Effect of pretreatment with solvents and solvent mixtures on the structure/properties and dye uniformity of textured polyester yarn

D P Chattopadhyay, R K Singh & T N Patra
The Technological Institute of Textile & Sciences, Bhiwani 127 021, India
and
A K Samanta
Textile Chemistry Section, Institute of Jute Technology, 35 Ballygunge Circular Road, Calcutta 700 019, India

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Textured polyester multifilament yarn was subjected to swelling in single and mixed solvents (with varying ratio) at room temperature for different durations. The changes in the structure and properties of the yarn were investigated by measuring birefringence, crystallinity, critical dissolution time, shrinkage on treatment, % change in bulk, residual shrinkage, crimp rigidity, dye uptake and dye uniformity. Among the four single solvents used, dimethyl formamide (DMF) and methylene chloride showed better balance of the above properties and dye uniformity. Use of a mixture of tetrachloroethane and DMF in the ratio of 1:3 gave dye uptake at par or slightly better than that given by the corresponding single solvent but showed more dye uniformity.

Keywords: Dye uniformity, Dye uptake, Polyester multifilament yarn, Solvent swelling, Structure-property relationship, Textured yarn

1 Introduction

The demand of textured yarns for the manufacture of various textile items has increased as the use of the textured yarns imparts bulkiness, stretchability, wearing comfort and aesthetic appeal in the resultant fabric. However, dye uniformity or dyeing non-uniformity is a practical problem for the dyers of textured filament yarns. It is known that occasional variations in texturing parameters cause structural as well as physical variations in the textured filament yarn. These variations cause dyeing non-uniformity and ultimately result in barriness or streakiness after dyeing.

There are essentially three ways in which the solvent pretreatment can be helpful in improving the disperse dyeing results on polyester. First, the solvents can modify the fibre structure in a more or less temporary way by some structural changes participating in dyeing process, even by small retention of solvent and/or helping transport of dyestuff into fibre structure. Second, the solvents can be used to modify fibre structure irreversibly or permanently by creating more voids, reducing glass transition temperature and crystallinity, making fibre structure more open and thus promoting not only the increased rate of dye transport but also enhancing the saturation dye uptake. Third, the solvents can dissolve out oligomers present, homogenize the fine structural differences and provide increased internal surface by more opening up of the structured assembly permitting increased deposition of more dyestuff, which on thermal aftertreatment at high temperature dyeing can collapse the openness of the structure trapping the dyestuff inside. Therefore, it is expected that the physical and structural variations induced in thermomechanical texturing process may be, to some extent, homogenized as well as the polyester oligomers migrated on the surface during texturing may be dissolved and more uniform dyeing may be achieved at a relatively lower temperature of dyeing for solvent pretreated textured polyester multifilament yarns.

The effects of pretreatment with single solvent and with mixture of solvents may not be the same; intersolvent interactions can lead to synergism or
may be proportional to composition of the solvent mixture.

Extensive studies\(^2\)\(^-\)\(^1\(^4\) have been made on solvent treatment (swelling) of untextured (flat) polyester multifilament yarns and its effect on dyeability. Moore and Sheldon\(^3\) correlated the shrinkage behaviour and ability of solvents to swell and crystallize unoriented amorphous polyester (PET) with the total solubility parameters of different swelling agents. Weigmann et al.\(^3\)\(^,\)\(^5\) studied the mechanical properties, swelling and shrinkage behaviour of oriented semi-crystalline PET fibres. The progressive swelling of continuous filament of polyester in phenol has been reported by Bobeth\(^6\). Brennecke and Richter\(^7\) studied the shrinkage and tensile behaviour of fifteen different swelling agents on PET yarn, but not dyeing. Ribnick et al.\(^8\)\(^,\)\(^9\) studied the kinetics of thermal- and solvent-induced shrinkage of polyester filaments using a broad range of solvents. Bredereck et al.\(^10\) systematically investigated the oligomer extraction from PET fibre in a number of solvents.

Samanta et al.\(^11\) reported the selective solvent pretreatment of PET multifilament yarn for achieving subsequent atmospheric dyeing. Knox et al.\(^1\)\(^2\)\(^,\)\(^1\(^3\) studied the isothermal shrinkage of PET in mixture of perchloroethylene and methanol.

The interactions of non-aqueous solvents with textured polyester yarns have been studied by Weigmann and Marjil\(^1\(^3\). They observed that the overall shrinkage as a result of solvent treatment produced further increase in bulkiness of the textured yarns. Knox et al.\(^1\(^4\) investigated in detail the physical and structural changes of polyester untextured yarn on solvent treatment.

However, no information is available on the dyeing non-uniformity or physical and structural variation in textured polyester filament induced in thermal texturing process.

The present study was, therefore, aimed at investigating the effect of pretreatment of polyester (PET) textured multifilament yarn with four different single solvents (DMF, acetone, methylene chloride, tetrachloroethane) and solvent mixtures (with varying ratio) on dye uniformity and related changes in structure and properties.

2 Materials and Methods

2.1 Materials

2.1.1 Yarn

Conventional false twist textured (friction crimped) polyester multifilament yarn (58 denier, 24 filaments, zero twist) supplied by M/s Modipon Ltd, Modinagar, was used.

2.1.2 Solvents, Dyes and other Chemicals

Dimethyl formamide (DMF), acetone, methylene chloride, tetrachloroethane (TCE), carbon tetrachloride and phenol, all of LR grade, were used.

A disperse dye, Foron Brown-S-5RL (C I Disperse Brown 9) of M/s Sandoz (India) Ltd, Bombay, was used for dyeing the experimental polyester multifilament yarns. A dispersing agent, Setamol-WS of BASF (India) Ltd and a carrier compound for disperse dyeing of polyester, Teraux-C (Carrier HC, a non-phenolic carrier based on a mixture of aliphatic hydrocarbons) of M/s. Auxichem, Bombay, were used as dyeing auxiliaries in disperse dyeing of the experimental PET yarns.

2.2 Methods

2.2.1 Solvent Treatment

For solvent treatment, the textured polyester multifilament yarns in hank form were dipped in each solvent separately under relaxed condition for different durations (15, 60, 480 and 960 min). In case of mixed solvents, the treatments were carried out for 60 min under relaxed condition. The samples were taken out and washed thoroughly under running water and then with carbon tetrachloride. Finally, the samples were washed with water and dried in air at room temperature till constant weight was obtained.

2.2.2 Measurement of Shrinkage

The shrinkage (%) of the yarns after solvent treatment was calculated by measuring the length of the PET filament yarn hank (before and after solvent treatment) applying a small pre-tension of 0.0016 g/den as per standard shrinkage test procedure\(^1\(^5\).

2.2.3 Determination of Weight Loss

The initial and final weights of conditioned yarn hank before and after solvent treatment were measured using Mettler micro-balance and the loss in weight was calculated accordingly.

2.2.4 Measurement of Denier

The denier of both the treated and untreated samples was measured as per the method followed
by Monsanto\textsuperscript{15} after removing the crimp with suitable pre-determined decrimping load.

2.2.5 Determination of % Change in Bulk

The bulk of the yarn was determined using the following formula\textsuperscript{15}:

$$\text{Bulk} (\%) = \frac{\text{Specific volume of textured yarn}}{\text{Specific volume of parent yarn}} \times 100$$

The % change in bulk for solvent-treated polyester textured yarns was determined using the following relationship:

$$\% \text{ Change in bulk} = \frac{\% \text{ Bulk of treated yarn} - \% \text{ Bulk of untreated yarn}}{\% \text{ Bulk of untreated yarn}} \times 100$$

For determining the % bulk, the specific volumes of the untreated and treated yarns were calculated in the usual way from the overall diameter of the yarn measured under projection microscope under a constant tension of 0.00536 g/den.

2.2.6 Measurement of Crimp Rigidity

Crimp rigidity of treated and untreated PET yarns was measured using modified HATRA crimp rigidity method after relaxing the yarns in hank form in water at 80°C for 2 min. The light weight and heavy weight taken were 0.002 g/den and 0.1 g/den respectively as per the method followed by Monsanto\textsuperscript{15}.

2.2.7 Measurement of Residual Shrinkage

Polyester textured yarn samples of known length ($L_0=30$ cm) were boiled in water under relaxed condition for 2 min. The samples were then dried in air and the change in length ($\Delta L$) was measured under a pre-tension of 0.25 g/den. The per cent residual shrinkage\textsuperscript{16} was expressed as percentage change in length.

$$\text{Residual shrinkage (\%)} = \frac{\text{Change in length (\Delta L)}}{L_0} \times 100$$

2.2.8 Measurement of Critical Dissolution Time

The yarn hank (diam., 1/4 inch) in the form of a single loop was hung from a stainless steel rod (using a hook) with a pre-tension of 0.007 g/den using appropriate weights made of copper, hung from the yarn skein. The yarn loop with the pre-tension load was then introduced into 100% phenol at 40°C and the time taken (sec) for the weights to fall down was recorded using a stop watch. Critical dissolution time gives a measure of intercrystalline free space in the fibre.

2.2.9 Measurement of Mechanical Properties

Breaking tenacity (g/den) and breaking elongation (%) for untreated and treated yarn samples were measured using USTER TENSORAPID-3 with a gauge length of 200 mm, cross-head speed of 200 mm/min, chart speed of 500 mm/min and full scale load of 0.5 gf. Pre-tension used was 0.1 g/den as specified for textured yarn by Monsanto\textsuperscript{15}. Tenacity was calculated on the basis of actual denier before and after the solvent pretreatment.

2.2.10 Measurement of Birefringence

The birefringence ($\Delta n$) of the yarn samples was measured by a Vicker’s polarizing microscope fitted with a Berek compensator\textsuperscript{16-18} using the following expression:

$$\Delta n = \frac{6.33 \times \text{Phase difference}}{100 \times \text{Filament diameter}}$$

2.2.11 X-ray Crystallinity

The wide angle x-ray diffraction patterns of finely powdered samples were obtained using a Philips x-ray diffractometer (model 1700). Rotation powder method with identical setting for all samples was used to obtain the diffraction patterns for the measurement of fibre crystallinity\textsuperscript{19}. Nickel-filtered CuK$_\alpha$ radiation was used for this purpose. The recordings were done for 20 values between 10° and 35°. After obtaining the x-ray diffraction patterns, the patterns were automatically scanned in a densitometer to obtain a suitable plot to compute % crystallinity using PW-1710 computation system.

2.2.12 Dyeing

The untreated and solvent-treated PET yarn samples were dyed with C.I Disperse Brown 9 in boiling aqueous bath using a non-phenolic carrier (Teraux-C). Use of non-phenolic carrier in disperse dyeing of experimental yarns at lower temperature was thought appropriate as such type of carrier is non-toxic and promotes levelling by aiding in migration of disperse dyes. Also, at lower temperature, for the slow rate of dye diffusion, the coverage of dye variation is usually better than that in HT-HP dyeing. In each case, the dye bath contained:
Cl Disperse Brown 9 — 3% (owm)
Setamol-WS — 0.5% (owm)
Glacial acetic acid — a few ml (to adjust pH 4-4.5)
Teraux-C — 5 g/L
M:L — 1:100

The dyeing was carried out at 100°C for 1 h following the conventional carrier dyeing process of PET dyeing. After the dyeing was over, the dyed yarn was subjected to reduction clearing treatment using 2-3% sodium sulphite at 60°C for 15 min followed by final washing and drying in air.

2.2.13 Measurement of Dye Uptake

The optical density of the dye solution (after extracting the dye from the dyed PET filament yarn using chlorobenzene extraction at 125°C) was measured using Perkin-Elmer UV-VIS spectrophotometer (Model LAMDA-2S). The concentration of dye in dye bath before and after the dyeing was determined by measuring the optical densities of the dye-bath liquor before and after dyeing to get an estimate of the dye exhaustion in each case.

2.2.14 Measurement of Dye Uniformity

Ten small yarn samples were collected, each at a minimum distance of 1 m or more, from each bobbin of the solvent-treated (for varying time or proportion for mixed solvents) and untreated PET textured yarns. Yarn samples from each bobbin were dyed together in the same bath by the usual carrier dyeing method with a disperse dye and the K/S values of dyed yarn samples (dried) were measured using Macbeth 2020+ computerised reflectance spectrophotometer and associated software by the usual method. Each dyed yarn sample was wound on a uniform white cardboard forming uniform multiple layer of yarns to get a sheet of coloured yarns to be exposed (at ten points) before the reflectance spectrophotometer to measure its K/S value. The K/S value recorded for yarn samples from each bobbin was an average of 10 readings for each sample. From the 10 point average values of K/S (each being average of another 10 readings), the coefficient of variation (CV%) of K/S data was statistically calculated to express the dye uniformity.

3 Results and Discussion

3.1 Single Solvent Treatment

3.1.1 Effect of Treatment Time on Weight Loss, Shrinkage and Physical Properties of Yarn

The data in Table I show gradual increase in weight loss along with increase in shrinkage on treatment as well as increase in linear density with increase in treatment time from 15 min to 960 min, irrespective of the type of solvent used. These

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Treatment time</th>
<th>Weight loss</th>
<th>Linear density</th>
<th>Shrinkage</th>
<th>Tenacity</th>
<th>Elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (Untreated)</td>
<td>0</td>
<td>—</td>
<td>58.0</td>
<td>—</td>
<td>3.25</td>
<td>34.60</td>
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<tr>
<td>Dimethyl formamide</td>
<td>15</td>
<td>1.67</td>
<td>76.7</td>
<td>24.5</td>
<td>2.40</td>
<td>36.50</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>1.87</td>
<td>80.5</td>
<td>28.7</td>
<td>2.30</td>
<td>38.59</td>
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<td></td>
<td>480</td>
<td>2.05</td>
<td>81.0</td>
<td>28.8</td>
<td>2.24</td>
<td>42.89</td>
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<tr>
<td></td>
<td>960</td>
<td>2.23</td>
<td>82.0</td>
<td>29.9</td>
<td>2.15</td>
<td>38.50</td>
</tr>
<tr>
<td>Acetone</td>
<td>15</td>
<td>1.66</td>
<td>76.0</td>
<td>23.5</td>
<td>2.45</td>
<td>38.25</td>
</tr>
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<td></td>
<td>60</td>
<td>1.75</td>
<td>79.0</td>
<td>26.4</td>
<td>2.45</td>
<td>40.0</td>
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<td>29.0</td>
<td>2.33</td>
<td>42.60</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>1.89</td>
<td>82.5</td>
<td>30.0</td>
<td>2.27</td>
<td>43.20</td>
</tr>
<tr>
<td></td>
<td>480</td>
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<td>84.0</td>
<td>30.5</td>
<td>2.20</td>
<td>39.40</td>
</tr>
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<td></td>
<td>960</td>
<td>2.24</td>
<td>85.0</td>
<td>31.0</td>
<td>2.14</td>
<td>38.90</td>
</tr>
<tr>
<td>Tetrachloroethane</td>
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<td>1.68</td>
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<td>2.56</td>
<td>35.00</td>
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<td>75.5</td>
<td>23.0</td>
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<tr>
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<td>480</td>
<td>1.88</td>
<td>76.5</td>
<td>24.8</td>
<td>2.33</td>
<td>36.90</td>
</tr>
<tr>
<td></td>
<td>960</td>
<td>2.16</td>
<td>83.0</td>
<td>29.0</td>
<td>2.18</td>
<td>38.49</td>
</tr>
</tbody>
</table>

Table 1 — Effect of treatment with different solvents on weight loss, linear density, shrinkage and tensile properties of textured polyester multifilament yarn

[Treatment temp., 30±2°C]
result from the following two opposing influences:
—mass loss by surface dissolution including the removal of finishing oil/agents, surface oligomers, etc.; and
—longitudinal shrinkage consequent to swelling and stress relaxation of the polymeric chain, causing overall increase in diameter/denier.

Obviously, the results obtained indicate the predominance of second influence for all the solvents used. However, the % increase of shrinkage is maximum in case of tetrachloroethane.

The data on tensile properties (Table 1) indicate that with the increase in treatment time the tenacity of the filaments is marginally decreased. The elongation to break after solvent treatment increases to some extent with the increase in treatment time except in some cases where the trend starts reversing for a very high time of treatment i.e for 960 min. The trends are the same for all solvents used except methylene chloride where the maximum elongation to break is found at 60 min treatment time. The quick action of methylene chloride showing maximum shrinkage consequent to disorientation, leading to maximum elongation to break, can be explained by its small molecular size compared to that of other solvents. The rapid diffusion and extremely high interaction of methylene chloride with PET fibre was reported earlier in the patent literature\(^{20,21}\). However, both the general trends of decrease in tenacity and increase in percentage elongation to break for all the experimental solvents used may be attributed to the possible disorientation of polymeric chain consequent to longitudinal shrinkage that occurs during swelling treatment and solvent-induced chain relaxation.

In general, it was observed that the treatments for 60 and 480 min for all the solvents used show very close results/changes and, therefore, it was thought appropriate not to employ 480 min treatment in the subsequent studies, though the treatment for 960 min for all subsequent studies was continued to get comparative result.

It is evident from Table 2 that the % change in bulk increases with the increase in treatment time for all the solvents used. % Change in bulk is maximum for the highest treatment time (960 min) and minimum for the lowest treatment time (15 min), irrespective of the type of solvent used. The increase in bulk (10.2-18%) may be attributed to increased longitudinal shrinkage on solvent treatment, which is higher for higher treatment time. However, the differences between the % change in bulk for 60 min and 960 min are not always significant for all the solvents used except tetrachloroethane, which shows dominant effect of time compared to the other solvents used, though the highest % change in bulk is found for methylene chloride solvent, probably due to its rapid diffusion characteristics, apparently on account of its smaller size. Therefore, it is advisable to carry out the solvent treatment for 60 min only in each case.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Treatment time</th>
<th>Change in bulk %</th>
<th>Crimp rigidity %</th>
<th>Residual shrinkage %</th>
<th>Crystallinity %</th>
<th>Birefringence Δn</th>
<th>Critical dissolution time s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (Untreated)</td>
<td>0</td>
<td>—</td>
<td>17.60</td>
<td>5.00</td>
<td>47.00</td>
<td>0.147</td>
<td>50</td>
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<tr>
<td>Dimethyl formamide</td>
<td>15</td>
<td>12.4</td>
<td>12.86</td>
<td>4.50</td>
<td>46.25</td>
<td>0.140</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>15.1</td>
<td>9.85</td>
<td>4.01</td>
<td>45.70</td>
<td>0.142</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>960</td>
<td>16.0</td>
<td>6.64</td>
<td>3.25</td>
<td>43.80</td>
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<td>23</td>
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<tr>
<td>Acetone</td>
<td>15</td>
<td>11.7</td>
<td>12.11</td>
<td>4.75</td>
<td>45.85</td>
<td>0.144</td>
<td>33</td>
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<td></td>
<td>60</td>
<td>14.0</td>
<td>11.51</td>
<td>4.25</td>
<td>45.50</td>
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<td>32</td>
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<tr>
<td>Methylene chloride</td>
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<td>10.82</td>
<td>4.60</td>
<td>46.08</td>
<td>0.142</td>
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<td>4.35</td>
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<td>18.0</td>
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<td>3.75</td>
<td>43.50</td>
<td>0.145</td>
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</tr>
<tr>
<td>Tetrachloroethane</td>
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<td>10.07</td>
<td>4.65</td>
<td>46.75</td>
<td>0.144</td>
<td>32</td>
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<tr>
<td></td>
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<td>11.5</td>
<td>8.70</td>
<td>4.15</td>
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<td>3.72</td>
<td>43.9</td>
<td>0.146</td>
<td>24</td>
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</tbody>
</table>
It may also be seen from Table 2 that the crimp rigidity (%) of the solvent-treated textured PET yarn samples decreases with the increase in treatment time. Crimp rigidity is a measure of resistance and recovery against deformation and stretch and it indicates the extent of chemical setting of the thermo-mechanically textured filament yarn.

Table 2 also shows that the residual shrinkage decreases with the increase in treatment time in case of all the solvents used and the values are lower compared to that for the control sample. Residual shrinkage provides a measure of dimensional stability of the textured polyester filament yarn; the lower the value, the higher the stability of the yarn. Higher residual shrinkage of the solvent-treated textured polyester yarn indicates a less effective swelling agent. Thus, comparing the residual shrinkage values obtained, DMF is considered as effective swelling agent among the single solvents used.

3.1.2 Effect of Treatment Time on Fine Structure of Yarn

Table 2 shows that the birefringence decreases initially with the increase in solvent treatment time in case of all the four single solvents used, but for a very high treatment time (960 min), it shows an increasing trend, the value still being lower than that for the control sample. Solvent swelling leads to achieve a relatively stable structure in a state of lower energy, so far molecular relaxation is concerned, causing some loss in amorphous orientation. The loss of amorphous orientation on solvent treatment was earlier noticed by Subramanian et al.\textsuperscript{22} The initial solvent-induced relaxation and disorientation during shrinkage is frequently followed by partial dissolving or melting and recrystallisation of imperfect crystalline domains, normally as a second step after shrinkage.

It is observed from Table 2 that the crystallinity and critical dissolution time (CDT) decrease with the increase in solvent treatment time, irrespective of the type of solvent used. The effect is more pronounced in case of DMF and methylene chloride treatments and less in case of acetone and tetrachloroethane (TCE). CDT values for acetone- and TCE-treated polyester filaments are relatively higher than those for the other two solvents used. The maximum drop in CDT on methylene chloride treatment is a clear indication of maximum increased accessibility of the PET polymer towards external agents. The increased accessibility towards external agents/dyes, etc on solvent treatment may be explained by better separation/segregation of crystalline and non-crystalline regions by partial dissolving and perfectioning of crystallites.\textsuperscript{22}

3.2 Mixed Solvent Treatment
3.2.1 Effect of TCE/DMF Ratio on Weight Loss, Shrinkage and Physical Properties of Yarn

The effect of mixture of organic solvents on shrinkage of polymeric fibres depends on the extent to which the components interact with each other. Such inter-solvent interactions can also lead to synergism. A similar effect has been observed by Weigmann et al.\textsuperscript{2,4} in the isothermal shrinkage of PET in mixture of perchloroethylene and methanol. In contrast, the shrinkage behaviour of PET in mixture of non-interacting solvents such as perchloroethylene and trichlorobenzene is directly proportional to the composition of the solvent mixture. Therefore, it is considered to be appropriate to use mixture of solvents instead of single solvent to bring the solubility parameter of the mixture of solvents much closer to that of total solubility parameter of PET fibre\textsuperscript{24} ($\delta=10.7$) so that the action of the mixture of solvents becomes rapid and more uniform for removal of oligomers and better homogenization of the structural assembly of the fibre to obtain better dye uniformity, etc. Moore\textsuperscript{24} reported the solubility parameter of PET to be 10.7, which is definitely more widely accepted though the total solubility parameter of PET is also reported\textsuperscript{2} to be 9.6 (cal/cm$^3$)$^{1/2}$, with two separate component solubility parameters\textsuperscript{6,5,25} ($\delta_1=9.8$ and $\delta_2=12.1$).

Weigmann and coworkers\textsuperscript{2,5,25} found bimodal distribution for various properties like equilibrium swelling, mechanical properties, shrinkage behaviour, etc. as a functions of solubility parameter. Moore and Sheldon\textsuperscript{3} also reported similar findings. In all these examples, it was found that the maximum interactions with PET polymer occur at two regions of solubility parameter values ($\delta_1=9.8$ and $\delta_2=12.1$). It is assumed that either in these regions the solvents interact preferentially with the aromatic or aliphatic residue of the PET repeat unit or that there are specific acid-base interactions between solvents and polymer groups. Knox\textsuperscript{26} explored this aspect in detail and found such bimodal interactions (having two ranges) of solvents with PET.
Table 3 — Effect of treatment with mixtures of TCE and DMF on weight loss, linear density, shrinkage and tensile properties of textured polyester multifilament yarn

[Treatment time, 60 min; and Treatment temp, 30±2°C]

<table>
<thead>
<tr>
<th>TCE : DMF</th>
<th>Weight loss %</th>
<th>Linear density den</th>
<th>Shrinkage %</th>
<th>Tenacity g/den</th>
<th>Elongation %</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:1</td>
<td>1.47</td>
<td>72.0</td>
<td>19.08</td>
<td>2.58</td>
<td>35.04</td>
</tr>
<tr>
<td>2:1</td>
<td>1.59</td>
<td>72.5</td>
<td>20.38</td>
<td>2.62</td>
<td>35.6</td>
</tr>
<tr>
<td>1:1</td>
<td>1.80</td>
<td>77.5</td>
<td>26.00</td>
<td>2.36</td>
<td>35.69</td>
</tr>
<tr>
<td>1:2</td>
<td>1.78</td>
<td>81.0</td>
<td>28.25</td>
<td>2.28</td>
<td>35.29</td>
</tr>
<tr>
<td>1:3</td>
<td>1.88</td>
<td>82.0</td>
<td>28.75</td>
<td>2.34</td>
<td>35.89</td>
</tr>
</tbody>
</table>

TCE — Tetrachloroethane; and DMF — Dimethyl formamide

Table 4 — Effect of treatment with mixtures of TCE and DMF on properties and fine structure of textured polyester multifilament yarn

[Treatment time, 60 min; and Treatment temp, 30±2°C]

<table>
<thead>
<tr>
<th>TCE : DMF</th>
<th>Change in bulk %</th>
<th>Crimp rigidity %</th>
<th>Residual shrinkage %</th>
<th>Birefringence</th>
<th>Critical dissolution time s</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:1</td>
<td>13.75</td>
<td>8.75</td>
<td>4.75</td>
<td>0.146</td>
<td>28</td>
</tr>
<tr>
<td>2:1</td>
<td>14.25</td>
<td>8.50</td>
<td>4.66</td>
<td>0.144</td>
<td>26</td>
</tr>
<tr>
<td>1:1</td>
<td>15.52</td>
<td>7.75</td>
<td>4.33</td>
<td>0.143</td>
<td>25</td>
</tr>
<tr>
<td>1:2</td>
<td>17.00</td>
<td>6.94</td>
<td>4.25</td>
<td>0.142</td>
<td>24</td>
</tr>
<tr>
<td>1:3</td>
<td>18.00</td>
<td>6.75</td>
<td>4.00</td>
<td>0.140</td>
<td>23</td>
</tr>
</tbody>
</table>

Weight loss, linear shrinkage and changes in tensile properties on treatment with different proportions of DMF, (solubility parameter, δ=12.14) and TCE (solubility parameter, δ=9.85) are shown in Table 3. These two solvents were chosen on the basis of data shown in Tables 1 and 2 as well as considering their individual solubility parameter values, which are very close to the two regions of solubility parameter values where PET polymers showed maximum interactions2,3,5,25

Table 3 shows that on treatment with mixture of TCE and DMF the loss in weight increases with either decrease in the proportion of TCE, keeping the proportion of DMF constant, or with the increase in the proportion of DMF, keeping the proportion of TCE constant.

It is observed from Table 3 that the breaking tenacity decreases marginally with either decrease in the proportion of TCE or increase in the proportion of DMF in the solvent mixture, whereas the elongation to break increases with the increase in DMF proportion in the solvent mixture. Highest elongation to break is observed for 1:3 TCE /DMF solvent-treated PET sample which shows highest increase in % bulk as well as highest linear shrinkage. This effect may be well attributed to the highest disorientation effect (corresponds to lowest birefringence, Table 4) to textured polyester yarn treated with 1:3 TCE/DMF mixture.

Table 4 shows that there is a gradual increase in % change in bulk with the use of higher proportion of DMF in the solvent mixture. Consequently, increase in bulk is also observed with the use of lower proportion of TCE in the solvent mixture. The optimum effect is observed in the case of 1:3 TCE/DMF solvent-treated sample.

It is also observed from Table 4 that the crimp rigidity decreases with either decrease of TCE proportion or increase of DMF proportion in the solvent mixture. It is further observed from Table 4 that the highest residual shrinkage is shown by 3:1 TCE/DMF solvent-treated sample. With the increase of DMF proportion the residual shrinkage decreases. The lowest residual shrinkage in case of 1:3 TCE/DMF solvent-treated sample is indicative of better setting action offered by this mixture in comparison to the other ratios of these two solvents. The changes in residual shrinkage by TCE/DMF mixed solvents, particularly 1:3 TCE/DMF, cannot be explained simply by the proportional compositions of those two solvents. It is presumed that some intersolvent interactions take place between these two solvents at this proportion, showing more than expected changes in properties.
of PET yarn. To understand the type of interactions, the kinetic study of the interaction of these two solvents mixture with PET polymer is to be carried out separately.

### 3.2.2 Effect of TCE/DMF Ratio on Fine Structure of Yarn

As shown in Table 4, the birefringence, i.e. the total orientation, of PET yarn sample decreases with the use of higher proportion of DMF in the TCE/DMF mixed solvent. The higher drop in polymeric chain orientation might have caused the polymer to achieve a relatively stable structure in a state of lower energy.

The critical dissolution time (CDT) is also decreased with the increase in the proportion of DMF in the solvent mixture. The lowest CDT value is observed in case of 1:3 TCE/DMF solvent-treated sample. The drop in CDT may be due to the increased localization of crystalline and non-crystalline regions which might have lead to increased accessibility to the polymer materials towards external agents, dyes, etc.

### 3.3 Effect of Single Solvent Treatment and Mixed Solvent Treatment on Dye Uptake and Dye Uniformity

The dyeing results of different single solvent treated PET yarns are shown in Table 5 and that for TCE/DMF solvent-treated yarns are shown in Table 6.

Dye uptake of single solvent treated samples increased by 2-5% with the increase in treatment time (Table 5) and it is maximum for the highest treatment time (960 min) in case of all the four single solvents. The improved dyeability of PET fibre pretreated with organic solvents is reported earlier and is achieved either through the retention of residual solvent in fibre structure even after the standard wash which acts like a carrier in subsequent dyeing or through semipermanent/permanent modification of fibre structure by reducing glass transition temperature and creating more voids and openness of fibre structure, which ultimately increases dye diffusion and dye accessibility, permitting increased rate of dye transport and enhancing saturation dye uptake.

The observed increase in dye uptake and consequent increase in average K/S values may therefore be explained by the increased dye accessibility in polymeric mass by the swelling action of solvents coupled with the structural changes and plasticizing effect of each solvent inducing increase in dye uptake. The swelling agent diffuses into polymer matrix and swells the polymer, causing increased accessibility in the non-crystalline zone for better segregation of crystallites and non-crystallites, which is also reported earlier by Warwicker et al.

The changes in percentage crystallinity, shrinkage and CDT after different single solvent treatments are also found consistent with the dye-uptake results (Tables 2, 4 and 5). Among the mixed solvent treated PET samples, the maximum dye uptake is observed for the sample treated with 1:3 TCE/DMF solvent mixture.

CV % of the K/S values of solvent pretreated and subsequently dyed PET samples indicate that the dye uniformity is increased substantially in all the cases of solvent-treated textured polyester yarns.
(Tables 5 and 6). Structural homogenization, removal of oligomers and plasticizing and carrier effect of retained solvents may be considered to be chiefly responsible for this. However, it is observed that the increase in solvent treatment time from 15 min to 60 min increases dye uniformity in case of all the single solvents used but the trend is reversed for use of very long treatment time (960 min). The observed reversing trend of increase in dye non-uniformity for a long time of solvent treatment may be due to the possible structural inhomogeneity superimposed on and above the relaxed/homogenized solvent-treated (limited time) sample by way of possible crystalline swelling coupled with the highest weight loss for a long time (960 min) of solvent treatment.

For the single solvents used, the best result for dye uniformity is obtained for TCE on treatment for 60 min, showing only 1.08 CV% of K/S. However, 1:3 TCE/DMF mixture pretreatment gives better or at least at par dye uniformity results. The order of dye uniformity given by different solvents is as follows:

TCE/DMF (1:3) ≈ TCE > DMF > CH₂Cl₂ > Acetone.

Again, between the TCE and 1:3 TCE/DMF, at otherwise comparable treatment condition, the dye-uptake is higher for the mixed solvent. So, the pretreatment of textured polyester multifilament yarn with 1:3 TCE/DMF solvent mixture at room temperature for 60 min may be of practical importance for increasing dye uniformity and saturation dye uptake.

4 Conclusions

4.1 Pretreatment of textured polyester multifilament yarns with the selected solvents has been found to be associated with an increase in weight loss, %change in bulk, linear density, treatment shrinkage, breaking elongation, dye-uptake and dye uniformity coupled with a decrease in crimp rigidity, tenacity, residual shrinkage, %crystallinity, birefringence and critical dissolution time.

4.2 Among the four different single solvents used, methylene chloride gives a better balance of the property parameters on pretreatment of ployester textured multifilament yarn at room temperature for 60 min. DMF and TCE both show at par performance to each other and are considered to be next to methylene chloride. TCE as single solvent gives very low CV% of K/S, indicating lower dye non-uniformity compared to other single solvents used.

4.3 Use of a selective proportion (1:3) of TCE and DMF in solvent mixture gives somewhat better balance of property parameters of the textured polyester filament yarn than the use of single solvents. Treatment with 1:3 TCE/DMF solvent gives the highest dye-uptake, lowest dye non-uniformity (lower CV% of K/S) and lowest residual shrinkage (highest setting) along with lower crimp rigidity, marginally higher increase in % bulk and lower critical dissolution time than the data obtained for methylene chloride treatment at otherwise comparable conditions of treatment for 60 min. These results may be practically useful for increasing dye-uptake, reducing dyeing variation and better balance of other properties of textured polyester filament yarns.

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References