

# Solvent-Induced Modifications in Polyester Yarns. II. Structural and Thermal Behavior

D. Chidambaram,<sup>1,\*</sup> R. Venkatraj,<sup>1</sup> P. Manisankar<sup>2</sup>

<sup>1</sup>Department of Textile Technology, P.A.C. Ramasamy Raja Polytechnic College, Rajapalayam-626108, India

<sup>2</sup>Department of Industrial Chemistry, Alagappa University, Karaikudi-630003, India

Received 21 June 2002; accepted 27 October 2002

**ABSTRACT:** The structural and thermal behaviors of polyester yarns treated with trichloroacetic acid–chloroform (TCAC) mixture were investigated by differential scanning calorimetric analysis (DSC), wide-angle X-ray scattering (WAXS), infrared spectroscopy (IR), and scanning electron microscopy (SEM). The effects of TCAC treatment on original fine filament (FFP) and microdenier (MDP) polyester yarns and on heat-set polyester yarns were studied. It was found that the glass transition temperature of TCAC-treated polyester yarns decreases with an increase in treatment concentration due to the plasticization effect, which is remarkable even at lower treatment concentration. The TCAC treatment on polyester yarns resulted in the formation of new crystallites in the extended noncrystalline domains of PET as well as growth and perfection of these new crystallites and the preexisting crystals. Further, the DSC thermograms re-

vealed that TCAC treatment with 3% concentration could be able to overcome the structural changes in PET produced by heat setting at 180°C. The substantial changes in noncrystalline and crystalline domains observed were related to the mechanical properties of yarns. From the WAXS studies, an increase in crystal size and lateral order of TCAC-treated polyester yarns was noted. The most distinct changes brought about by TCAC treatment include overall orientation determined by the *trans-gauche* ratio from IR measurements. The removal of oligomers and smoothening out of the fiber surface by TCAC treatment were observed from SEM studies. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1555–1566, 2003

**Key words:** poly(ethylene terephthalate); solvent treatment; fibers; heat treatment; structural and thermal behavior

## INTRODUCTION

Poly (ethylene terephthalate) (PET) has a compact fiber structure with a high degree of crystallinity and high glass transition temperature and without recognized dye sites.<sup>1</sup> Because of this, satisfactory dyeing of PET below 130°C is difficult to achieve. The dyeing behavior of PET can be improved by reducing the glass transition temperature of PET by suitable modification of polymer matrix.<sup>2</sup>

Both annealing and solvent pretreatment are important technological processes that induce extensive structural modification in PET yarns. Annealing of PET yarns confers dimensional stability to the material through the relaxation of residual stresses. Detailed investigations<sup>3–5</sup> have been carried out on structure and properties of PET yarns heat set at various temperatures. The transition in properties such as tensile modulus, shrinkage, and oxygen permeability of polyester yarns which are heat set at 180°C have been reported<sup>6</sup> on the basis of microstructural changes caused by processes such as crystallization, solid-state

thickening, melting, molecular relaxation, as well as melting and recrystallization. It has been observed<sup>3–6</sup> that up to a heat-setting temperature of 180°C, the number and size of the crystallites increases steadily. At temperatures above 180°C, the recrystallization process results in a further increase in crystallite size but a decrease in their number. Further, the studies of polymer–solvent systems have received much attention for environmental protection and industrial processes.<sup>7</sup> Investigations have been carried out on the interactions of organic solvents with PET to understand the morphological and structural changes taking place because of solvent treatment.<sup>8,9</sup> The majority of work on PET–solvent interaction has been on the solvent-induced crystallization (SINC). SINC is attributed to the disruption of secondary interchain bonds, which increases the segmental mobility of polymer chains and permits internal structural rearrangement to the desired configuration.<sup>9</sup> It results in the formation of new crystallites in glassy polymers<sup>10</sup> and perfection and growth of existing crystallites in semicrystalline polymers.<sup>11</sup> Solvents whose solubility parameter is closer to PET is likely to cause SINC in PET films<sup>12</sup> and PET fibers.<sup>13</sup>

Hence, both solvent pretreatment and heat setting of polyester yarns induce crystallization in the polymer, alter the glass transition temperature, and enhance the segmental mobility of polymer chains. The

Correspondence to: D. Chidambaram (dchidambaram@rediffmail.com).

major difference between them is that in the former case, external low molecular weight species is involved in the treatment and results in swelling of fiber structure, whereas in the latter, during thermal treatment, no swelling occurs and disorientation is rapidly followed by crystallization in the newly disoriented domains.<sup>14</sup> Most of the solvents and solvent mixtures are capable of inducing enough structural modification in PET at high-temperature or long-duration treatment time.<sup>15</sup> From our preliminary investigations,<sup>16–18</sup> it has been observed that the interaction of solvents with PET could be made more rapid by the addition of organic acids with solvents in suitable proportions. Hence, the investigation on structural and thermal behavior of PET yarns subjected to both heat and solvent–acid mixture pretreatment can lead to better a understanding of structure–property relationship in PET fibers and contribute significantly to the field of applied polymer science.

A considerable amount of research<sup>19–21</sup> has been done to modify PET fiber with a view to develop silklike, soft, and light drapeable articles. Advancements in spinning technology and quality of polymers has made it possible to reduce the denier of the filament to achieve the fineness of natural silk, its soft feel and luster in PET fiber.<sup>22</sup> In this context, fine filament and microdenier polyester filament assumes significance in commercial exploitation. In the first part of this series, the mechanical properties of fine filament and microdenier polyester yarns treated with trichloroacetic acid–chloroform (TCAC) reagent was discussed.<sup>23</sup> It is inferred that the changes in tensile properties reflect the structural modification induced by TCAC treatment. The studies reported in this article are mainly on structural and thermal behavior of polyester yarns modified by TCAC treatment based on the measurements from differential scanning calorimetry (DSC), wide-angle X-ray scattering (WAXS), infrared spectroscopy (IR), and scanning electron microscopy (SEM).

## METHODS

### Materials

The following polyester yarn samples were selected for the present study: (1) Fine Filament Polyester Yarn (FFP), 55.5 dtex/48; (2) Micro Denier Polyester Yarn (MDP), 75.5 dtex/72. The samples were obtained from Sanghi Polyesters Ltd., Hyderabad, India.

### Heat setting

PET yarn skeins weighing approximately 2 g were prepared by using a Shirley yarn winding device. These yarn skeins were subjected to isothermal an-

Materials used	Fine filament polyester yarns (FFP) Microdenier polyester yarns (MDP) Heat-set FFP yarns (HFFP) Heat-set MDP yarns (HMDP)
Solvent used	Trichloroacetic acid–chloroform (TCAC)
Concentration of the reagent (TCAC) used (w/v)	1%, 3%, 5%
Treatment temperature	Room temperature
Material-to-liquor ratio	1 : 100
Time	5 min
After treatment	Washing with chloroform for 5 min, followed by washing with acetone for 5 min

nealing in loose state in a hot-air oven. The heat setting was carried out at 180°C for 60 s.

### Chemicals

Laboratory grade (LR) trichloroacetic acid (CCl<sub>3</sub>COOH), chloroform (CHCl<sub>3</sub>), and acetone (CH<sub>3</sub>CO·CH<sub>3</sub>) were used.

### Pretreatment

The samples tested and the pretreatment conditions adopted in this investigation are given in Table I. TCAC reagent in desired concentrations (1, 3, 5% w/v) were prepared for the treatment of polyester yarn samples. The original and heat-set polyester yarn skeins were treated with TCAC reagent in a specially made closed trough at room temperature (30–32°C). The yarn samples were treated in the reagent with various concentrations in a relaxed state for 5 min, keeping the material-to-liquor ratio 1 : 100. The contents were agitated manually at regular intervals to ensure uniform treatment. The treated samples were rinsed with chloroform and then with acetone to remove any adhering reagent from the treated samples. The yarn samples were squeezed by using filter paper and then air dried at atmospheric condition, taking the advantage of quick evaporation of acetone at room temperature. The samples were conditioned at the standard testing atmosphere of 27° ± 2°C and at 65 ± 2.37 relative humidity (RH) for 24 h before testing.

### Yarn count

A direct method of weighing a definite length of yarn as per Bureau of Indian Standards<sup>24</sup> (BIS) was used. A Mettler microbalance (0.0001 mg precision) was used to determine accurately the weight of the samples. The mass in grams of 1000 meters length of yarn was calculated for determining the count of yarn.

### DSC analysis

DSC (Perkin–Elmer DSC 7) was used to obtain the thermograms. Glass transition temperature ( $T_g$ ) was taken as the midpoint of baseline shift region in the DSC thermograms. The thermograms were taken from the first scan of DSC run and all the scanning was done under inert atmosphere with a heating rate of 10°C/min. The crystallinity was calculated from the area of the melting endotherm, which is a measure of heat of fusion of the sample ( $\Delta H_{\text{exp}}$ ) and degree of crystallinity was calculated from the formula,

$$\text{Degree of crystallinity} = \frac{\Delta H_{\text{exp}}}{\Delta H_c} \quad (1)$$

where  $\Delta H_c$  is the absolute value of heat of fusion of fully crystalline polymer. For the present calculations,  $\Delta H_c$  was taken to be 119.8 J/g, a value given by Waunderlich.<sup>25</sup> For each sample, two specimens were taken for DSC measurements. Student *t*-tests were performed on the experimental results to show the significant difference due to TCAC treatment.

### WAXS studies

The WAXS diffraction patterns of finely powdered samples were obtained by using a Philips X-ray diffractometer. For each sample, two specimens were taken. Rotation powder method with an identical setting for all the samples was used to obtain diffraction patterns.<sup>26</sup> Nickel-filtered  $\text{CuK}\alpha$  radiation was used for this purpose. WAXS measurements were used to calculate the crystal size (CS) and percentage lateral order (%LO) as described in detail in the literature.<sup>27,28</sup> The PET fibers presented a characteristic three-peak equatorial X-ray scattering pattern. The observed peak maxima were  $2\theta_1 \cong 17.5^\circ$ ,  $2\theta_2 \cong 22.5^\circ$ , and  $2\theta_3 \cong 25.5^\circ$ , corresponding to the crystal planes, (010), (110), and (100), respectively. The width of the crystalline peak at  $2\theta \cong 17.5^\circ$  was considered for the crystal size calculations through the basic Scherrer equation<sup>28</sup>:

$$\text{CS} = \frac{K\lambda}{\beta \cos\theta} \quad (2)$$

where *K* is a shape factor that varies between 0.9 and 1.1. A value of 1.0 has been considered for our calculations,  $\lambda$  is the wavelength of the radiation used (for  $\text{CuK}\alpha$ ,  $\lambda = 1.5418 \text{ \AA}$ ),  $\beta$  is the half-maximum breadth in radians, and  $\theta$  is the Bragg's angle.

The  $\text{LO}^{29,30}$  parameter can be related to several factors such as crystallinity of the samples, perfection, size, and distribution of the crystallites, and it was calculated from the equation:

$$\% \text{ LO} = (1 - \text{RF}) \times 100 \quad (3)$$

where RF is the resolution factor which is given by:

$$\text{RF} = \frac{m_1 + 2m_2 + m_3 + \dots + m_n - 1}{h_1 + h_2 + h_3 + \dots + h_n} \quad (4)$$

where  $m_1, m_2$ , etc., are the heights of minima from the appropriate baseline, and  $h_1, h_2$ , etc., are the heights of maxima from the same baseline. Therefore, the resolution factor for PET fibers can be written as:

$$\text{RF} = \frac{m_1 + 2m_2}{h_1 + h_2 + h_3} \quad (5)$$

where  $m_1$  and  $m_2$  correspond to the minima between the planes (010) and (110) and between the planes (110) and (100), respectively;  $h_1, h_2$ , and  $h_3$  are the observed maxima diffraction peaks corresponding to the planes (010), (110), and (100).

### Infrared studies

Infrared spectra were recorded on a Perkin–Elmer infrared spectrophotometer model 783. The powdered samples were dispersed in KBr and pressed into pellets for these measurements. For each sample, two specimens were taken. Peak intensities in percentage transmission were taken at wave numbers  $973 \text{ cm}^{-1}$  (*trans*),  $898 \text{ cm}^{-1}$  (*gauche*), and  $795 \text{ cm}^{-1}$  (internal reference). Measurements of  $973$  and  $898 \text{ cm}^{-1}$  bands were normalized over the intensity of the  $795 \text{ cm}^{-1}$  band. Because the aliphatic ester segments of PET are either in *trans* or in *gauche* conformation, the relative percentage of each conformation was calculated by assuming the summation of two becomes one.<sup>31</sup>

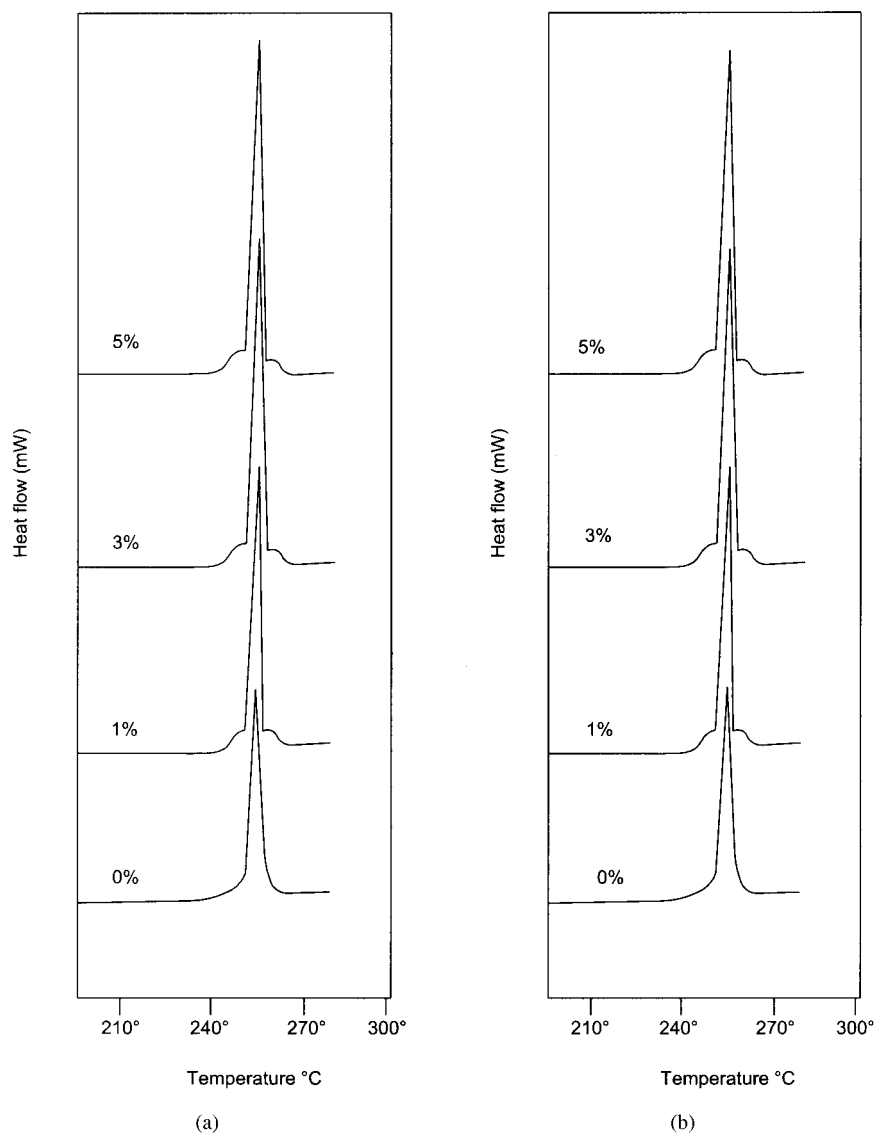
### SEM topography

SEM studies were carried out on the samples after mounting them on specimen stubs and coating with Au–Pd in a vacuum fine-coat ion sputter. For each sample, two specimens were taken. The thickness of the coating and time was optimized before the samples were examined in JOEL SEM model 84 0A.

## RESULTS AND DISCUSSION

### Thermal behavior

Figure 1 shows the main melting endotherms of original FFP and MDP yarn samples treated with various concentrations of TCAC reagent. For each sample, the starting melting temperature ( $T_1$ ), onset melting temperature ( $T_o$ ), final melting temperature ( $T_2$ ), and the peak melting temperature ( $T_m$ ) are shown in Tables II and III. Melting range is the phenomenon of the progressive melting of the crystallites of varying stability. The temperature  $T_1$  is the start of the melting endo-



**Figure 1** DSC thermograms showing the main melting peak of polyester yarns. (a) Untreated and TCAC-treated FFP yarns; (b) untreated and TCAC-treated MDP yarns.

**TABLE II**  
Thermal Behavior of TCAC-Treated FFP and HFFP Yarns

Yarns	TCAC concentration (w/v)	$T_1$ (°C)	$T_o$ (°C)	$T_2$ (°C)	$T_m$ (°C)	$T_g$ (°C)	pm (°C)	$X_p$ (%)	$X_m$ (%)	$X_c$ ( $X_p + X_m$ ) (%)	Max. heat flow (mW)
FFP	0%	234.51	251.82	264.86	255.69	96	—	—	45.2	45.2	19.7
	1%	234.50	253.26	264.87	255.78	81	162	1.2	47.5	48.7	25.3
	3%	234.58	253.32	264.86	255.71	79	182	2.3	46.5	48.8	26.7
	5%	234.57	253.33	264.87	255.67	76	182	2.8	45.9	48.7	27.2
HFFP	0%	233.42	251.74	266.92	255.99	112	168	1.7	47.1	48.8	19.7
	1%	233.75	251.75	265.25	255.96	98	170	1.8	46.8	48.6	19.7
	3%	233.90	252.15	265.27	255.27	86	181	2.3	46.7	49.0	20.4
	5%	234.81	252.44	265.27	255.38	80	182	2.8	46.7	49.5	21.9

$T_1$ ,  $T_o$ , and  $T_2$ , correspond to starting, onset, and final temperatures of the main melting peak, respectively;  $T_m$ , melting temperature at the max heat flow;  $T_g$ , glass transition temperature; pm, premelting temperature;  $X_p$  and  $X_m$  correspond to the crystallinities calculated from the premelting peak and main melting peak, respectively;  $X_c$ , total crystallinity.

TABLE III  
Thermal Behavior of TCAC-Treated MDP and HMDP Yarns

Yarns	TCAC concentration (w/v)	$T_1$ (°C)	$T_o$ (°C)	$T_2$ (°C)	$T_m$ (°C)	$T_g$ (°C)	pm (°C)	$X_p$ (%)	$X_m$ (%)	$X_c$ ( $X_p + X_m$ ) (%)	Max. heat flow (mW)
MDP	0%	231.12	251.26	264.0	254.6	93	—	—	43.8	43.8	19.9
	1%	231.12	252.79	264.12	255.57	78	165	1.1	45.4	46.5	25.3
	3%	231.20	252.82	264.57	255.45	75	179	2.3	45.3	47.6	25.9
	5%	231.21	252.74	264.87	255.03	73	181	3.1	45.4	48.5	26.3
HMDP	0%	233.37	251.34	266.00	254.77	108	170	1.7	45.3	47.0	19.9
	1%	234.25	251.46	264.87	254.58	97	170	1.8	45.4	47.2	20.3
	3%	234.21	251.46	264.85	254.59	86	178	2.3	45.5	47.8	21.9
	5%	234.12	251.90	264.87	254.68	80	180	3.0	45.3	48.3	22.1

$T_1$ ,  $T_o$ , and  $T_2$ , correspond to starting, onset, and final temperatures of the main melting peak, respectively,  $T_m$ , melting temperature at the max heat flow;  $T_g$ , glass transition temperature; pm, premelting temperature;  $X_p$  and  $X_m$  correspond to the crystallinities calculated from the premelting peak and main melting peak, respectively;  $X_c$  total crystallinity.

therm and can be regarded as the melting of the smallest perfect crystals present in the sample. The temperature  $T_o$  is regarded as melting of the less stable bigger crystals. The temperature  $T_2$  corresponds to the melting of the most stable bigger crystallites.  $T_m$  is taken at the maximum heat flow in the melting endotherm. The original FFP yarn samples presented higher values of  $T_1$ ,  $T_2$ , and  $X_c$  compared to the MDP yarns. The original MDP yarns presented an exothermic peak at 102.5°C (with heat flow of  $-4.02$  J/g), whereas the thermogram of FFP yarns do not show any characteristic exothermic peak.

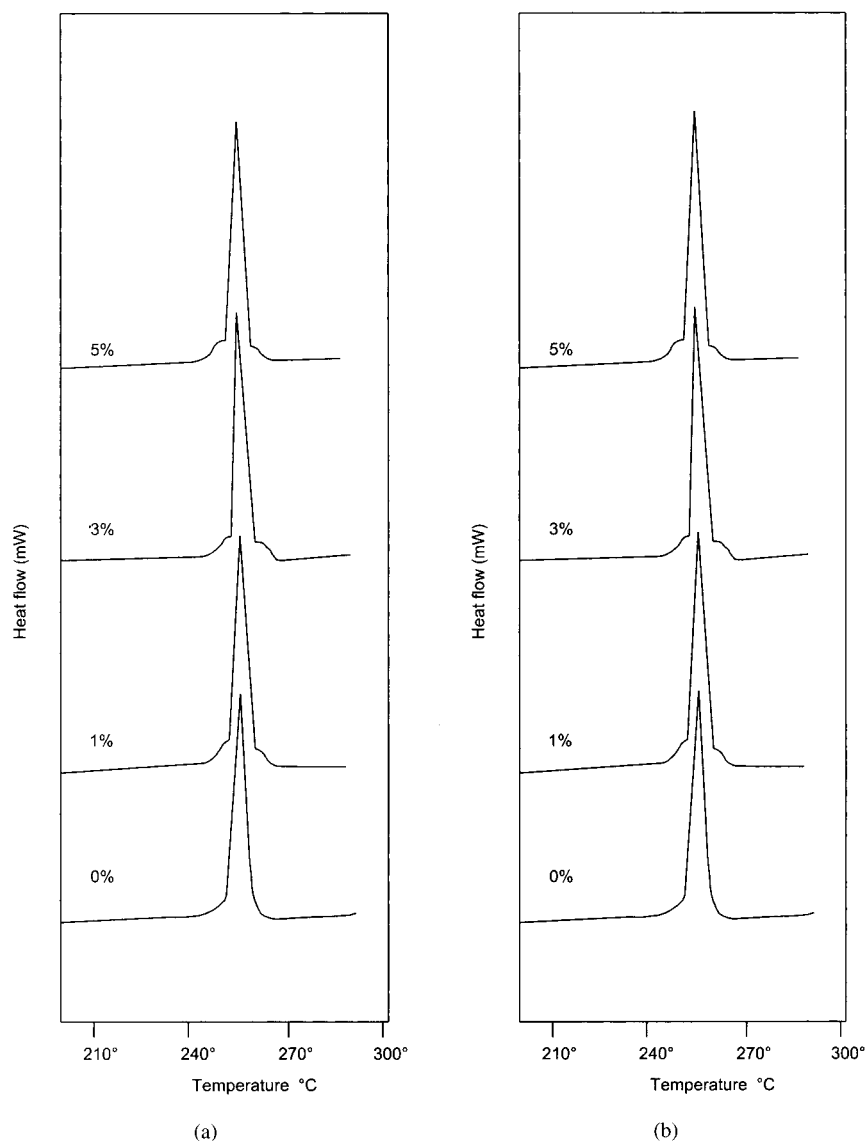
In general, PET can be quenched from the melt to produce a material that is amorphous at room temperature.<sup>32</sup> Under suitable process conditions, the polymer molecules transform from the melt to a folded chain conformation and then undergo enhanced lamellar thickening and transform into extended crystals. Hence,  $T_m$  is the phenomenon of progressive melting of crystallites of varying stability in terms of folded chain lamella, crystallite thickness, and crystal perfection. It is known that the heat of fusion of fibers (area under the curve) depends on the degree of crystallinity and the distribution of crystal size. A large range of  $T_m$  has been associated with a wide distribution of small crystals and small range has been associated with narrow distribution of bigger crystals.<sup>33</sup> Hence, it is possible to predict that the MDP yarns have a wider distribution of small crystals than FFP yarns.

The interaction of the polymer with solvent is strongly influenced by the morphological and structural parameters. In general, the solvent enters into the polymer structure, replaces, and weakens polymer-polymer interaction with polymer-solvent interaction. The interaction of solvent with polymer may be of two types (i.e., intercrystalline interaction and intracrystalline interaction). In the case of intercrystalline interaction, the solvent penetrates inside the noncrystalline domains and results in the rearrangement of the mo-

lecular chains. In this case, crystallization takes place in the swollen state.<sup>34</sup> On the other hand, in the case of intracrystalline interaction, the solvent penetrates inside the crystalline region, decrystallizes the sample, and affects the lateral order of the fiber.<sup>35</sup>

As can be seen from Tables II and III, PET treated with TCAC results in higher values of  $T_o$ , total crystallinity ( $X_c$ ), and heat flow at the melting peak for both FFP and MDP yarn samples. However, temperatures  $T_1$ ,  $T_2$ , and  $T_m$  of solvent-treated samples remain constant. In the case of MDP yarns, the exothermic peak disappears due to TCAC treatment. This suggests that TCAC penetrates into PET structure. The penetration results in complete swelling of the smaller crystallites and may be a partial swelling of the bigger crystallites. The swelling associated with segmental mobility of the polymer chains induces crystallization in the swollen state with the formation of most stable crystallites. This causes a shift in values of  $T_o$ ,  $X_c$ , and heat flow at melting peak without any change in the values of  $T_m$ . The increase in  $T_o$  can also be attributed to the increase in crystal size as well as crystal perfection due to TCAC treatment.

Based on the thermograms of TCAC-treated FFP and MDP yarns, some interesting features have also been observed. The  $T_g$  of PET fiber decreases with an increase in concentration of TCAC treatment. The reduction of  $T_g$  is believed to be the plastization effect of TCAC reagent on polyester yarns. The solvents with solubility parameter closer to those of the polymer are known to provide sufficient energy for chain interaction,<sup>36</sup> facilitate molecular movement, and reduce the effective glass transition temperature of the material. As can be seen from Tables II and III, the  $T_g$  of FFP and MDP yarns reduced by 15°C even at the 1% concentration suggests that the solubility parameter of TCAC is closer to PET. Further, premelting peak (pm) is observed in thermograms of TCAC-treated PET yarns (Figs. 3 and 4). Such a formation of premelting peak for heat-set PET fibers has been explored by many



**Figure 2** DSC thermograms showing the main melting peak of polyester yarns. (a) Untreated and TCAC-treated HFFP yarns; (b) untreated and TCAC-treated HMDP yarns.

researchers.<sup>37</sup> Based on three-phase model, PET fibers consist of a sequence of amorphous, crystalline, and extended noncrystalline domains. In general, the pre-melting peaks are associated with the melting of new crystallites formed in the extended noncrystalline domains.<sup>38</sup> Thus, the formation of pm around 160°C in 1% TCAC-treated FFP and MDP yarns suggests that tiny crystallites are generated in the extended noncrystalline domains of PET by TCAC treatment. The increase in value of pm for 3 and 5% TCAC-pretreated samples suggests that these crystals increase in perfection and size with an increase in concentration of TCAC pretreatment.

Figure 2 shows the thermograms for the HFFP and HMDP yarn samples treated with various concentrations of TCAC reagent. It can be seen that  $T_m$  remains constant for both original and heat-set PET yarns. The

increase in crystallinity and narrow distribution of larger crystals can be observed by a change in the heat of fusion area.<sup>39</sup> Thus, the applied heat treatment seems to be generating a new structure for FFP and MDP yarn samples. The appearance of pm around 170°C (Figs. 3 and 4) in the thermograms of heat-set fibers suggests that very small crystals are being formed in addition to perfection of crystals due to annealing. These effects are more pronounced in HMDP samples. When the heat-set fibers are treated with TCAC reagent, the increase in  $T_0$ ,  $X_c$ , and heat-flow value at the melting peak is not appreciable compared to changes occurred in original FFP and MDP samples. The  $T_g$  of heat-set PET yarns decreases more linearly and gradually than the original PET yarns due to TCAC pretreatment. As annealing causes more regular packing of crystals and of chains in the

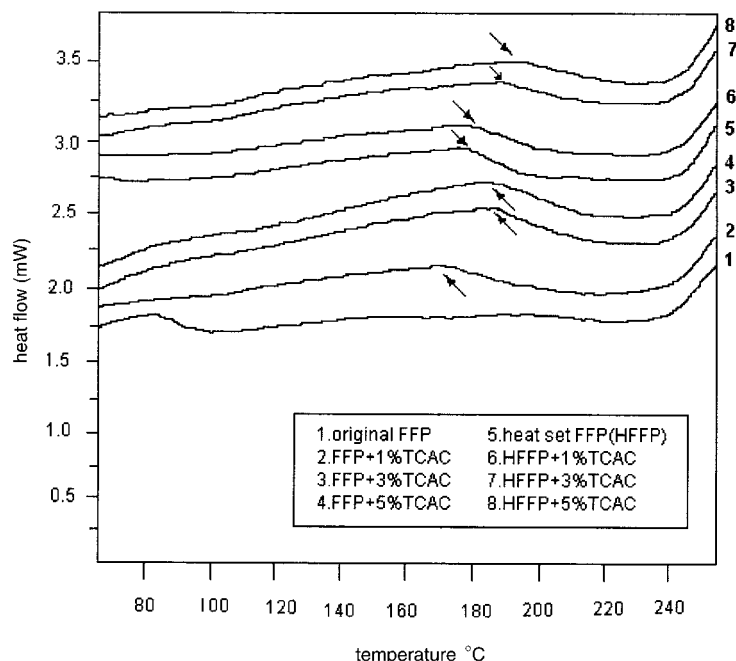


Figure 3 DSC thermograms of TCAC-treated FFP yarns. Arrows indicate the premelting peak in the thermograms.

noncrystalline regions, the TCAC reagent is not capable of fully penetrating into the polymer matrix to induce enough structural modification as in the case of original FFP and MDP yarns. In samples treated with 3 and 5% TCAC, pm is observed at 180°C (170°C for untreated HFFP and HMDP samples). Thus, the premelting peak formed by heat setting is transformed to a new melting peak around 180°C by subsequent TCAC treatment. Simal et al.<sup>11</sup> have observed similar

behavior in the treatment of heat-set polyester yarns with benzoic acid. It has been reported that premelting peak formed by heat setting (related to small and imperfect crystals) could be transformed to a new melting peak (related to small and perfect crystals) at higher temperature by subsequent solvent treatment. Further, it can be observed from the thermograms that the premelting peak formed by TCAC treatment occurs at a wide range of temperature than the premelt-

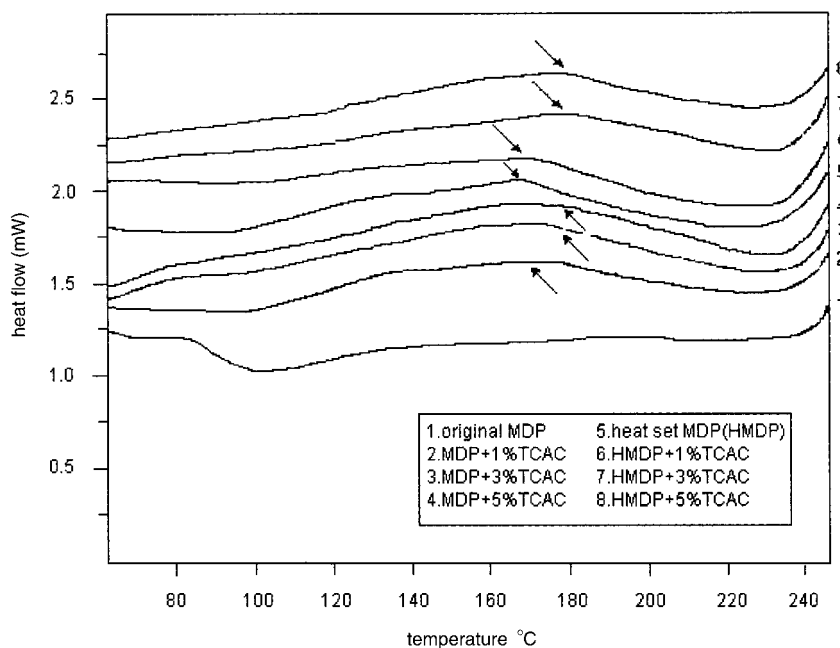


Figure 4 DSC thermograms of TCAC-treated MDP yarns. Arrows indicate the premelting peak in the thermograms.

TABLE IV  
Statistical Analysis for Thermal Behavior of TCAC-Treated FFP and HFFP Yarns

Yarns	Percent concentration	$T_o$		$X_c$		$T_g$			
		S.D.	$t_a$	S.D.	$t_a$	S.D.	$t_a$	$t_b$	$t_c$
FFP	0%	0.071	—	0.28	—	0.25	—	—	—
	1%	0.056	22.50	0.42	9.90	0.23	62.50	—	—
	3%	0.071	21.13	0.28	12.86	0.17	79.81	10.00	—
	5%	0.042	26.03	0.14	15.91	0.18	91.74	23.81	17.14
HFFP	0%	0.042	—	0.14	—	0.25	—	—	—
	1%	0.042	0.23	0.11	1.54	0.23	58.33	—	—
	3%	0.042	8.37	0.127	3.08	0.20	113.04	54.55	—
	5%	0.028	20.00	0.11	5.56	0.23	133.33	78.26	27.27

$t_a$ ,  $t_b$ , and  $t_c$  correspond to the calculated significance value of  $t$  with respect to values of control, 1%, and 3% TCAC-treated samples, respectively.

ing peak formed by heat setting. This behavior shows the formation of wider distribution of new crystals due to TCAC treatment.

It can be seen from thermograms (Figs. 1 and 2) that TCAC-pretreated polyester yarns presented double melting peak, whereas the control samples have one melting peak. It has been reported<sup>40</sup> that these multiple fusion endotherms are associated with melting of different morphological crystals such as chain-folded lamella, extended chain, or fringed micelle crystals. The melting endotherm with double melting peak could be due to the melting distribution of single morphological form differing in size and perfection.<sup>41</sup> Based on the above discussion, it can be postulated that TCAC treatment on polyester yarns increases the segmental mobility of polymer chains that favors the formation of small crystallites within the extended noncrystalline domains of PET and simultaneously promotes the growth and perfection of the existing crystals.

The statistical analysis for thermal behavior of TCAC-treated polyester yarns are presented in Tables IV and V. In the case of TCAC-treated FFP and MDP yarn samples,  $T_o$  and  $X_c$  values are significantly different from the respective control ones. For the heat set yarn samples, an increase in  $T_o$  and  $X_c$  with signif-

icant difference is observed only at 5% treatment condition. Further, it can be observed that  $T_g$  values of all the TCAC-treated polyester yarn samples are significantly different not only compared to the control samples but also the difference exists with respect to treatment concentration. Thus, TCAC treatment in PET involves two distinct processes. Primarily SINC occurs because of the generation of new crystallites in the extended noncrystalline domains of PET. On the other hand, TCAC treatment on PET breaks the intermolecular bonds and relaxes the residual orientations, with the result being  $T_g$  is reduced. It has already been reported<sup>23</sup> that TCAC treatment increases the elongation, plastic flow, and work of rupture and reduces the tenacity of polyester yarns. The extent of change in mechanical properties depends on the treatment conditions and type of yarns. It has been postulated that the oriented noncrystalline domains are plasticized during TCAC–PET interaction and could result in considerable structural rearrangement. Further, a linear correlation can be noticed between  $T_g$  depression and tenacity and breaking elongation values (Figs. 5 and 6) of TCAC-treated FFP and MDP yarns, This suggests that the plasticizing effect is predominant compared to solvent-induced crystallization in PET due to TCAC pretreatment.

TABLE V  
Statistical Analysis for Thermal Behavior of TCAC-Treated MDP and HMDP Yarns

Yarns	Percent concentration	$T_o$		$X_c$		$T_g$			
		S.D.	$t_a$	S.D.	$t_a$	S.D.	$t_a$	$t_b$	$t_c$
MDP	0%	0.023	—	0.14	—	0.23	—	—	—
	1%	0.042	42.5	0.28	12.27	0.28	57.69	—	—
	3%	0.042	43.3	0.35	14.07	0.25	75.00	11.54	—
	5%	0.056	33.64	0.42	15.16	0.30	74.07	17.24	7.14
HMDP	0%	0.028	—	0.11	—	0.25	—	—	—
	1%	0.042	3.33	0.12	1.67	0.28	40.74	—	—
	3%	0.042	3.33	0.11	7.27	0.31	78.57	36.67	—
	5%	0.028	20.00	0.13	10.83	0.30	100.00	58.62	19.35

$t_a$ ,  $t_b$ , and  $t_c$  correspond to the calculated significance value of  $t$  with respect to values of control, 1%, and 3% TCAC-treated samples, respectively.



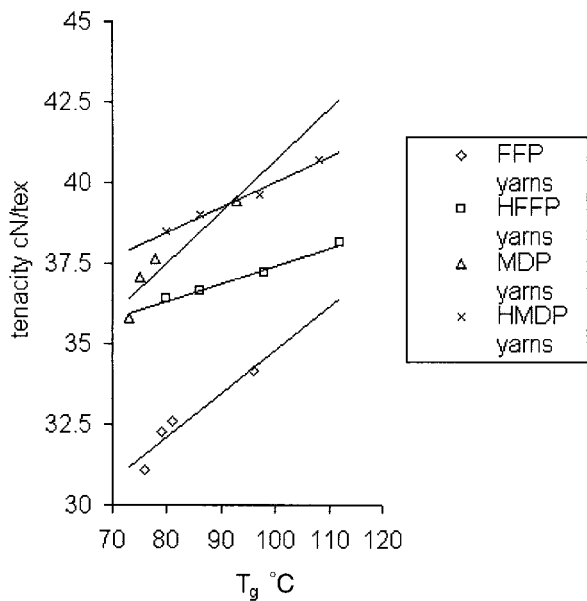


Figure 5 Relation between  $T_g$  and tenacity values.

**Structural changes**

Figures 7 and 8 show the wide-angle diffraction patterns of original and TCAC-treated FFP and MDP samples. The original FFP yarns exhibit broad and diffuse patterns. The diffraction pattern of original MDP sample does not show any sharp reflection in (010), (110), and (100) planes. This suggests the more amorphous nature of MDP yarns than the FFP yarns. In contrast, all the samples treated with TCAC reagent show clear crystalline reflections, although the each diffraction is broad and diffuse compared to heat set yarn samples. The broadness of the WAXS pattern of

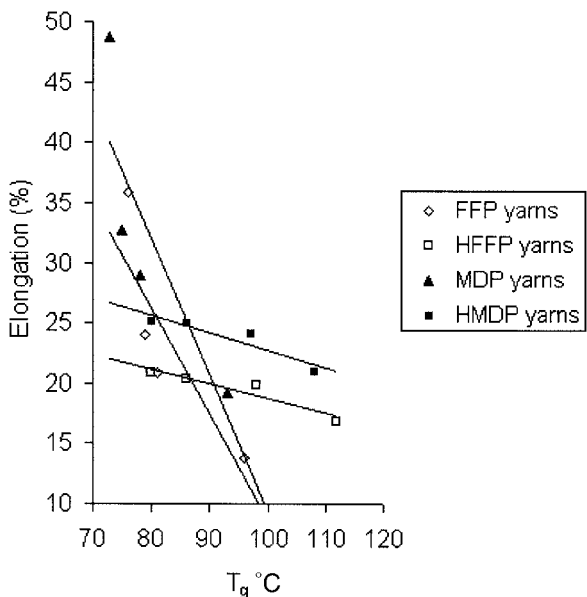


Figure 6 Relation between  $T_g$  and elongation of polyester yarns.

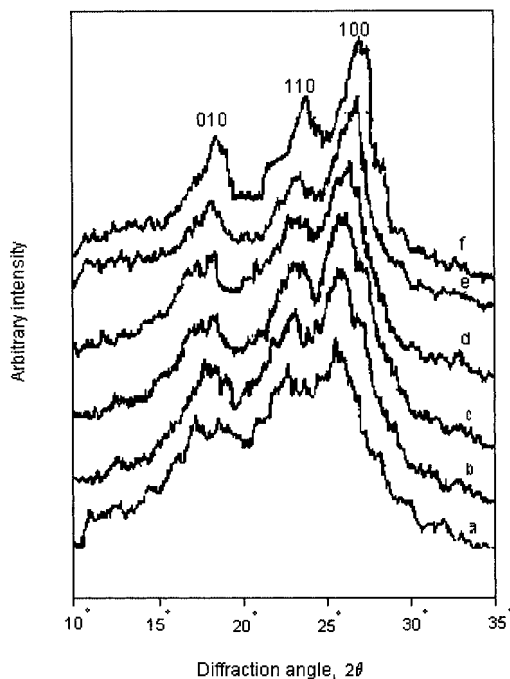


Figure 7 X-ray diffractograms of TCAC-treated FFP yarns. (a) Untreated FFP; (b) FFP, 1% TCAC; (c) FFP, 3% TCAC; (d) FFP, 5% TCAC; (e) heat-set FFP (HFFP); (f) HFFP, 5% TCAC treatment.

TCAC-treated yarns decreases with an increase in treatment concentration of TCAC. Further, the diffraction ring still becomes sharp for the heat set samples

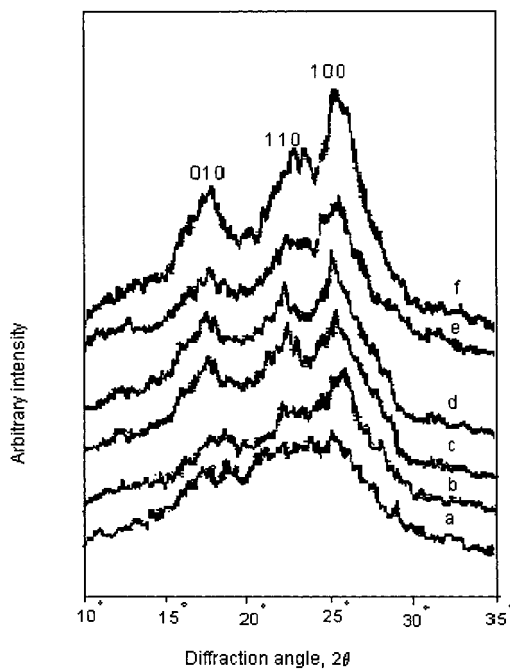


Figure 8 X-ray diffractograms of TCAC-treated MDP yarns. (a) Untreated MDP; (b) MDP, 1% TCAC; (c) MDP, 3% TCAC; (d) MDP, 5% TCAC; (e) heat-set MDP (HMDP); (f) HMDP, 5% TCAC treatment.

**TABLE VI**  
Crystalline Parameters of TCAC-Treated Polyester Yarns

Yarns	TCAC concentration (w/v)	Crystal size (Å)	Lateral order <sup>a</sup> (%)
FFP	0%	34	23.49 (0.24)
	1%	38	31.07 (0.32)
	3%	40	32.18 (0.36)
	5%	41	33.57 (0.32)
HFFP	0%	40	39.44 (0.21)
	1%	41	39.64 (0.20)
	3%	43	40.81 (0.24)
MDP	0%	—	—
	1%	34	30.06 (0.21)
	3%	35	30.14 (0.22)
	5%	38	32.82 (0.25)
HMDP	0%	37	34.92 (0.20)
	1%	38	35.10 (0.20)
	3%	38	35.70 (0.21)
	5%	40	36.65 (0.21)

<sup>a</sup> Average values calculated ( $n = 2$ ).

Values in parentheses show the standard deviations.

treated with TCAC. These patterns confirms the better interacting power of TCAC with PET and suggests that SINC takes place and the crystals become perfect and/or their sizes are growing, with this tendency more predominant with increasing concentration of TCAC.

It can be seen from Table VI that the original FFP and MDP yarns treated with TCAC reagent show an increase in crystal size and %LO as the treatment concentration of TCAC increases. The increase in LO parameter for the treated samples at 1% concentration is more pronounced and the LO at 1% treatment concentration is almost maintained at high concentration

levels (3 and 5%). Further, it can be observed that when HFFP and HMDP yarns are treated with TCAC reagent, the increase in %LO is more or less linear with treatment concentration but not appreciably improved by TCAC treatment. These changes reveal that TCAC treatment influences the crystallinity of polyester yarns. In SINC, the change in degree of crystallinity depends on the type of polymer, interacting power of penetrant with polymer, concentration of the reagent, and treatment environment such as time and temperature. The formation of new crystallites within the extended noncrystalline domains of PET and the increase in size and perfection of existing crystals are responsible for the increase in LO parameter of TCAC-treated PET yarns.

The *trans* (T) and *gauche* (G) content and structural absorbance ratio (T/G ratio) of TCAC-treated polyester yarns are shown in Table VII. In PET structure, the ethylene glycol segments (EG) can exist in either *trans* or *gauche* conformation. The *trans* conformation, which is related to straight parts of the molecules, can be present in both crystalline and amorphous regions in the fibers. The *gauche* conformation related to disorganized parts of the molecules can exist only in amorphous regions.<sup>42</sup> Thus, the changes in the structural absorbance ratio between *trans* and *gauche* bands (T/G) provide the detailed information about the structural changes due to any pretreatment. The *trans* conformation of original FFP and MDP yarns are 72 and 68%, respectively. This suggests the less stable structure of MDP yarns than FFP. It can be seen from the Table VII that the *trans* conformation of EG segment of PET yarns increases because of heat treatment. Hence, it seems that chains located in the amorphous

**TABLE VII**  
*Trans* (T) and *Gauche* (G) by % and Structural Absorbance Ratio (T/G) of TCAC-Treated Polyester Yarns

Sample	Percent concentration (w/v)	<i>Trans</i> <sup>a</sup>	<i>Gauche</i> <sup>a</sup>	T/G ratio
		A 973/A 795 (%)	A 896/A 795 (%)	
FFP	0	72.7 (0.24)	27.3 (0.20)	2.66
	1	64.0 (0.26)	36.0 (0.21)	1.77
	3	63.6 (0.22)	36.4 (0.22)	1.75
	5	62.9 (0.18)	37.1 (0.21)	1.70
HFFP	0	78.9 (0.18)	21.1 (0.17)	3.74
	1	70.0 (0.17)	30.0 (0.17)	2.33
	3	69.8 (0.17)	30.2 (0.16)	2.31
	5	69.6 (0.19)	30.4 (0.17)	2.29
MDP	0	68.2 (0.20)	31.8 (0.24)	2.15
	1	66.7 (0.19)	33.3 (0.18)	2.00
	3	66.2 (0.18)	33.8 (0.20)	1.96
	5	65.6 (0.19)	34.4 (0.22)	1.91
HMDP	0	78.2 (0.19)	21.8 (0.20)	3.59
	1	75.0 (0.17)	25.0 (0.17)	3.00
	3	74.8 (0.18)	25.2 (0.18)	2.96
	5	74.5 (0.20)	25.5 (0.20)	2.92

<sup>a</sup> Average values calculated ( $n = 2$ ).

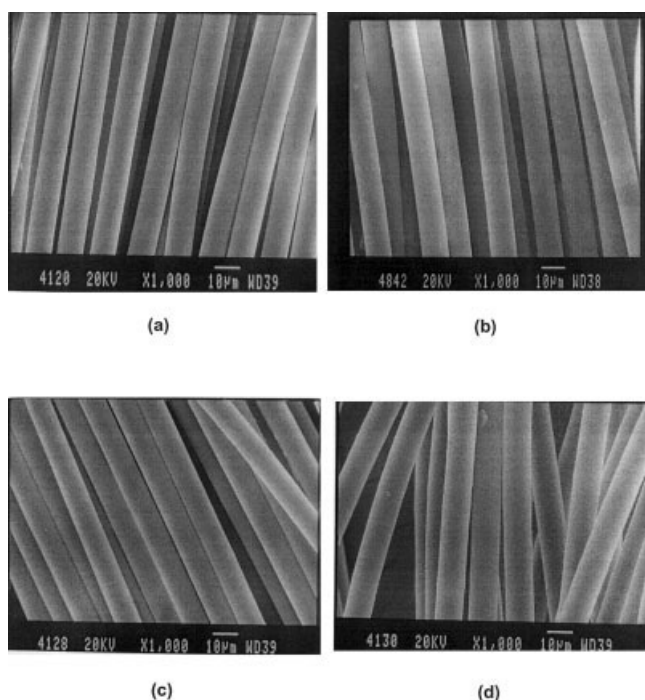
Values in parentheses indicate the standard deviations.

regions are transformed from the original more random conformation to a new and more oriented conformation due to heat setting. Further, it has been reported that the *trans* isomer allows a closer packing of molecules than the *gauche* isomers.<sup>43</sup> It implies that the increase in *trans* conformation of heat-set samples suggests an increase in intermolecular packing.

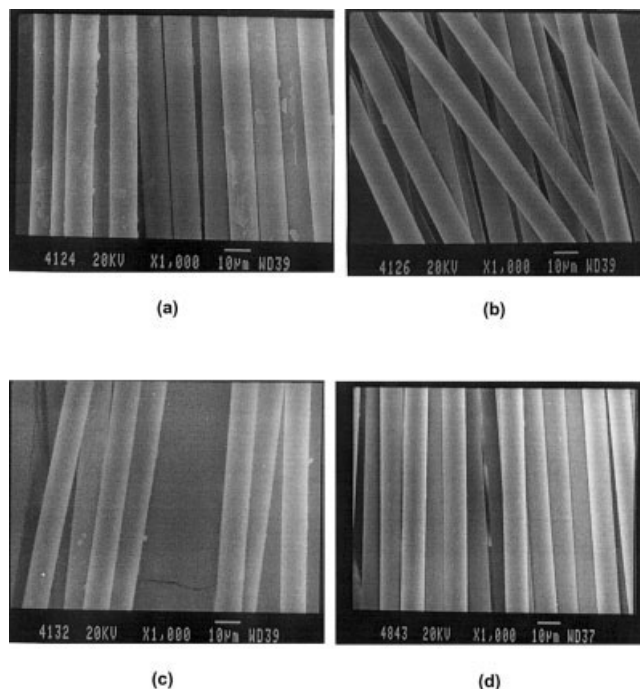
When the original and heat-set samples are treated with TCAC reagent, a decrease in T/G ratio is observed. This behavior can be related to changes in *trans* conformation not only in the amorphous regions but also in the crystalline regions, as described previously. However, it can be seen from Tables II, III, and VI that the structural parameters such as the degree of crystallinity, crystal size, and the percentage lateral order (measured by DSC and WAXS studies) increases due to TCAC treatment on polyester yarns. Thus, these changes related to crystalline regions are not overcoming the events related to amorphous regions. Hence, the decrease in T/G ratio could be mainly due to decrease in *trans* conformation in amorphous region. The morphological changes of PET fibers by solvent treatment could be the contributing factor for disorientation of the amorphous phase of TCAC treated PET yarns.

### Surface morphology

The scanning electron micrographs of TCAC-treated FFP, HFFP, MDP, and HMDP-treated samples (5%)



**Figure 9** SEM micrographs of (a) untreated FFP yarn; (b) treated FFP yarn (5% TCAC); (c) untreated MDP yarn; (d) treated MDP yarn (5% TCAC).



**Figure 10** SEM micrographs of (a) untreated HFFP yarn; (b) treated HFFP yarn (5% TCAC); (c) untreated HMDP yarn; (d) treated HMDP yarn (5% TCAC).

along with their untreated controls are shown in Figures 9 and 10. The untreated FFP and MDP yarns exhibit smooth surface texture without any other characteristic features. The surface of the treated yarns is still smoother than the respective untreated ones and swells significantly, indicating detectable morphological changes. On the other hand, the surface of the heat set fibers is not smooth as expected and reveals a large number of tiny particulates. It is likely that the exposure of PET fiber to heat gives rise to sublimation of cyclic trimers from the interior of the fibers that eventually set on the fiber surface.<sup>44</sup> The particulates on the surface of heat-set fibers could be due to the high viscosity liquid containing some crystalline material exuding to the surface. Thus, they represent low molecular weight fractions (oligomers). It can be observed that the surface of all TCAC-treated yarns is smoother than the respective untreated samples. It has been reported in the literature that certain solvents are able to remove the oligomers from polyester fibers.<sup>45</sup> Thus, the smooth surface of TCAC-treated polyester fibers could be due to removal of the low molecular weight fractions (oligomers) from polyester. The smooth surface of the treated fibers may also be due to the increase in perfection of crystals. This observation is consistent with the findings of Rajendran et al.,<sup>46</sup> in which they found that the solvent treatment on PET improves the smoothness of fibers and changes the crystal structure and increases the lateral order.

## CONCLUSION

This investigation revealed that TCAC treatment modifies the structure and morphological characteristics of original and heat-set fine filament and microdenier polyester yarns. When PET fibers are treated with TCAC reagent, plasticization, SINC, disorientation of amorphous phase, and dissolution of oligomers occurred in the treated fibers. DSC analysis revealed the presence of wide distribution of small crystals in MDP yarns than FFP yarns. The depression of glass transition temperature by TCAC treatment even at 1% concentration in 5 min duration showed its effectiveness to plasticize both original and heat-set PET fibers. Further, the DSC analysis indicated that premelting peak was formed in thermograms of TCAC-treated PET fibers, suggesting the formation of tiny microcrystallites in the extended noncrystalline domains of PET by TCAC treatment. In the case of heat set fibers, the premelting peak appeared after heat setting was dislocating toward higher temperature that could be attributed to the morphological changes by TCAC treatment.

The linear correlation observed between  $T_g$  depression and the change in mechanical properties suggests that the plasticizing effect is predominant compared to SINC due to TCAC pretreatment. The WAXS studies showed an increase in crystal size and lateral order of TCAC-treated polyester yarns. Further, when the original and heat-set fibers are treated with TCAC reagent, a decrease in *trans* conformation was observed, suggesting that TCAC treatment was affecting the chain packing of the amorphous regions of PET. The TCAC-treated polyester yarns showed smoother surfaces than the untreated control samples. The smooth surface of heat-set yarns by TCAC treatment showed the capability of the reagent to remove the low molecular weight compounds from polyester.

The authors are thankful to Dr. Manjeet Jassel, Assistant Professor, Indian Institute of Technology, New Delhi, Dr. A. Shanmugasundaram, Head of Department Chemistry, VSVN College, Virudhunagar, and Thiru Gurulinga, Indian Institute of Science, Bangalore for the help rendered by them in testing certain parameters. The authors gratefully acknowledge the cooperation from Sanghi Polyesters, Hyderabad for providing yarn samples for this work.

## References

- Simal, A. L.; De Araujo, M. S. *J Appl Polym Sci* 1996, 60, 2453.
- Shukla, S. R.; Mathur, M. R. *J Soc Dyers Color* 1997, 113, 178.
- Gupta, V. B.; Ramesh, C.; Gupta, A. K. *J Appl Polym Sci* 1984, 29, 3115.
- Ramesh, C.; Gupta, V. B.; Radhakrishnan, J. *J Macromol Sci, Phys* 1997, B36(2), 281.
- Kequiang, C.; Zhongxun, C.; Jianwei, X. *Text Res J* 2002, 72(4), 367.
- Gohil, R. M. *J Appl Polym Sci* 1994, 52, 925.
- Mi, Y.; Zhou, S.; Stern, S. A. *Macromolecules* 1991, 24, 2361.
- Makarewicz, P. J.; Wilkes, G. L. *J Appl Polym Sci* 1978, 16, 1559.
- Kulshreshtha, A. K.; Khan, A. H.; Madan, G. L. *Polymer* 1978, 19, 819.
- Billovits, G.; Durning, C. J. *Polymer* 1988, 29, 1468.
- Simal, A. L.; De Araujo, M. S. *J Appl Polym Sci* 1996, 60, 2437.
- Durning, C. J.; Rebenfeld, L.; Russel, W. B.; Weigmann, H. D. *J Polym Sci, Part B: Polym Phys* 1986, 24, 1341.
- Durning, C. J.; Scott, M. G.; Weigmann, H. D. *J Appl Polym Sci* 1982, 27, 3597.
- Weigmann, H. D.; Scott, M. G.; Ribnick, A. S.; Matkowsky, R. D. *Text Res J* 1977, 47, 745.
- Chattopadhyay, D. P.; Singh, R. K.; Panta, T. N.; Samanta, A. K. *Indian J Fiber Text Res* 1998, 23, 267.
- Chidambaram, D.; Muralidharan, B. *Indian Text J* 1999, 1, 81.
- Chidambaram, D.; Venkatraj, R.; Manisankar, P. *Indian J Fiber Text Res* 2002, 27, 199.
- Chidambaram, D.; Venkatraj, R.; Manisankar, P. *Rapid Blend Analyzing Technique for P/C Blends*; unpublished report, Apr 9, 2000.
- Su, C.; Lo, K. *Text Res J* 2000, 70(2), 93.
- Fukuhara, M. *Text Res J* 1993, 63, 387.
- Matsui, M. *Multi Component Fibres and Microfibres, Textile Fibres: Developments and Innovations*; IAFL Publications: New Delhi, India, 2000; p 9.
- Kiang, C. T.; Cuculo, J. A. *J Appl Polym Sci* 1992, 46, 83.
- Chidambaram, D.; Venkatraj, R.; Manisankar, P. *J Appl Polym Sci* 2002, 87, 1500.
- Bureau of Indian Standards; I S 10014 (Part II); 1981.
- Wunderlich, B. *Polym Eng Sci* 1978, 18, 431.
- Dumbleton, J. H.; Bell, J. P.; Murayama, T. *J Appl Polym Sci* 1968, 12, 2491.
- Cullerton, H. M.; Ellison, M. S.; Aspland, J. R. *Text Res J* 1990, 50, 594.
- Alexander, L. E. *X-ray Diffraction Methods in Polymer Science*; Wiley Interscience: New York, 1969.
- Bhat, N. V.; Naik, S. G. *Text Res J* 1984, 54, 868.
- Manjunath, B. R.; Venkataraman, A.; Stephan, T. V. *J Appl Polym Sci* 1973, 17, 1091.
- Timm, D. A.; Hsieh, Y. L. *J Appl Polym Sci* 1994, 51, 1291.
- Seigmann, A. *J Polym Sci, Polym Phys Ed* 1980, 18, 2181.
- Rao, M. S. V.; Kumar, R.; Dweltz, N. E. *J Appl Polym Sci* 1986, 32, 4439.
- Weigmann, H. D. *Handbook of Fiber Science and Technology, Vol. I, Part A: Fundamentals and Preparations*; Lewin, M., Sello, S. B., Eds.; Marcel Dekker: New York, 1983; p 3.
- Rajendran, S.; Ramasamy, S. S.; Mishra, S. P. *Indian J Fiber Text Res* 1996, 21, 179.
- Weast, R., Ed., *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*; CRC Press: Boca Raton, FL, 1985.
- Gupta, V. B.; Ramesh, C.; Gupta, A. K. *J Appl Polym Sci* 1984, 29, 3727.
- Khanna, Y. P. *J Appl Polym Sci* 1990, 40, 569.
- Urbanczyh, G. W.; Michalak, G. *J Appl Polym Sci* 1986, 32, 3841.
- Groeninckx, G.; Reynaers, H.; Berghmans, H.; Smets, G. *J Polym Sci, Polym Phys Ed* 1980, 18, 1311.
- Qudah, A.; Alraheij, I. A. *Polym Int* 1995, 38 (4), 367.
- Heuvel, H. M.; Huisman, R. *Integration of Fundamental Polymer Science and Technology*; Kleintjens, L. A., Lemstra, P. J., Eds.; Elsevier: London, 1986; p 536.
- Lin, S. B.; Koenig, J. J. *J Polym Sci, Polym Phys Ed* 1983, 21, 2067.
- Patel, V. H.; Bhat, N. V. *Indian J Fiber Text Res* 1986, 11, 181.
- Bredereck, K.; Dolmetsch, H.; Koch, E.; Schoner, R. *Melliand Textilber* 1975, 56, 50.
- Rajendran, S.; Ramasamy, S. S.; Mishra, S. P. *J Appl Polym Sci* 1996, 62, 989.