute concentration range, the absorbances of these solutions, when plotted against their concentrations, gave the linear plot, which is in accordance with the Beer-Lambert Law. From this plot, the concentration of the dye extracts were found by interpolation. The absorbances were measured at a constant wavelength of 512 nm. The dye percent absorbed is related to absorbance by the equation given below:

$$\% \text{ Dye absorbed} = \frac{\text{absorbance} \times \text{extract volume} \times \text{dilution} \times 100\%}{\text{extinction coefficient} \times \text{wt of dye sample} \times 1000}$$

Measurement of Mechanical Properties

The mechanical properties of poly(ethylene terephthalate) filaments were measured on an Instron tensile testing machine using a gauge length of 5 cm and cross-head speed of 5 cm/min. Measurements were carried out on original (untreated), solvent-treated and heat-set fiber samples as well as on solvent-treated samples dyed for 4 and 144 min. The original (control) sample which was dyed for 144 min was also tested. All tests were carried out at 65% relative humidity and 22°C. Twenty specimens were used for each sample.

Determination of Density

The Davenport 2-column density measuring apparatus was used to determine the densities of all the fiber samples whose mechanical properties were measured as described previously. The density gradient column was filled with a mixture of carbon tetrachloride (CCl_4) and n-heptane at $23.0 \pm 0.1°C$. The column was previously calibrated with glass floats of known densities. Before suspension in the column, the fiber samples were soaked in CCl_4 for 20 h and then allowed to equilibriate in the column for 24 h, after which their respective heights were noted. Their densities were subsequently found from the calibration plot by interpolation.

RESULTS AND DISCUSSION

Physical Properties of the Fibers

Table I shows the densities of various treated PET fibers and their corresponding crystallinities. It must be emphasized that the density changes due to the disorientation of the ordered amorphous regions should be considered in the calculation of crystallinity values from density determination.[6] Studies by Samuels[13] and Wilson[19] have shown that the semicrystalline PET fibers can be treated as a two-phase system, and that macroscopic shrinkage results from a disorientation of oriented amorphous regions. In this study, heat setting and solvent treatment led to increase in density compared to the original untreated sample. N,N-dimethyl formamide-treated sample had a

TABLE I
Results of Density Measurements

PET filament samples	Density (g/cm^3)	Crystallinity (%)
Untreated	1.404	57.5
CH$_3$CN-treated, 74°C, 15 min	1.422	72.5
DMF-treated, 74°C, 15 min	1.452	97.5
Heat-set samples		
Heat-set		
99°C, 360 min	1.410	62.5
114°C, 360 min	1.433	81.7
130°C, 360 min	1.450	95.8
Dyed samples		
DMF-treated and dyed 4 min	1.433	97.5
DMF-treated and dyed 144 min	1.452	97.5

TABLE II
Density and Crystallinity of Polyester Yarns after Treatment in DMF (Unrestrained)
at Various Times and Temperatures Determined by Two Liquid Systems
in Density Gradient Columns

	Liquid system			
	Heptane-carbon tetrachloride		Water-calcium nitrate	
Treatment conditions	Density (g/cm^3)	Crystallinity (%)	Density (g/cm^3)	Crystallinity (%)
60°C, 180 min.	1.383	40	1.386	42.3
80°C, 180 min.	1.387	43.3	1.388	44.4
100°C, 180 min	1.391	46.7	1.392	47.5
120°C, 100 min	1.396	50.8	1.395	49.8
140°C, 15 min	1.428	77.5	1.401	54.8
140°C, 180 min	1.444	90.8	1.409	61.7
150°C, 2 min	1.440	87.5	1.400	53.9
150°C, 15 min	1.447	93.3	1.400	54.3
150°C, 180 min	1.450	95.8	1.401	55.4

higher density than the acetonitrile-treated sample. In certain cases densities of 1.452 g/cm^3 suggesting crystallinities as high as 98% were recorded. Such values are considered unrealistic in that they suggest the virtual disappearance of an amorphous phase through selective chain scission at the interphase between crystalline and amorphous phases. It is inferred that unrealistically high density values were a result of preferential absorption of carbon tetrachloride (CCl_4), the heavier component of the carbon tetrachloride −n-heptane mixture in the density gradient column.

Unrealistically high density values can be avoided if a liquid system such as calcium nitrate solution that does not permit preferential absorption is used. This is illustrated in Table II, where density values observed with DMF-treated samples at various times and temperatures are given.[6]

It must be emphasized that the fibers used in this work are drawn PET filaments; generally, stretching or drawing of PET fibers imparts a greater degree of morphological order to them. This is usually accompanied by improved crystallinity owing to better alignment of chain molecules.

Effect of Solvent Treatment on Shrinkage of PET Filaments

It has been established[12] that active solvents such as DMF can cause longitudinal shrinkage. In this work, the three distinct regions identifiable from the plot of shrinkage percentage against time as shown in Figure 1 (kinetics curve) are the following:

1. Induction period of 6 s in the case of DMF-treated filaments and about 60 s for CH_3CN-treated filaments; in this region only the diffusion[12] of the solvents into the fiber structure took place.

2. A period where shrinkage varied linearly with time. A linear region within the first 4 min was observed and this agreed with previous investigators.[12]
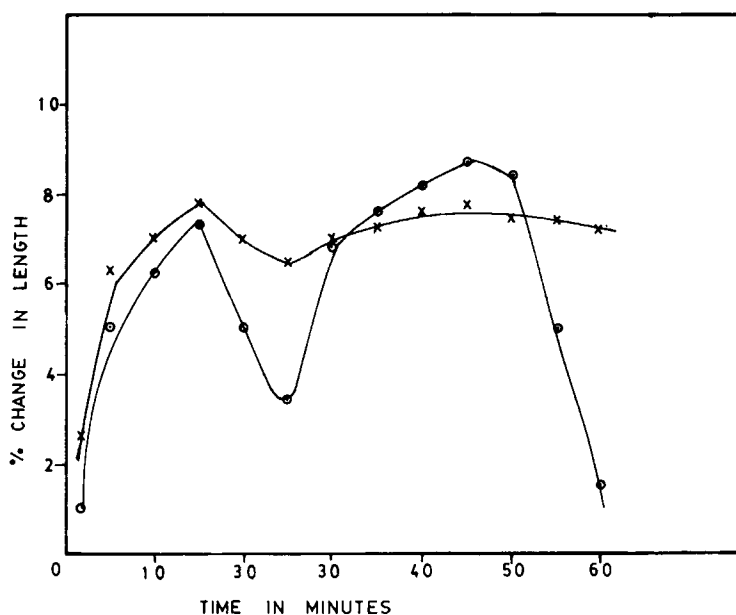
Fig. 1.   Effect of solvent treatment on shrinkage property of PET filaments. (×) DMF-treated, (⊙) CH_3CN-treated filaments.

3. A period in which the rate shrinkage decreased tending toward equilibrium with time was observed for the PET filaments treated at 74°C with DMF. However, the "equilibrium state" of the shrinkage with time is observed to start gradually after the 20th minute. The shrinkage results of CH_3CN-treated filaments after the 20th minute is less consistent and no equilibrium was observed within the 60 min experimental time.

The curves in Figure 1 showed a tendency to rise to a peak after a period of 15 min and then dropped before another peak was again observed after 45 min, this second peak being most pronounced in the case of CH_3CN-treated filaments.

The action of solvents is believed to be twofold: the disruption of intermolecular forces in the swollen state by a solubilizing action and a secondary crystallization process involving chain folding of the newly relaxed chains.[2] In a particular study, the magnitude of the observed swelling and shrinkage will depend upon the original structure of the fiber.

Effect of Solvent Treatment on Dyeability

It is known[7,8,20] that increased temperature accelerates dye diffusion within the fiber while increased dye concentration and stirring rate increase dye uptake. Berndt[20] suggested that effects of these variables can be overcome by determining a relative dye uptake in which the dye uptake of the test sample is normalized by the dye uptake of an untreated, control sample dyed simultaneously in the same bath. This technique was used in this investigation and relative dye uptakes given in Table III are, therefore, used to characterize the dyeability of the solvent-treated samples. As these values do

TABLE III
Relative Dye Uptake of Solvent-Treated PET Filaments (74°C, 15 min)

Description	Absorbance	Concentration $(g/cm^3 \times 10^{-3})$	% Dye absorbed	Normalized value
Untreated and dyed for 144 min	0.150	4.13	2.06	100.00
DMF-treated and dyed for 144 min	0.235	6.63	3.31	160.7
CH_3CN-treated and dyed for 144 min	0.155	4.25	2.13	103.4

not represent equilibrium values, they are indicative of dye diffusion characteristics.

Tables IV and V give values for the dye-absorbed percent by fibers that had been pretreated with N,N-dimethyl formamide and acetonitrile. The effect of the solvent treatment is to create voids within the fiber structure, which cause the dyestuff to migrate more rapidly and to achieve saturation at much earlier dyeing time. In other studies[1] a close correlation was observed between dye uptake and void volume, calculated from density data. Compared to the untreated sample, acetonitrile treatment improved dye uptake by 3%, whereas DMF treatment enhanced relative dye uptake by about 61%. Compared to acetonitrile-treated samples, DMF treatment also resulted in improved diffusivity, as can be determined[11] from the slope of the initial portion of the rate of dyeing curves.

TABLE IV
Percentage Dispersol Red B-23 Dye Absorbed by DMF-Treated PET Filaments (74°C, 15 min)

Time of dyeing (min)	Absorbance	Concentration $(g/cm^3 \times 10^{-3})$	% Dye absorbed
4	0.100	2.75	1.38
16	0.130	3.50	1.75
36	0.170	4.75	2.38
64	0.172	4.76	2.38
100	0.175	4.78	2.39
144	0.235	6.63	3.31

TABLE V
Percentage Dispersol Red B-2B Dye Absorbed by Acetonitrile-Treated
PET Filaments (74°C, 15 min)

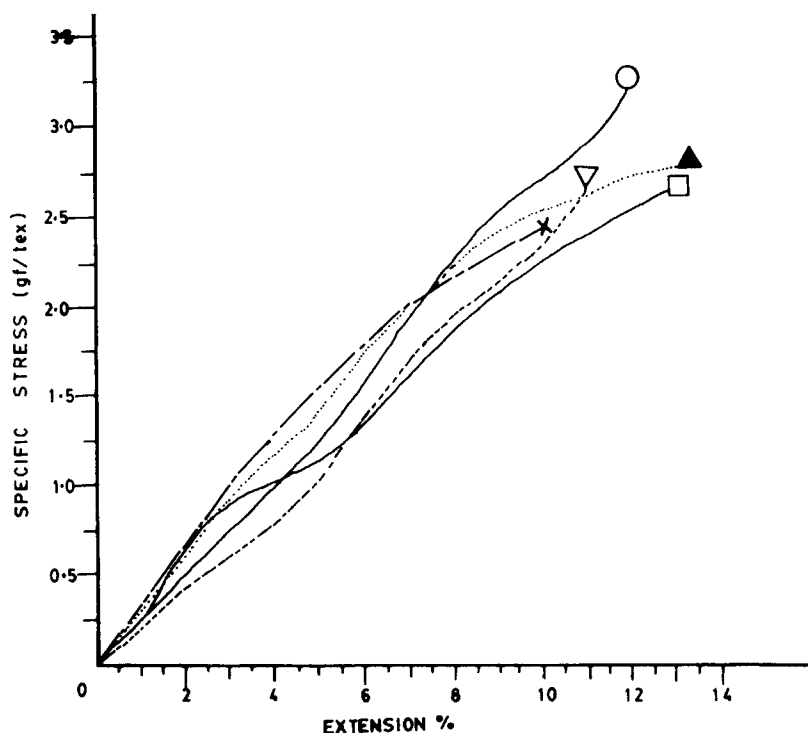| Time of dyeing (min)	Absorbance	Concentration $(g/cm^3 \times 10^{-3})$	% Dye absorbed
4	0.055	1.50	0.75
16	0.070	2.00	1.00
36	0.080	2.25	1.13
64	0.095	2.50	1.25
100	0.095	2.63	1.31
144	0.155	4.25	2.13

Fig. 2. Stress–strain curves for some untreated and DMF-treated and dyed PET fibers. (O)
Untreated fiber; (□) untreated and dyed for 144 min; (×) DMF-treated and dyed for 4 min; (▽)
DMF-treated and dyed 144 min; (▲) DMF-treated 74°C for 15 min.

Effect of Dyeing on the Mechanical Properties of Various Treated PET Fibers

Table V illustrates the mechanical properties of the untreated, untreated and dyed, solvent-treated, and solvent-treated and dyed samples. The stress–strain profiles are shown in Figures 2 and 3. A full characterization of the effect of solvent-induced modification of PET fiber on its dyeability cannot be achieved unless cognizance is also taken on the side effects of such treatment on mechanical properties. Ugbolue and Aula[18] observed that disperse dyes initially caused a reduction in tensile strength of undrawn PET fibers and that at saturation the original tensile strength was restored. They also observed[18] a monotonic decrease in the extensibility and an increase in initial modulus of the undrawn PET fibers. The decrease in tensile strength and the increase in extensibility suggest that the dye is acting as a plasticizer. Okajama et al.[21] have in their studies on the dichroism of the PET disperse dye system confirmed that disperse dyes act as weak plasticizers. They have also shown[21] that a distribution of lateral order exists in the amorphous region and that dye molecules do not distribute homogeneously throughout the entire amorphous region but exist only within the region of lowest lateral order.

Table VI also shows that DMF and acetonitrile treatment at 74°C for 15 min led to a weakening of the tensile strength of PET fibers, with the DMF
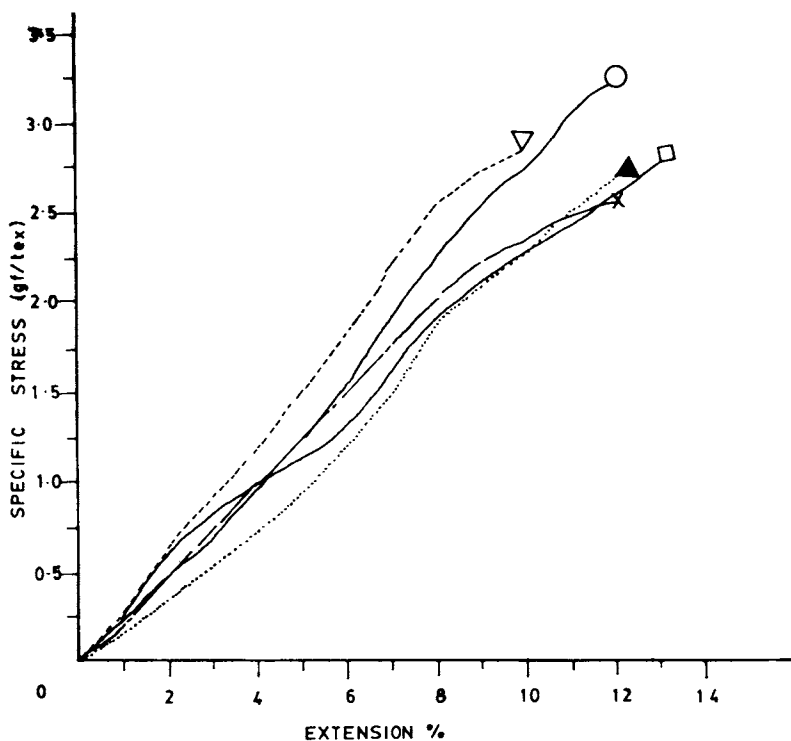
Fig. 3. Stress–strain curves for some untreated, CH_3CN-treated, and CH_3CN-treated and dyed PET fibers. (O) Untreated fiber; (□) untreated and dyed for 144 min; (×) CH_3CN-treated and dyed 4 min; (▽) CH_3CN-treated and dyed 144 min; (▲) CH_3CN-treated fibers.

having a more pronounced effect. An increase in extensibility was observed for the DMF-treated fibers while no apparent change in extensibility was found for acetonitrile-treated fibers. A decrease in initial modulus is to be expected because of plasticization, and while this was observed for acetonitrile-treated fibers, no significant change was observed for DMF-treated fibers; the changes in mechanical properties are consistent with a fiber that is undergoing a reduction in orientation. The extent to which this reduction manifests itself in terms of observed changes depends on the physical characteristics of the fiber, especially its degree of orientation and crystallinity, treatment conditions as well as the effectiveness of the solvent. The treatment condition used, that is 74°C and 15 min, is considered not sufficiently drastic to produce very marked changes on drawn PET fibers when acetonitrile is used as a solvent because of the lower interacting ability of acetonitrile. The constancy of the extensibility value, despite acetonitrile treatment may be understood in light of the preceding statement. It is probable that extensibility may well be a less sensitive test for evaluating mechanical properties of modified poly(ethylene terephthalate) fibers.

The basis of structural modification during DMF treatment of PET is solvent-induced crystallization, which occurs while the PET structure is swollen with the solvent. After removal of the solvent and dyeing with disperse dyes at 100°C for 144 min, some changes in the mechanical properties

TABLE VI
The Mechanical Properties of Various Treated PET Fibers

Measurement	Untreated	Untreated dyed for 144 min	DMF treated only	DMF treated and dyed for 4 min	DMF treated and dyed for 144 min	CH_3CN treated only	CH_3CN treated and dyed for 4 min	CH_3CN treated and dyed for 144 min
Mean[a] Tensile strength (gf/tex)	3.23	2.65	2.57	2.42	2.67	2.68	2.50	2.83
Mean[a] extension at break %	12	13	13.5	10	11	12	12	10
Initial Modulus (gf/tex) at 1% strain	25	32.6	24.8	26.2	20.7	22.9	24.7	29.5
Secant Modulus (gf/tex)	26.92	20.38	21.42	24.20	22.25	22.33	20.83	28.30

[a] Mean of 20 tests.

were observed as detailed in Table VI. However, there was no significant change in the tensile strength of the solvent-treated and dyed filaments compared to their solvent-treated counterparts. The effect of dyeing was to cause some reduction in the initial modulus and, to some extent, the extensibility of DMF-treated and dyed fibers. It is surmised that no appreciable deterioration in mechanical properties is induced on the PET filaments subject to these solvent treatments at 74°C before dyeing. The pretreated dyed filaments gave acceptable shade/dyeings, thereby providing alternative method of application of disperse dyes on PET filaments without the use of carriers or high temperature dyeings.

CONCLUSION

Solvent treatment and heat setting lead to improvement in the crystallinity of the PET fibers. It is observed that strongly interacting solvent such as N,N-dimethyl formamide improved the dyeability of PET which had been treated with the solvents at 74°C for 15 min before dyeing with disperse dyes at 100°C. The relative dye uptake after DMF treatment was 20 times greater than after acetonitrile treatment. Pretreatments in both solvents resulted in a lowering of tensile strength.

References

1. C. L. Bird, F. Manchester, and P. Harris, *Disc. Faraday Soc.*, **16**, 85 (1954).
2. B. H. Knox, H. D. Weigmann, and M. G. Scott *Text. Res. J.*, **46**, 574 (1976).
3. R. J. B. Marsden and A. R. Urqhart, *J. Text. Inst.*, **33**, T105, (1942).
4. A. E. Stubbs, *J. Soc. Dyers and Colourists*, **70**, 120 (1954).
5. T. Vickerstaff, *The Physical Chemistry of Dyeing*, 2nd Ed., Oliver and Boyd, London, 1954.
6. H. D. Weigmann, M. G. Scott, A. S. Ribnick, and L. Rebenfeld, *Text. Res. J.*, **46**, 578 (1976).
7. W. Ingamells, R. H. Peters, and S. R. Thornton, *J. Appl. Polym. Sci.*, **17**, 3733 (1973).
8. D. N. Marvin, *J. Soc. Dyers Colour.*, **70**, 16 (1964).
9. J. H. Dumbleton, *J. Polym. Sci.* Pt. A-2, **7**, 667 (1969).
10. H. U. Echmidlin, *Preparation and Dyeing of Synthetic Fibres*, Chaplin and Hall Ltd., London, 1963, p. 24.
11. O. E. Ekpenyon, M.Sc. thesis, Department of Chemistry Ahmadu Bello University, Zaria, Nigeria, June, 1979.
12. A. S. Ribnick and H. D. Weigmann, *Text. Res. J.*, **43**, 316–324 (1973).
13. R. J. Samuels, *J. Polm. Sci.*, Pt. A-2, **9**, 781 (1972).
14. S. C. O. Ugbolue and O. E. Ekpenyon, *Acta Polymerica* **32** (10), 634 (1981).
15. A. S. Ribnick, H. D. Weigmann, and L. Rebenfeld, *Text Res. J.*, **46**, 574–587 (1975).
16. H. D. Weigmann, M. C. Scott, and A. S. Ribnick, *Text. Res. J.*, **48** 4, (1978).
17. E. Kissa, *Text. Res. J.*, **45**, 298 (1975).
18. S. C. O. Ugbolue and S. M. Aula, *J. Appl. Polym. Sci.*, **25**, 1071 (1980).
19. M. P. W. Wilson, *Polymer*, **15**, 277 (1974).
20. Berndt, *Melliand Texilber*, **54**, 676 (1973).
21. S. Okajama, K. Nakayama, K. Kayama, and T. Kato, *J. Appl. Polym. Sci.*, **14**, 1069 (1970).
22. W. O. Statton, L. Keening, and M. Hannon, *Bull. Am. Phys. Soc.*, **11**, 14 (1969).
23. H. J. White, *Text. Res. J.*, **30**, 329 (1960).