

Solvent-Induced Modifications in Polyester Yarns. I. Mechanical Properties

D. Chidambaram,¹ R. Venkatraj,¹ P. Manisankar²

¹Department of Textile Technology, P.A.C. Ramasamy Raja Polytechnic College, Rajapalayam - 626 108, India

²Department of Industrial Chemistry, Alagappa University, Karaikudi - 630 003, India

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ABSTRACT: The mechanical properties of polyester (PET) yarns, fine filament, and microdenier (original and heat-set), treated with a trichloroacetic acid–chloroform (TCAC) mixture were investigated. The treatments were carried out in an unstrained state with various concentrations of the TCAC reagent at room temperature. The TCAC treatment on PET yarns resulted in notable changes in the tensile behavior. The TCAC-treated yarns exhibited higher extensibility and work of rupture without much loss in strength. The improvement in elongation was less in the case of heat-set polyester yarns due to solvent treatment. The depression of the glass transition temperature (T_g) of TCAC-treated PET yarns, even at the minimum concentration, showed its effectiveness to plasticize the fibers and the closeness of the

solubility parameter of TCAC and PET. The T_g depression favors molecular relaxation, which has resulted in a higher shrinkage percentage of TCAC-treated PET yarns and the effective shrinkage was reached more easily for the original fine-filament polyester (FFP) and microdenier polyester (MDP) yarns at the lowest concentration. The effects of the concentration of TCAC on the strength, elongation, yield behavior, and work of rupture on PET were also investigated. A significant plastic flow was observed in the TCAC-treated yarns. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1500–1510, 2003

Key words: poly(ethylene terephthalate); solvent treatment; fibers; heat treatment; shrinkage; mechanical properties

INTRODUCTION

Poly (ethylene terephthalate) (PET) fibers do not carry any functional groups and possess limited chemical reactivity. PET fibers are generally dyed by a high temperature/high pressure (HT/HP) method or using carrier chemicals. The HT/HP method involves high-energy consumption, and the use of a carrier has many disadvantages. Improvement in dyeability in PET can also be achieved through a swelling and/or plasticizing action of solvents either by opening up the fiber structure or by increasing the segmental mobility of the polymer chains at the dyeing temperature.¹ Most of the solvents and solvent mixtures are capable of inducing enough structural modification in PET at high temperature or at long treatment time.²

A synergic solvent interaction was observed by Weigmann³ in the isothermal shrinkage of PET in solvent mixtures of perchloroethylene and methanol. On the other hand, in the mixture of noninteracting solvents such as perchloroethylene and trichlorobenzene, it was observed that the shrinkage behavior of PET is proportional to the composition of the solvent mixture. The interaction of the solvent mixture with PET fibers in a given composition increases with an

increasing treatment temperature.⁴ This is attributed to the penetration of the solvent mixture into more compact regions of PET, less accessible at lower temperatures. In the present investigation, the use of a solvent–acid mixture is considered instead of a pure solvent or solvent mixtures to bring the solubility parameter of the solvent–acid mixture much closer to that of the PET fiber⁵ ($\delta = 10.7$) so that the action of the solvent–acid mixture could be more rapid and induce better reorganization of the internal structure of the fiber.

The mechanical properties of a polymer can be attributed to factors such as the structural and molecular orientation and also environmental factors. It is a well-known fact that textile polymers are partially crystalline in nature. The tensile properties of a semicrystalline polymer like PET is generally influenced by the degree of crystallinity and the crystal morphology, such as spherulite size, fibril width, molecular tying between fibrils, and degree of orientation. The various processing parameters such as spinning speed, winding speed, drawing, heat-setting, and treatment with various chemicals/solvents also influence the mechanical properties of the textile substrate.⁶

Heat-setting and solvent pretreatment are the important processes that induce extensive structural modification in PET yarns, with the result that there could be a change in the dye uptake. An investigation on the properties of yarn samples so prepared can lead

Correspondence to: D. Chidambaram.

to a better understanding of the structure–property relationship in PET fibers, which will be helpful in process development and lead to a good contribution in the field of applied polymer science.

From our preliminary investigations,^{7,8} it was observed that the interaction of a trichloroacetic acid–chloroform (TCAC) solvent system with PET is very high and that the reagent dissolves out of PET at a 30% (w/v) concentration in 5 min at room temperature (30°C). This indicates that the solubility parameter of TCAC is closer to that of PET. Hence, it is expected that, at a lower concentration of TCAC treatment, the compact structure of PET opens up and could result in improvement in the dyeability.

The practical utility of any process that induces structural modification is largely dependent upon the mechanical behavior of the material. Here, we report on the mechanical properties of fine-filament and microdenier polyester yarns (with and without annealing) that have been treated with the TCAC reagent in various concentrations at room-temperature conditions.

EXPERIMENTAL

Materials

The following polyester yarn samples were selected for this study:

- (i) Fine-filament polyester (FFP) yarn, 55.5 dtex/48;
- (ii) microdenier polyester (MDP) yarn, 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 using a Shirley yarn-winding device. These

TABLE I
Pretreatment Conditions

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

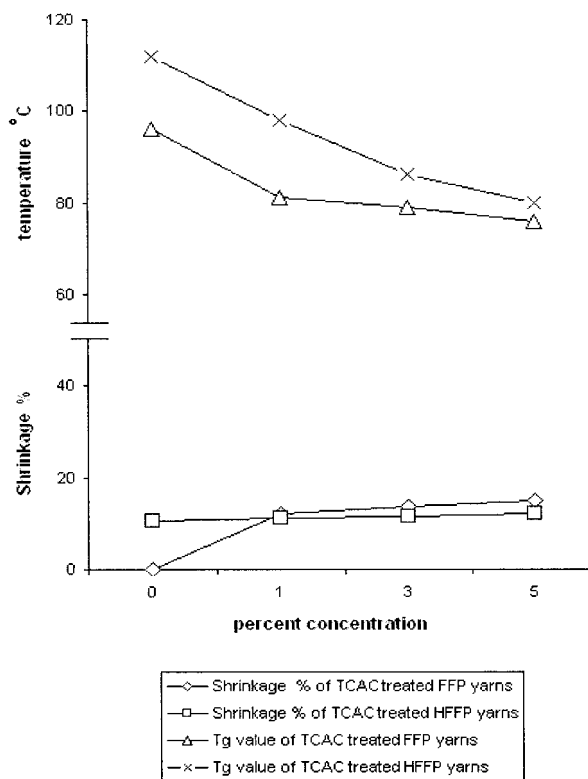


Figure 1 Shrinkage behavior and glass transition temperature of TCAC-treated FFP and HFFP yarns.

yarn skeins were subjected to isothermal annealing in a 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 (CCl₃ · COOH), chloroform (CHCl₃), and acetone (CH₃ · CO · CH₃) were used.

Pretreatment

The pretreatment conditions adopted in this investigation are given in Table I. The TCAC reagent in various concentrations (1, 3, and 5% w/v) was prepared for the treatment of polyester yarn samples. The original and heat-set polyester yarn skeins were treated with the TCAC reagent in a closed trough at ambient temperature between 30 and 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 as 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 using filter paper and then air-dried at an atmospheric condition, taking advan-

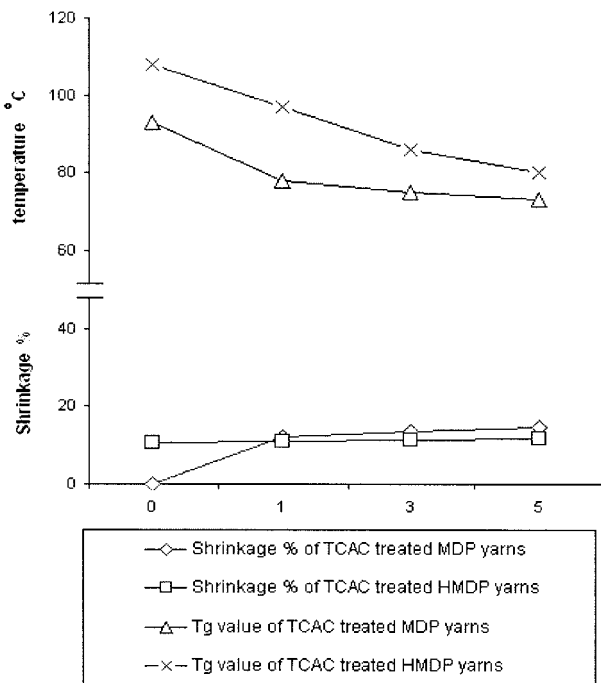


Figure 2 Shrinkage behavior and glass transition temperature of TCAC-treated MDP and HMDP yarns.

tage of the quick evaporation of acetone at room temperature. The samples were conditioned at the standard testing atmosphere of $27 \pm 2^\circ\text{C}$ and at $65 \pm 2\%$ RH for 24 h before testing.

Yarn count

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

Shrinkage test

The shrinkage percentage of polyester yarns due to annealing and TCAC treatment was calculated by measuring the length of the PET yarn hank (before

and after annealing and TCAC treatment) by applying a pretension of 0.5 cN/tex.⁹ The shrinkage percentage (% S_f) was calculated through the following expression:

$$\% S_f = \frac{S_1 - S_2}{S_1}$$

where S_1 and S_2 are the initial and final lengths of the specimens, respectively. For each sample, the shrinkage percentage was calculated from the average value of 10 specimens.

T_g measurements

A differential scanning calorimetry (DSC) Perkin-Elmer Model DSC 7 was used to obtain the thermograms of the PET yarn samples. The runnings were effectuated under an inert atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$. The glass transition temperature (T_g) was taken as the midpoint of the baseline-shift region in the DSC thermograms. The T_g measurement was taken from the first DSC run for all the samples. For each sample, the T_g was estimated from the average value of two specimens.

Tensile test

The tensile properties of the yarn samples were measured using an USTER®Tensorapid4 instrument. A specimen length of 250 mm was used at an extension rate of 250 mm/min with a clamp pressure of 30% and suction-off pressure of 10%. The tenacity, elongation at break, and work of rupture were determined from the average value of 30 tests in each sample. For each sample, five load-elongation curves whose breaking load was closer to the average value were selected and superimposed to obtain the characteristic curve. This curve was reconstructed in terms of stress in cN/tex and strain in percentage. The yield stress, yield strain, and percentage plastic flow were calculated from the stress-strain curves.

RESULTS AND DISCUSSION

Shrinkage behavior

The shrinkage behavior and T_g depression of PET yarns treated with various concentrations of the

TABLE II
Strength and Elongation of Untreated and Treated FFP and HFFP Yarns

Percent concentration (w/v)	FFP yarn			HFFP yarn		
	Tenacity (cN/tex)	Elongation (%)	Shrinkage (%)	Tenacity (cN/tex)	Elongation (%)	Shrinkage (%)
0	34.14	13.79	—	38.16	16.79	10.50
1	32.58	20.86	12.14	37.20	19.80	11.20
3	32.26	24.03	13.79	36.64	20.40	11.50
5	31.08	35.85	15.01	36.42	20.80	12.10

TABLE III
Strength and Elongation of Untreated and Treated MDP and HMDP Yarns

Percent concentration (w/v)	MDP yarn			HMDP yarn		
	Tenacity (cN/tex)	Elongation (%)	Shrinkage (%)	Tenacity (cN/tex)	Elongation (%)	Shrinkage (%)
0	39.44	19.25	—	40.72	20.96	10.60
1	37.64	28.99	12.12	39.60	24.10	11.00
3	37.06	32.65	13.64	39.00	24.96	11.20
5	35.79	48.75	14.56	38.50	25.10	11.70

TCAC reagent are shown in Figures 1 and 2. It can be seen that the FFP and MDP yarns heat-set at 180°C at a recorded shrinkage of 10.5%. It is a fact that, when drawn fibers are subjected to higher annealing temperatures, the intermolecular bonds possessing the energy will dissipate away,¹⁰ with the result that they start melting. This local melting behavior allows a local crystallization of folded chains to occur, which increases in the number of folded chain segments.¹¹ The refolding of chains is the main cause for the shrinkage of PET fibers due to heat-setting. Further, the shrinkage of an oriented polymer occurs as a result of the molecular relaxation of orientational strains. This molecular relaxation involves a substantial movement of the polymer-chain segments. This can be achieved either by increasing the temperature of the polymer above its glass transition temperature (T_g) or by lowering the T_g value of the polymer by treating it with strongly interactive penetrants.¹² It is evident from Figures 1 and 2 that the T_g of the PET fibers is lowered by 10–15°C with a 1% TCAC treatment condition. It shows the better interacting power of the penetrant with the polymer structure and is attributed to the closeness of the solubility parameter of PET and

the TCAC reagent. Thus, the T_g depression favors the molecular relaxation, which has resulted in a higher percentage of shrinkage of PET yarns treated with the TCAC reagent and the effective shrinkage is reached more easily for the original FFP and MDP yarns at the lowest treatment concentration. Further, when FFP and MDP yarns are heat-set, the T_g is increased. The increase in the T_g of heat-set PET fibers was explored on the basis of the size and size distribution of the crystallites.^{13,14} A high T_g corresponds to large number of small crystals, which reduces the segmental mobility of the polymer chains. Further, it can be observed that the T_g of heat-set PET yarns decreases linearly and more gradually than does that of the original PET yarns due to TCAC pretreatment.

Mechanical properties

The change in tenacity, elongation percentage, and shrinkage percentage due to TCAC treatment for the original FFP and MDP, heat-set FFP (HFFP), and heat-set MDP (HMDP) yarns are shown in Tables II and III. When the PET fibers are heat-set at 180°C, the tenacity of FFP is increased to 12%, and of MDP, to 4%. The

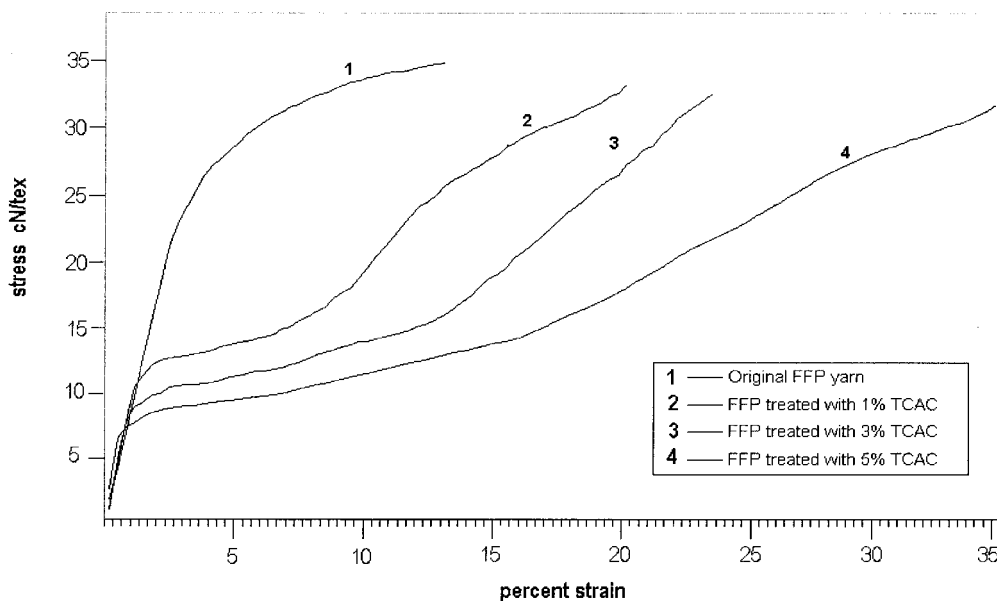


Figure 3 Stress-strain behavior of FFP yarns.

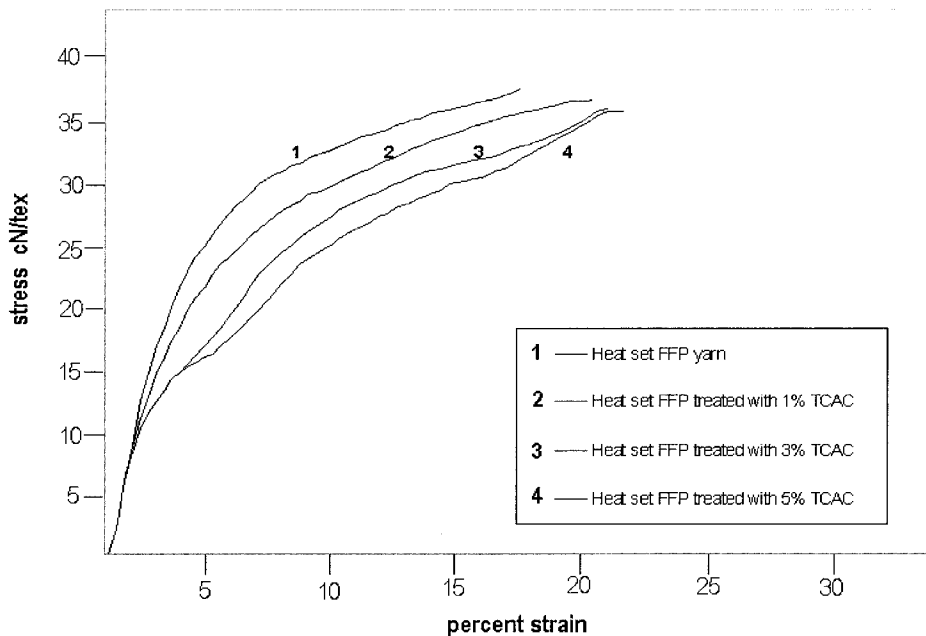


Figure 4 Stress-strain behavior of heat-set FFP yarns.

improvement in the elongation for FFP is 22%, and for MDP, 9%, with a shrinkage of 10.5% in both yarns due to heat-setting. It was observed by the researchers that the crystallization rate is maximum at 180°C, which is independent of the PET characteristics and measurement technique.¹⁵⁻¹⁷ With an increasing heat-setting temperature to 180°C, the crystal dimensions and crystallinity increase. The constraint on the amorphous phase also increases with the heat-setting temperature to 180°C. The increase in constraint is due to the increase in the physical tie points (due to an in-

crease in crystallinity), which forms an effective network.¹⁸ Further, the increase in the crystal size and degree of crystallinity is accompanied by the loss of crystal orientation and a decrease in van der Waal forces due to annealing.¹⁹ All the aforesaid factors contribute to an increase in tenacity and breaking elongation values of heat-set PET fibers. The strength-elongation behavior and other related properties like yield behavior and work of rupture of TCAC-treated yarns are discussed below, making use of their respective stress-strain curves.

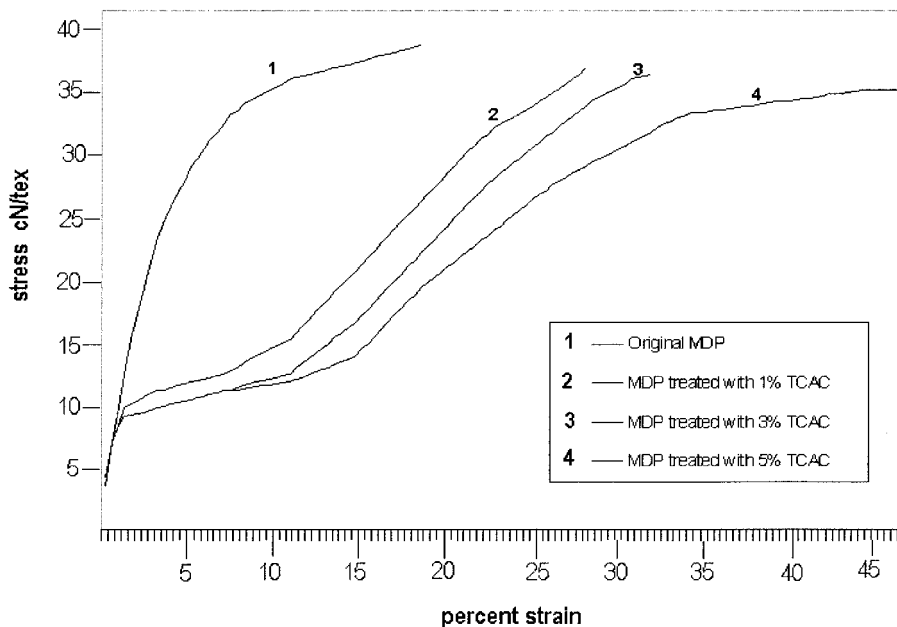


Figure 5 Stress-strain behavior of MDP yarns.

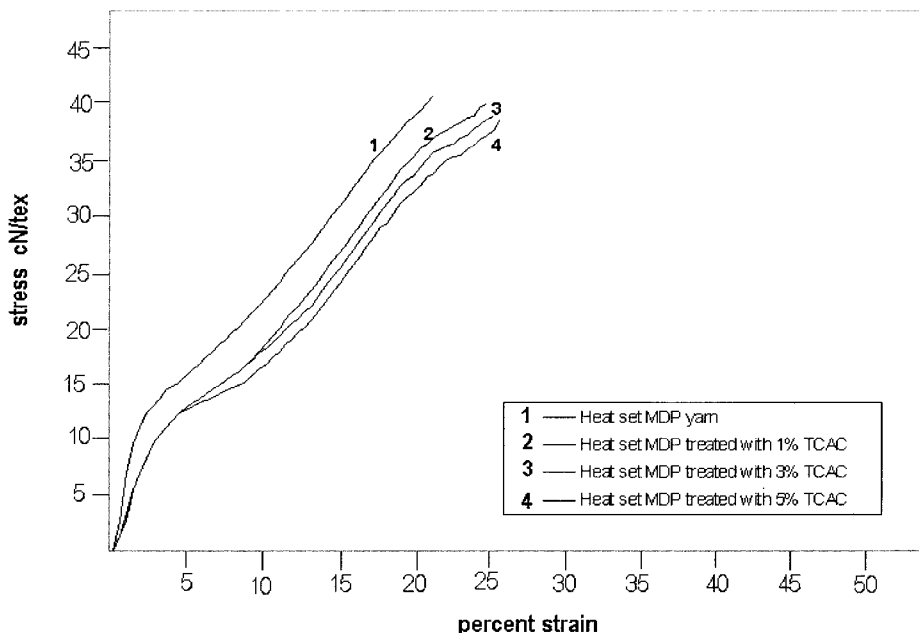


Figure 6 Stress-strain behavior of heat-set MDP yarns.

Influence of TCAC treatment on strength

It can be seen from Tables II and III and Figures 3–6 that the tensile strength of TCAC-treated PET yarns decreases with increase in the concentration of the reagent. The strength loss is about 4.5–9.0 % for FFP yarns, 4.5–9.25 % for MDP yarns, 2.5–4.5 % for HFFP yarns, and 2.75–5.45 % for HMDP yarns, the extent of which varies with the concentration of the reagent. The change in the shape of the stress-strain curves of the TCAC-treated FFP and MDP yarns, even at the lowest concentration, shows the high interacting power of the penetrant with PET. Thus, a wide range of structural modifications might be possible in PET yarns depending upon the extent of interaction of the TCAC reagent with PET. The high interacting power

of TCAC with PET can be explained with a three-phase model of PET, which quantitatively describes the relationship between the polymer structure and the tensile properties.

Besides the crystalline phase and randomly oriented amorphous phase, there is an intermediate phase in semicrystalline PET fibers. The chains of the intermediate phase are partially oriented along the fiber axis. The intermediate phase is present mainly between fibrils, whereas the crystallites are separated in the fiber direction mainly by a more random amorphous phase. Prevorsek²⁰ found that this intermediate phase comprises oriented noncrystalline domains consisting of more or less extended polymer chains. These extended domains are plasticized during solvent-poly-

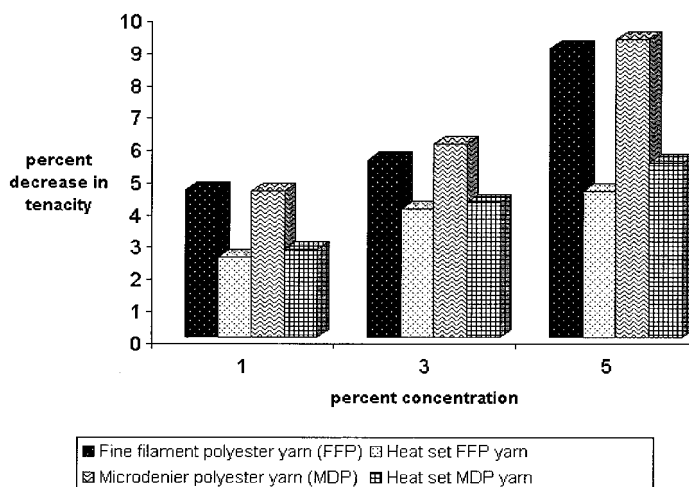


Figure 7 Effect of concentration on tenacity.

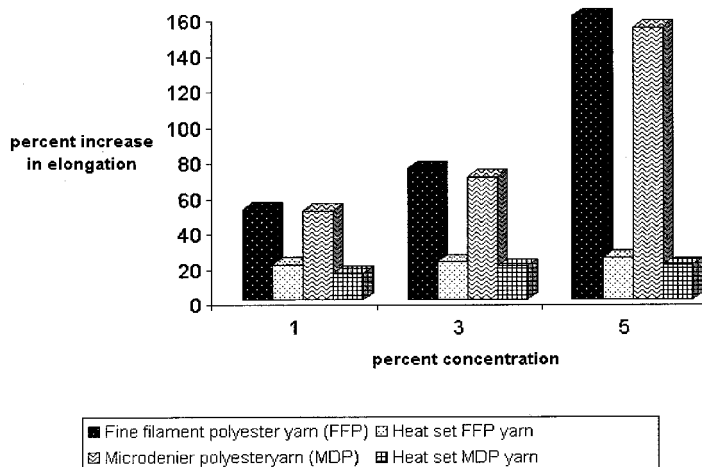


Figure 8 Effect of concentration on elongation.

mer interaction, the extent of which depends upon the closeness of the solubility parameter values, treatment time, temperature, environment, etc.²¹ Thus, the changes in the mechanical properties of the TCAC-treated PET yarns are due to the increased mobility of the polymer chains by the reagent, resulting in a considerable structural rearrangement. This hypothesis is in good agreement with the findings of Weigmann et al.²² Further, it is the general findings of the researchers that heat treatment, even at 70°C of PET, will have no effect on the structural modification by subsequent solvent treatment at room temperature. The solvents cannot penetrate into the compact crystalline region and, thus, it will not affect the tenacity values appreciably.²³ However, in the present investigation, it was observed that the strength reduction for FFP and MDP yarns is 9%, and for HFFP and HMDP yarns, 5–6% (at an extreme 5% concentration level) (Fig. 7). This implies that the higher concentration of the TCAC reagent is capable of penetrating even the well-defined crystalline zones of the PET polymer matrix after attacking the amorphous region of the polymer chains, resulting in lower tenacity values. In the man-made fiber wet-processing industries, the strength reduction of 10% by any chemical treatment is the accepted level. Hence, the strength loss on polyester yarns due to TCAC treatment to a 5% concentration level is insignificant.

The diffusion of low molecular weight substances is interpreted in terms of either the free-volume model or the pore model. The free-volume model describes the amorphous regions as a single-phase system in which the segmental mobility of the polymer chains is the contributing factor, as described previously. The pore model describes the amorphous region as a two-phase system made of polymer chains and voids. The volume fraction of pores decreases in the dry heat-setting process. The decrease in the volume fraction of pores is likely due to the partial melting and recrystallization of the polymer at high heat-setting temperatures.¹⁹ Further annealing causes more regular packing of crystals and of chains in the noncrystalline regions. This suggests that, in the case of heat-set PET fibers, the TCAC reagent is not capable of fully penetrating into the polymer matrix to induce enough structural modification as in the case of the original FFP and MDP yarns. Hence, the decrease in the tenacity value is less in the case of the HFFP and HMDP yarns.

Effect of treatment on breaking elongation

The extension behavior of a fiber is due to the specific structure of polymers, the presence of two kinds of linkages differing sharply in energy and length: One is of the strong chemical bonds between the atoms in the

TABLE IV
Yield Behavior of Untreated and Treated FFP and HFFP Yarns

Percent concentration (w/v)	FFP yarn			HFFP yarn		
	Yield stress (cN/tex)	Yield strain (%)	Plastic flow (%)	Yield stress (cN/tex)	Yield strain (%)	Plastic flow (%)
0	25.42	3.80	—	17.08	2.28	—
1	11.67	2.14	29.67	14.58	1.82	—
3	9.17	1.43	47.57	10.36	1.37	8.90
5	6.25	0.95	52.36	10.36	1.37	17.55

TABLE V
Yield Behavior of Untreated and Treated MDP and HMDP Yarns

Percent concentration (w/v)	MDP yarn			HMDP yarn		
	Yield stress (cN/tex)	Yield strain (%)	Plastic flow (%)	Yield stress (cN/tex)	Yield strain (%)	Plastic flow (%)
0	31.38	4.19	—	13.50	2.43	—
1	11.11	1.61	30.04	9.00	1.87	—
3	9.16	1.29	36.56	9.00	1.87	33.58
5	9.16	1.29	37.01	9.00	1.87	37.91

chains, and the other, much weaker, of intermolecular bonds between the chains.²⁴ Besides highly elastic material and crystalline solids, there are certain polymers which can undergo large-scale deformation without significant fracture up to certain level, but do not completely return to their original length upon the removal of stress. However, they show elastic behavior at smaller strains at the Hookean region.²⁵ This behavior is observed in the stress-strain curves of the FFP and MDP yarns treated with the TCAC reagent.

Elongation results are shown in Tables II and III. The results indicate that the TCAC-treated PET yarns (both original and heat-set yarns) exhibit higher deformation. The extension percentage increases gradually as the concentration of the reagent increases. The improvement in the breaking elongation percentage of TCAC-treated FFP, MDP, HFFP, and HMDP yarns for various concentrations of the reagent are shown in Figure 8.

The highly elastic nature of a polymer is influenced by the presence of a continuous spatial entanglement network formed by flexible macromolecules and their associates. The chain molecules in a fiber are held together by lateral forces such as covalent bonds, hydrogen bonds, and van der Waal forces. Further, high elasticity could be due to the change of the chain configuration, which can take place by the rotation of chain bonds and by slippage of the polymer segments. Both processes occur naturally due to the micro-Brownian motion of the segments. Based on the above discussion, it appears that TCAC treatment on the FFP and MDP yarns produced some degree of molecular movement by relaxing the above-mentioned lateral forces and resulted in higher extensibility.

As discussed earlier, the increase in the degree of crystallinity of PET by annealing causes the tying of polymer chains together and hinders the segmental mobility of polymer chains by solvent treatment. Thus, the improvement in elongation percentage by TCAC treatment is less in heat-set yarns compared to the original FFP and MDP yarns.

Changes in yield behavior

The shape of the stress-strain curve depends on the aggregation and phase state of the polymer and is characterized into three regions: The initial portion of the curve corresponds to very small strains, which obey Hook's law. In this portion, the modulus is constant and not very large. The second portion of the curve corresponds to the development of rubberlike strain (i.e., the plastic region), which shows the flow behavior. The third portion is the strain-hardening region in which the modulus increases sharply.

The changes in yield behavior of PET yarns are shown in Tables IV and V. The yield point is the point where the polymer transits from elastic behavior to plastic behavior. Based on the molecular theory of yield, it has been postulated that plastic behavior in polymers is due to the shear component of tensile stress that is capable of inducing flow.²⁶ When FFP and MDP yarns are treated with a lower concentration of the TCAC reagent, the yield stress is changed to a larger extent. This indicates that the sorption of TCAC molecules modifies the PET structure and induces plastic flow in the stress-strain behavior of the PET yarns.

TABLE VI
Work of Rupture of Untreated and Treated Polyester Yarns

Percent concentration (w/v)	FFP yarn		HFFP yarn		MDP yarn		HMDP yarn	
	Work of rupture (cN cm)	Percent increase	Work of rupture (cN cm)	Percent increase	Work of rupture (cN cm)	Percent increase	Work of rupture (cN cm)	Percent increase
0	505.6	—	642.9	—	1054	—	1109.1	—
1	585.4	15.78	672.2	4.56	1275	20.96	1183.3	6.69
3	659.3	30.40	707.5	10.05	1368	29.79	1222.4	10.21
5	771.6	52.61	731.2	13.73	1460	38.52	1272.9	14.76

TABLE VII
Statistical Analysis of Tenacity Values of Polyester Yarns

Percent concentration (w/v)	FFP yarn						HFFP yarn					
	Standard deviation	Standard error	Coefficient of variation	t_a	t_b	t_c	Standard deviation	Standard error	Coefficient of variation	t_a	t_b	t_c
0	0.58	0.11	1.70	—	—	—	0.79	0.14	2.07	—	—	—
1	0.53	0.10	1.63	10.54	—	—	0.71	0.13	1.90	5.02	—	—
3	0.52	0.09	1.61	13.23	2.58	—	0.69	0.13	1.88	7.96	3.04	—
5	0.48	0.09	1.54	21.53	11.15	9.27	0.67	0.12	1.84	9.44	4.23	1.24

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

It is seen from Tables IV and V that the original FFP and MDP and heat-set yarns do not show any plastic-flow behavior. When PET yarns are treated with the TCAC reagent, it modifies the structure, thereby all the TCAC-treated FFP and MDP yarns show a plastic-flow region and exhibit the highest value at a 5% treatment concentration. As discussed in the foregoing section, the segmental mobility of polymer chains is restricted by the annealing conditions. Hence, the heat-set samples, when treated with the TCAC reagent, do not show any plastic flow at a lower concentration, and only at a 5% treatment level, a marginal plastic flow is observed.

Changes in work of rupture

The work of rupture is the energy required to break the specimen. It is proportional to the elongation behavior of yarns. The TCAC treatment influences the work of rupture of PET yarns as seen in Table VI. It is obvious that high energy is required to break the TCAC-treated PET samples. The percentage increase in the work of rupture is more or less linear with the treatment concentration and was recorded at 52% for FFP and 38.5% for MDP yarns at an extreme concentration. In the case of heat-set samples, the subsequent TCAC treatment recorded a marginal increase in the work of rupture (13.7% for HFFP and 14.7% for HMDP yarns at a 5% concentration), but not an appreciable one compared to the original samples. This

is because when the substrate is heat-treated a consequence is that the PET structure becomes more compact, leading to a decrease in penetration capacity of the solvent to induce enough structural modification.

Statistical analysis of experimental results

The tenacity and breaking elongation values of all the samples were statistically analyzed and are presented in Tables VII–X. It can be observed (Tables VII and VIII) that, in the case of the FFP and MDP yarn samples, the CV % of the tenacity values for treated samples is lower than that of the control samples. The relative dispersion of the tenacity values is lower and the CV % of the treated yarns is maintained almost constant compared to the control samples in HFFP and HMDP yarns. This shows the greater uniformity of the treatment adopted in this investigation. To determine the significant difference between the control and the TCAC-treated yarn samples, Student’s “ t ” tests were performed, as suggested by Uster.²⁷ Since the calculated “ t ” values are more than 1.96 (significance limit value) in all cases (except t_c in the HFFP yarns), the difference between the mean tenacity values are significant at the 5% level, and it can be said that the tenacity values of polyester yarns decrease with an increasing reagent concentration.

TABLE VIII
Statistical Analysis of Tenacity Values of Polyester Yarns

Percent concentration (w/v)	MDP yarn						HMDP yarn					
	Standard deviation	Standard error	Coefficient of variation	t_a	t_b	t_c	Standard deviation	Standard error	Coefficient of variation	t_a	t_b	t_c
0	0.60	0.11	1.52	—	—	—	0.72	0.13	1.76	—	—	—
1	0.58	0.11	1.54	11.57	—	—	0.69	0.13	1.74	6.09	—	—
3	0.56	0.10	1.51	16.01	3.90	—	0.67	0.12	1.71	9.72	3.39	—
5	0.54	0.09	1.51	25.68	13.02	9.44	0.65	0.12	1.68	13.08	6.48	2.9

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

TABLE IX
Statistical Analysis of Breaking Elongation of Polyester Yarns

Percent concentration (w/v)	FFP yarn						HFFP yarn					
	Standard deviation	Standard error	Coefficient of variation	t_a	t_b	t_c	Standard deviation	Standard error	Coefficient of variation	t_a	t_b	t_c
0	1.00	0.18	7.25	—	—	—	1.10	0.20	5.96	—	—	—
1	1.00	0.18	4.79	27.19	—	—	1.15	0.21	5.87	10.38	—	—
3	1.10	0.20	4.58	37.93	11.74	—	1.20	0.22	5.88	12.03	2.70	—
5	1.30	0.24	3.63	73.53	39.40	38.12	1.25	0.23	5.89	13.37	3.23	1.25

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

In the breaking elongation, it can be seen from Tables IX and X that the deviation values of the TCAC-treated samples are slightly higher than are those of the respective control samples. The ultimate CV % of the treated samples is well below the CV % of the corresponding control samples for the FFP and MDP yarns. In the case of the HFFP and HMDP yarns, the CV % is almost maintained constant, irrespective of the concentration of the reagent. Hence, it can be concluded that the variation in the breaking elongation values of all the samples is within the acceptable limit. The "t" tests performed on the breaking elongation values show that a significant difference exists at the 5% level for all treated samples compared to the corresponding control samples.

CONCLUSIONS

The TCAC treatment increases the elongation and reduces the tenacity of the polyester yarns. The extent of the change in the tensile behavior depends on the treatment conditions and the type of yarn. The increase in elongation observed for FFP and MDP yarns is 150% with a 10% decrease in strength at a 5% concentration and 5-min treatment condition. The heat-set yarns registered a strength loss of 5% with an improvement in elongation of 20–25% at a 5% concentration of TCAC. At a 5% treatment condition, the

percentage improvement in the work of rupture for FFP yarns is 52%; for MDP yarns, it is 38.5%; and for heat-set yarns, it is 13–14%. The changes in the mechanical properties of FFP and MDP yarns (with and without annealing) reflect the solvent-induced morphological changes due to the TCAC treatment. Further, there exists a strong interaction between TCAC and polyester yarns at room-temperature treatment conditions. The high interacting power of the reagent even at the minimum concentration shows that the solubility parameter of TCAC is closer to that of PET. The depression of the glass transition temperature of PET yarns by TCAC treatment even at a 1% concentration shows its effectiveness to plasticize both the original and heat-set PET fibers. The reagent changes the yield behavior of the polyester yarns, suggesting the solvent effect on intermolecular bonding within the fiber structure. A statistical analysis was carried out on the variability of the test results for both tenacity and breaking elongation, which indicates the greater uniformity of the treatment adopted in this investigation.

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TABLE X
Statistical Analysis of Breaking Elongation of Polyester Yarns

Percent concentration (w/v)	MDP yarn						HMDP yarn					
	Standard deviation	Standard error	Coefficient of variation	t_a	t_b	t_c	Standard deviation	Standard error	Coefficient of variation	t_a	t_b	t_c
0	1.15	0.21	5.97	—	—	—	1.18	0.22	5.63	—	—	—
1	1.23	0.23	4.24	31.42	—	—	1.25	0.23	5.19	9.81	—	—
3	1.28	0.23	3.92	43.23	11.44	—	1.30	0.24	5.21	12.12	2.61	—
5	1.40	0.26	2.87	89.39	56.46	46.00	1.32	0.24	5.20	12.55	3.03	2.95

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

References

1. Shukla, S. R.; Mathur, M. R. *J Soc Dyers Colour* 1997, 113, 178.
2. Chattopadhyay, D. P.; Singh, R. K.; Panta, T. N.; Samanta, A. K. *Indian J Fiber Text Res* 1998, 23, 267.
3. Weigmann, H. D. In *Chemical Processing of Fabrics, Fundamentals and Preparations*; Lewin, M.; Sello, S. B., Eds.; Marcel Dekker: New York, 1983; Part A, pp 1-49.
4. Gacén, J.; Cayuela, D.; Gacén, I. *J Text Inst* 1999, 2, 265.
5. Moore W. R. *J Soc Dyers Colour* 1957, 73, 500.
6. Anvy, Y.; Rebenfeld, L. *J Appl Polym Sci* 1986, 32, 4009.
7. Chidambaram, D.; Venkatraj, R.; Manisankar, P. *Indian J Fiber Text Res*, in press.
8. Chidambaram, D.; Venkatraj, R.; Manisankar, P., unpublished report.
9. Huisman, R.; Heuvel, H. M. *J Appl Polym Sci* 1989, 37, 595.
10. Simal, A. L.; Martin, A. R. *J Appl Polym Sci* 1998, 68, 441.
11. Hearle, J. W. S.; Greer, R. *Text Inst* 1970, 2, 65.
12. Knox, B. H.; Weigmann, H. D.; Scott, M. G. *Text Res J* 1975, 45, 203.
13. Dingleton, J. H.; Murayama, T. *Kolloid Z Z Polym* 1967, 41, 220.
14. Greener, J.; Tsou, A. H.; Blanton, T. N. *Polym Eng Sci* 1999, 39, 2403.
15. Cobbs, W. H.; Burton, R. L. *J Polym Sci* 1953, 10, 275.
16. Statton, W. O. *Am Chem Soc Div Polym Chem Prepr* 1966, 7, 31.
17. Baranov, V. G.; Kenerov, A. V.; Valkov, T. I. *J Polym Sci Polym Phys Ed* 1972, 11, 2423.
18. Gohil, R. M. *J Appl Polym Sci* 1994, 52, 925.
19. Murthy, N. S.; Reimschuessel, A. C.; Kramer, V. *J Appl Polym Sci* 1990, 40, 249.
20. Prevorsek, D. C. *J Appl Polym Sci C* 1975, 32, 343.
21. Peterlin, A. *J Appl Polym Sci C* 1971, 32, 97.
22. Weigmann, H. D.; Ribnik, A. S.; Rebenfeld, L. *Text Res J* 1972, 42, 720.
23. Makerewicz, P. J.; Wilkes, G. L.; Budnitsky, Y. *J Appl Polym Sci Polym Phys Ed* 1978, 16, 1545.
24. Tager, A. In *Physical Chemistry of Polymers*; Sobolev, D., Bobrov, N., Eds.; Mir: Moscow, 1978; p 236.
25. Rajendran, S.; Ramasamy, S. S.; Mishra, S. P. *J Appl Polym Sci* 1996, 59, 99.
26. Arridge, R. G. C. *Mechanics of Polymers*; Clarendon: Oxford, 1975; p 201.
27. Zellweger Uster Application Handbook, *Tensile Testing of Single and Ply Yarns for USTER®Tensorapid*; Zellweger Uster AG: Uster/Schweiz, Switzerland, p 63.