

Shrinkage and Mechanical Properties of Poly(ethylene Terephthalate) Filaments Treated with Various Organic Solvents

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Synopsis

The effects of a number of chemically nonreacting organic solvents on shrinkage and stress-strain properties of preoriented semicrystalline poly(ethylene terephthalate) filaments have been studied. The changes in shrinkage and mechanical properties are found to be highly dependent on time and temperature, as well as on tension applied on the yarn during the treatment. The changes brought about by the solvents at lower temperatures (i.e., below 100°C) are either comparable with or more than those produced by thermal treatments in air or silicone oil above 200°C. The possibility of using solvent treatment for setting polyester for dimensional stability at low temperatures as an alternative to the normal dry-heat-setting method has been discussed.

INTRODUCTION

Relaxation of strains built into thermoplastic fibers such as polyester, nylon, etc., during melt spinning, drawing, or textile processing (spinning, weaving, and wet processing), and setting the material in a more favorable state in order to achieve dimensional stability during subsequent use, are important textile operations. However, during the process of achieving relaxation and dimensional stability, structural changes take place that affect the mechanical properties of fibers and also their subsequent dyeing behavior. Minor changes in the conditions during heat setting have been found to be responsible for the undesirable uneven or Barré dyeing.¹ Setting of thermoplastic textile material is usually carried out in industry at high temperatures in an atmosphere of dry air or steam. Apart from temperature, the time of heat setting and the tension, as well as the medium of setting, has considerable influence on the extent of relaxation and consequent dimensional stability achieved during heat setting.

In recent years, considerable interest has been shown in developing wet finishing processes using nonaqueous solvents as processing media with a dual objective of reducing environmental pollution and conserving energy. As a result, a number of technologically feasible processes have been developed. However, not much information is available²⁻¹⁰ on the effect of temperature and time, as well as tension, on the interaction between the nonaqueous solvents and synthetic textile fibers. It is known that some solvents are capable of swelling fibers, particularly synthetic fibers, resulting in the relaxation of built-in strains. Whenever there is interaction between polymer and solvent, shrinkage, which

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is a manifestation of an irreversible structural change presumably within the disordered domains of the polymer, occurs with the concomitant changes in the structural and mechanical properties. However, it is essential to have a quantitative understanding of the effects of nonaqueous solvents in conferring dimensional stability to the textile material treated under varying experimental conditions. In this article the results of a study on the shrinkage and mechanical properties of polyester filament yarns treated in different nonaqueous solvents under varying experimental conditions will be discussed.

EXPERIMENTAL

Material. Commercially available medium tenacity multifilament (76/24/0) (courtesy of J. K. Synthetics Ltd., Kota) was used in this investigation.

Treatments. Poly(ethylene terephthalate) (PET) filament yarns were treated in slack or constant length conditions with a number of solvents such as perchloroethylene, *s*-tetrachloroethane, dimethylformamide, nitrobenzene, etc. Treatments were carried out over a wide range of temperatures in an oil thermostat. The time of treatment was varied from 2 min to 24 hr.

Free Shrinkage. PET yarn samples of 10 cm length were allowed to shrink freely in various solvents at different temperatures for specified times and the percent of shrinkage was determined from the initial and final lengths.

Residual Shrinkage. The samples tested in various solvents in the slack condition, as well as at constant length, were allowed to undergo free shrinkage in boiling distilled water and the percent residual shrinkage was determined in each case.

Load-Elongation Curves. Single filaments of 1 cm test length were extended on an Instron tensile tester. The crosshead speed was varied from 2 to 5 cm/min depending on the extensibility of the sample being tested in order to keep the rupture time around 20 sec. Some of the highly extensible fiber samples were broken at the crosshead speeds of 2 and 5 cm/min. The tenacity values obtained at both crosshead speeds were found to be more or less the same. In each case, 25 filaments were broken. From the load-elongation curves, the mean breaking strength (g/denier), the percent extension at break, and the work of rupture (g wt cm) were determined. The load-elongation curves of the samples having the breaking strength and extension close to the mean values in each case are reproduced in Figures 9-14.

Crease Recovery Angle. The crease recovery angles of parallelized bundles of filament yarn were determined by the method described elsewhere.¹¹

RESULTS AND DISCUSSION

Partially oriented PET filament starts shrinkage when exposed to dry heat at temperatures in excess of its glass transition temperature (about 90°C). As the temperature of heat treatment increases, the shrinkage increases, reaching a value of 2.1% at 100°C and 26.4% at 240°C. Solvents such as water, primary alcohols, and aliphatic and aromatic hydrocarbons have little or no effect on the dimensional property of the drawn polyester yarn up to about 80°C. It is self-evident that the shrinkage occurs only after the entire cross section of the individual filament is completely penetrated by the solvent. The absence of

shrinkage can be attributed to the lack of interaction of the PET yarn with the solvent. In the absence of any interaction, the filament is not swollen, and consequently the rate of diffusion of the solvent into the filament is extremely slow. It will be shown later that the interaction depends on the presence of certain active groups of atoms in the solvents which will interact with the aromatic (A) or the aliphatic ester residue^{12,13} (B) of the poly(ethylene terephthalate) repeat unit shown in Figure 1, producing swelling and shrinkage of polyester yarn.

The free shrinkage of PET yarn obtained in 2 min in a number of solvents is shown in Figure 2 as a function of temperature of treatment. In the case of perchloroethylene, the most widely used solvent for solvent processing of textiles, a significant effect on the dimensional stability of the yarn is noted only at the boiling point (120°C). In the case of methylene chloride [dichloromethane (DCM)], a powerful plasticizing agent, PET shows considerable shrinkage even at 5°C. The temperature dependence of shrinkage in methylene chloride appears to be linear over the entire temperature range investigated, from 5 to 40°C. PET hardly shrinks at room temperature *s*-tetrachloroethane (TCE), another powerful plasticizing agent, and even at 50°C, the shrinkage of PET is negligible. However, there is a dramatic increase in shrinkage with further increase in temperature of treatment, reaching a value of 38% at 120°C. Moderate plasti-

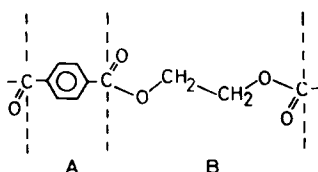


Fig. 1. Schematic representation of the monomer repeat unit of poly(ethylene terephthalate): (a) aromatic residue centered around A, and (b) aliphatic ester residue centered around B from Knox, Weigmann and Scott (ref. 12).

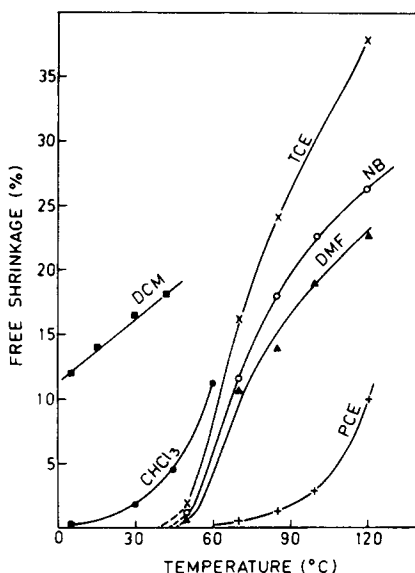


Fig. 2. Free shrinkage of PET filament yarn as a function of temperature in different solvents.

cizing agents such as dioxane, nitrobenzene (NB), and dimethylformamide (DMF) exhibit similar behavior. However, the increase in shrinkage with increasing temperature is not as rapid as that observed in the case of TCE. Except for the initial portion, the shrinkage of PET yarn in various solvents appears to increase almost linearly as a function of temperature. Treating the shrinkage-versus-temperature data as linear and extrapolating to zero shrinkage one gets zero shrinkage temperatures (T_0) for different solvents. The T_0 values for different solvents are given in Table I, along with the T_0 values obtained by Ribnick and co-workers^{6,7} from the extrapolation of the final or equilibrium shrinkage-versus-temperature curves, and also of the dynamic shrinkage-versus-temperature relations. The T_0 values obtained in the present study are much higher than those obtained by Ribnick et al.^{6,7}

As indicated earlier, solvent molecules must first diffuse into the core and swell the fiber before any shrinkage can occur. Since the distance penetrated depends on both time and temperature,¹⁴ it is likely that in about 2 min the total realizable or equilibrium shrinkage might not have occurred. In order to examine this, PET yarns were treated in different solvents for varying periods ranging from 3 to 24 hr. In Figure 3, the shrinkage obtained in 2 min in different solvents is compared with the shrinkage obtained after several hours of treatment. The most dramatic effect of the time of treatment is seen at lower temperatures of treatment and that, too, in the case of chlorinated solvents. Among the chlorinated solvents, tetrachloroethane shows the maximum effect. In the case of DMF and nitrobenzene, the effect of the time of treatment is only moderate, especially above 65°C. It is interesting to note that the shrinkage data again appear to have an approximately linear relation with temperature, except for the initial portion. Further, as the time of treatment increases, the linear portion of the shrinkage-versus-temperature curve extends to lower temperatures. It has been shown in other articles^{15,16} that PET yarn attained the temperature of the furnace in about 5 sec when treated in silicone oil and in about 2 min (minimum time studied) when subjected to dry heat in nitrogen atmosphere. It has also been shown that as the temperature of treatment increases, the percent free shrinkage increases, reaching a value of 50% when treated in silicone oil at 240°C for 1 min and about 26% when treated in dry air at 240°C for 5 min. In order to examine whether the free shrinkage during high-temperature treatment

TABLE I
Estimation of Zero Shrinkage Temperature of Various PET-Solvent Systems

Solvent	Zero shrinkage temperature (°C) obtained from				Temperature (°C) T_α
	Isothermal shrinkage ^a	Dynamic shrinkage ^b	2-min shrinkage	3-hr shrinkage	
Dry	83	83	—	—	83
Perchloroethylene	22	20	—	25	50
Nitrobenzene	—	-61	28	8	-42
Dioxane	-63	-63	55	—	—
Dimethylformamide	-70	-72	23	10	-40
<i>s</i> -Tetrachloroethane	-180	-134	30	-35	-104
Methylene chloride	—	—	-64	—	95
Chloroform	—	-143	—	-64	-85

^a Data from Ribnick et al. (ref. 6).

^b Data from Ribnick and Weigmann (ref. 7).

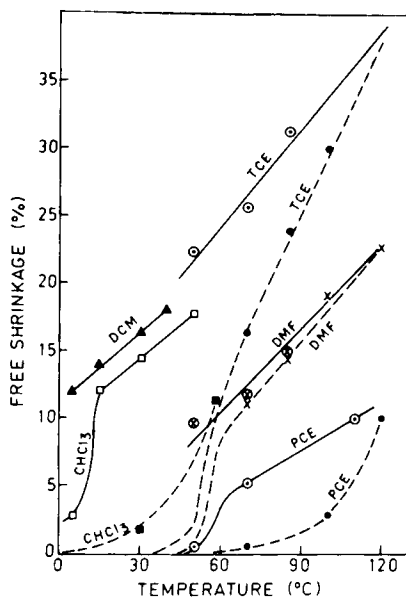


Fig. 3. Effect of time of treatment on the temperature dependence of shrinkage of PET yarns in different solvents; (■ ● × ▲) 2-min data; (○ ⊗ □) 3- to 5-hr data.

is dependent on the time of treatment, as in the case of solvents, PET samples were subjected to heat treatment for 7 hr in air as well as for 3 hr in silicone oil. The shrinkage data thus obtained are compared in Figures 4 and 5 with the corresponding shrinkage data obtained in 1 and 5 min, respectively, in silicone oil and air. It is evident from Figures 4 and 5 that the free shrinkage of PET when exposed to heat treatment temperatures in excess of its glass transition temperature does not appreciably depend on the time of treatment, unlike in the case of solvent treatment.

Extrapolation of the linear portions of the shrinkage-versus-temperature curves shown in Figure 3 leads to considerable shifting of the zero shrinkage

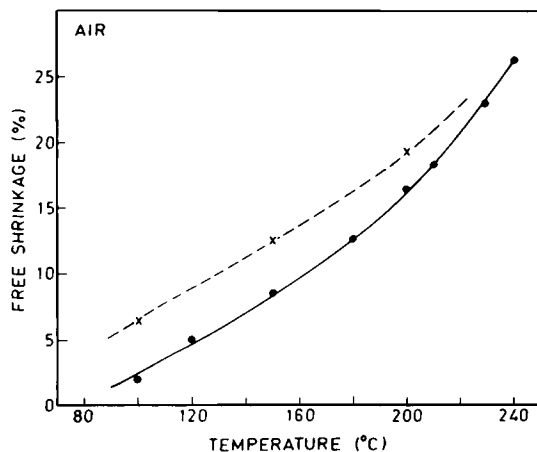


Fig. 4. Effect of time of treatment on the temperature dependence of shrinkage of PET yarn subjected to dry heat; (●) 5-min data; (×) 3-hr data.

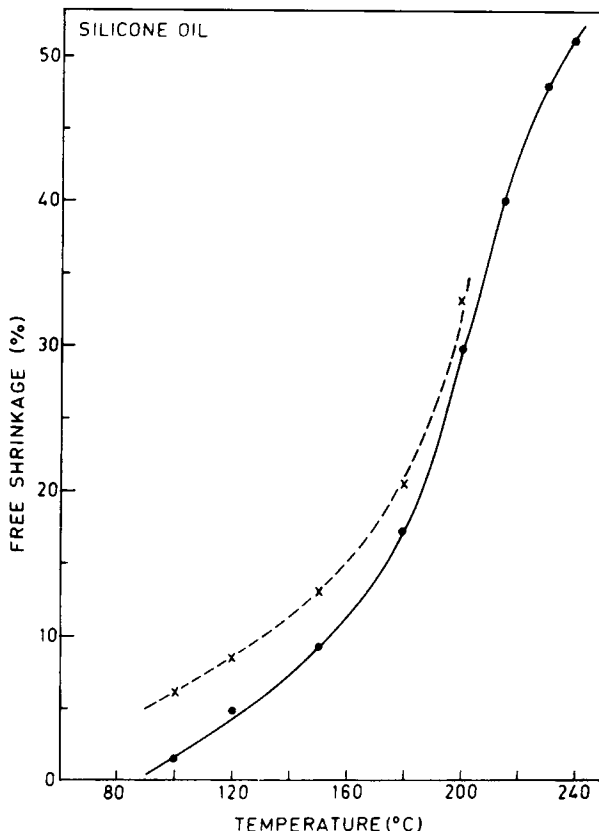


Fig. 5. Time dependence of shrinkage of PET yarns heat treated at different temperatures in silicone oil; (●) 1-min data; (×) 3-hr data.

temperatures (T_0) to lower values for different solvents. Still, these T_0 values are higher than those obtained by Ribnick et al.^{6,7} The difference in T_0 values may be explained by again assuming that the equilibrium has not been reached in the present study. However, careful scrutiny of the isothermal shrinkage data of Ribnick et al. leads to a proper explanation of the observed differences in the T_0 values. The free shrinkage observed after treatments in DMF and TCE for durations lasting 5 hr, along with the data obtained by Ribnick et al.,⁶ is plotted in Figure 6. It is seen that Ribnick et al. have examined the shrinkage data over a limited temperature range (150–90°C). On the other hand, the treatment in the present study was extended to much higher temperatures. At the highest temperature studied, the free shrinkage in both TCE and DMF is about 1.5 times the corresponding value at 90°C. Because of the limited temperature range in their experiments,⁶ the linear portion of the shrinkage temperature curve is less steep, and consequently extrapolation to zero shrinkage has resulted in significantly lower T_0 values for different solvents. However, Ribnick and Weigmann⁷ have studied the dynamic shrinkage data over a much wider range of temperature (i.e., up to 150°C in solvents and up to 240°C in air) at heating rates ranging from 4.0 to 0.26°C/min. Ribnick and co-workers^{6,7} have extrapolated to zero shrinkage temperature the equilibrium shrinkage values from the isothermal

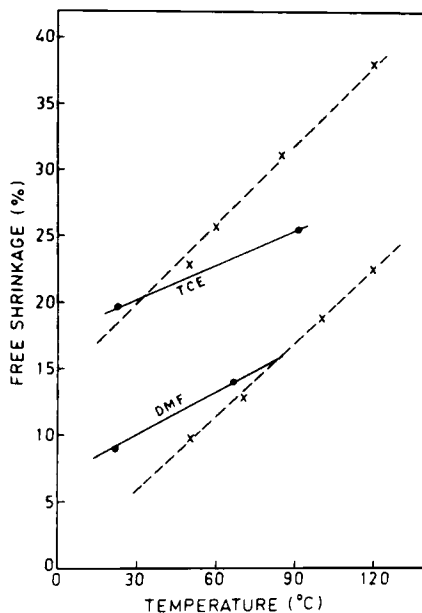


Fig. 6. Free shrinkage of PET yarns in TCE and DMF as a function of temperature. (—) Data of Rubnick et al.; (---) present data.

and dynamic shrinkage measurements under the premises that solvent-induced shrinkage is essentially a relaxation phenomenon of orientation stresses introduced during the melt-spinning and drawing processes and that no crystallization effects interfere with the shrinkage process. However, it has been shown elsewhere that slack treatment for 2 min in *s*-tetrachloroethane at 90°C produces significant increase in the intensity of the trans band at 973 cm^{-1} and also in the regular chain-folding band at 988 cm^{-1} (both indicative of the increased crystallinity). It is doubtful that even the highest heating rate employed in the measurement of dynamic shrinkage in solvents in the temperature range of 20–130°C has not resulted in increased crystallinities. It thus appears likely that crystallization effects interfere with the shrinkage process in both the isothermal and dynamic shrinkage studies.

Rubnick et al.⁶ made another interesting observation, namely, that the temperature dependence of the equilibrium shrinkage curve is similar in shape for different solvents. This is evident from Figure 3. The observed shrinkage data were fitted to a master shrinkage curve by a suitable shift along the temperature axis, as was done by the earlier workers.^{6,7} The shift in the temperature (T_α) has been shown to be directly proportional to the glass transition temperature (T_g or T_0) of the solvent–polyester system. The resulting curve is shown in Figure 7. The data for the treatment in various solvents and in air fit the linear portion of the curve very well. However, the shrinkage data in silicone oil deviate considerably from linearity. This is because the shrinkage values in silicone oil up to 180°C are comparable to those obtained in air, suggesting that the T_g values in air and oil are the same. However, above 180°C the shrinkage in silicone oil is much more than that in air.

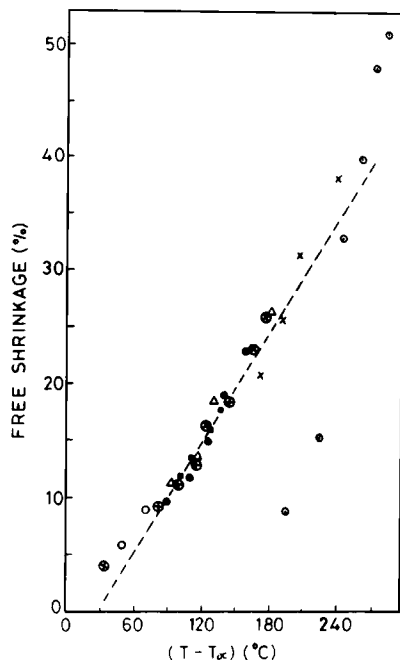


Fig. 7. Master shrinkage curve of PET yarn in various solvents [(●) DMF, (×) TCE, (○) PCE, (Δ) NB, (■) DCM, (⊗) N₂, (⊙) oil] as a function of $(T - T_d)$.

Solubility Parameter

The observations made so far indicate that the nature and extent of interaction between PET and organic solvents depend on various factors, such as the nature of the solvent, time and temperature of treatment, state of tension in the polymer during treatment, and the initial morphology of the material. No theoretical model, however, that could completely characterize the interaction between organic solvents and thermoplastic polymers exists yet. The solubility parameter principle of Hildebrand and Scott,¹⁸ which was subsequently extended by Hansen,¹⁹ has recently been shown^{6,7} to be a promising guideline to understand the PET-solvent interactions. We, however, observe that perchloroethylene, though with a total solubility parameter ($\delta = 9.36$) very near to that of the aromatic residue of PET ($\delta = 9.85$), does not cause appreciable shrinkage or changes in mechanical properties even at 100°C, and, on the other hand, methylene chloride ($\delta = 9.93$) causes very high shrinkage instantaneously at temperatures as low as 5°C. It can also be noted that *s*-tetrachloroethane ($\delta = 9.85$) takes several hours before appreciable shrinkage can occur at room temperature, whereas at 100°C, the solvent interacts instantaneously and very strongly with the polymer. These observations appear to be inexplicable in the light of the present solubility parameter concept. Further limitations of the bimodal distribution of the Hildebrand solubility parameter to represent PET-solvent interactions have been discussed previously.^{12,13}

Residual Shrinkage

The residual shrinkage in boiling water is a measure of the dimensional stability of the treated material. From the shrinkage data given in Table II it is clear that the residual shrinkage decreases with increasing temperature of treatment in all the solvents. The samples treated in the slack condition show lower shrinkage in boiling water than those treated at constant length. Similar observations have been made in the case of nylon and polyester samples subjected to dry heat¹⁶ or heat set in silicone oil.¹⁵ Only the PET slack treated in perchloroethylene at the boiling point (120°C) shows about 1% shrinkage in boiling water, indicating that the treatment in the slack condition at 120°C can only confer dimensional stability on the treated polyester material. Treatment in tetrachloroethane, dimethylformamide, and nitrobenzene at or above 70°C or in methylene chloride at or above 5°C in the slack condition results in low shrinkage in boiling water. The PET yarn slack treated at 5°C shows less than 1% shrinkage when exposed to dry heat at 200°C. The samples solvent treated at constant length at different temperatures undergo relatively lower residual shrinkage in boiling water than the untreated control. However, the residual

TABLE II
Free and Residual Shrinkage of PET Filaments Treated with Solvents

Solvent	Treatment temperature (°C)	Free shrinkage (%)	Residual shrinkage (%) in boiling water	
			Treated (slack)	Treated (constant length)
Control	—	—	7.7	—
Perchloroethylene	70	0.8	4.2	6.8
	85	1.4	2.6	4.8
	100	2.9	2.2	4.4
	120	10.1	0.7	3.8
Methylene Chloride	5	12.2	0.8	6.5
	15	13.7	0.5	—
	30	16.5	0.3	6.5
	40	17.9	0.0	5.5
<i>s</i> -Tetrachloroethane	50	2.1	4.5	6.1
	70	19.3	1.6	5.2
	85	24.4	0.7	4.7
	100	30.3	0.5	4.2
	120	38.0	0.0	3.6
Nitrobenzene	50	1.2	4.7	6.4
	70	12.3	1.1	6.2
	85	18.5	1.0	5.3
	100	22.7	0.0	3.8
	120	26.3	0.0	2.4
Dimethylformamide	50	0.7	3.9	7.0
	70	11.0	1.9	4.7
	85	15.0	0.5	2.9
	100	19.0	0.0	2.6
	120	25.7	0.0	2.0

shrinkage in all cases is still high. It appears unlikely that satisfactory dimensional stability can be achieved for PET solvent treated at constant length at any temperature. Some predetermined shrinkage should be allowed during the treatment in order to achieve satisfactory dimensional stability. Separate mixtures of methylene chloride with perchloroethylene, trichloroethylene, and tetrachloroethane were prepared, and the free shrinkage of PET yarn at room temperature was determined in each of these mixtures. The material-to-liquor ratio was infinitely large in these experiments. The residual shrinkage in boiling water of the samples slack treated in the above mixtures for 2 min at room temperature (30°C) was also determined. These results are shown in Figures 8(A) and 8(B). As pointed out earlier, perchloroethylene (PCE), trichloroethylene (TrCE), and tetrachloroethane do not swell PET fiber within about 2 min, and hence no shrinkage could be observed at room temperature. As the methylene chloride content (DCM) in the PCE/DCM mixture increases, the free shrinkage increases rather slowly initially. To cause a free shrinkage of 10% the methylene chloride content should be about 70%. In the case of TCE/DCM mixtures the free shrinkage is low even in a 60/40 mixture. However, a very sharp increase in shrinkage is observed with further increase in the methylene chloride content. The 50/50 mixture produces as much shrinkage in PET as DCM alone. The residual shrinkage data [Fig. 7(b)] suggests that mixtures of methylene chloride with TCE, TrCE, and PCE in order of preference could be used for setting polyester material at room temperature. However, a word of caution is necessary here to emphasize the need to allow large shrinkage during the treatment and to carry out further processing under relaxed conditions. This is necessary because tension on the fibers plays an important role in solvent setting. It was found that PET treated in tetrachloroethane at 70°C in the slack condition and stretched back to original length while still in the solvent showed as high as 7% shrinkage in boiling water.

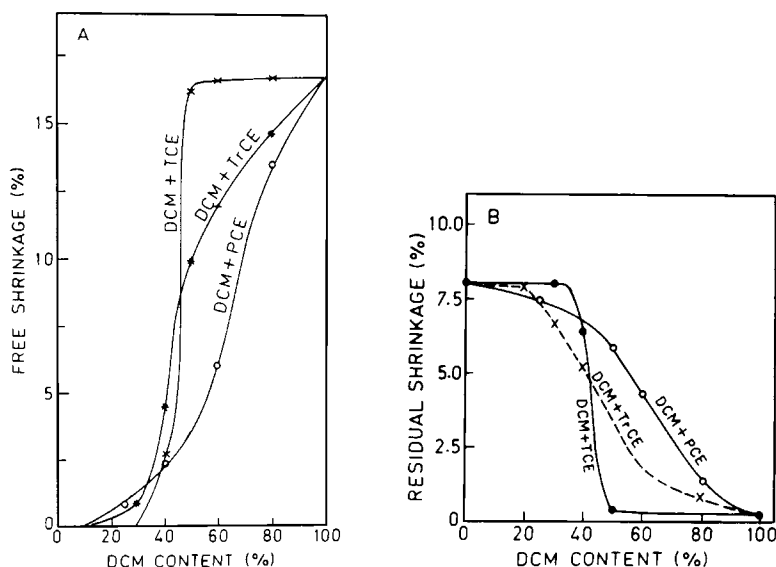


Fig. 8. Free shrinkage (A) and residual shrinkage (B) of PET yarns treated at 28°C in mixtures of DCM and TCE, PCE, or trichloroethylene (TCE) in the slack condition.

Mechanical Properties

Before concluding whether or not the solvent treatment can be an alternative to the conventional thermal treatment, it is essential to have data on the mechanical properties of solvent-treated samples.

The load–elongation curves of PET filaments treated in different solvents are represented in Figures 9–14. The load–elongation curves of PET samples treated in perchloroethylene at 50 and 70°C, either in the slack condition or at constant length, are more or less indistinguishable from that of the control (Fig. 9). The mechanical properties of the sample slack treated even at 90°C are only slightly modified (Fig. 9). The initial modulus, as well as the yield stress, has decreased, while the extension at break has increased. On the other hand, the PET slack treated at 120°C behaves very differently, especially in regard to yield stress which has been drastically reduced. However, the fiber hardens quickly and thereafter exhibits normal load–elongation behavior. When the treatment is carried out at constant length the mechanical properties are more or less unchanged.

Dramatic changes in the mechanical properties of PET yarns occur for the samples treated in strongly plasticizing solvents such as tetrachloroethane, dimethylformamide, nitrobenzene, and dichloromethane. In the case of the sample treated in tetrachloroethane at 50°C in the slack condition, the yield stress is modified only to a minor extent. On the other hand, slack treatment at 70°C drastically reduces the yield stress (Fig. 10). Further increase in the temperature of treatment has only a minor effect on the yield stress, though the extension at break continues to increase with temperature. TCE causes a largely extended flow region following the yield point. However, the yarn hardens quickly and thereafter shows a normal behavior. This sort of recovery of the yarn depends greatly on the temperature of treatment. The higher the temperature of treatment, the slower the recovery, and hence the higher the extension at break. The increase in the extension at break conforms with the shrinkage data. The

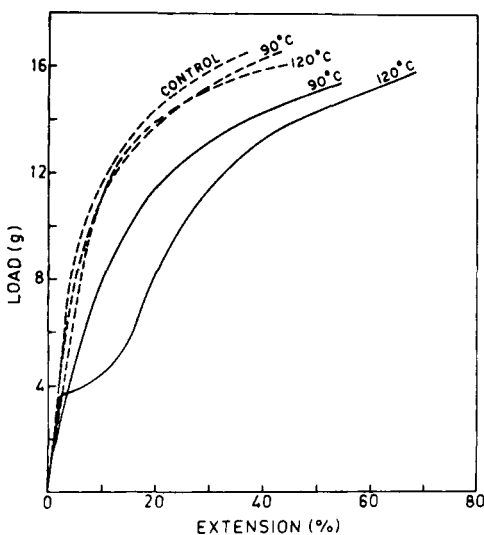


Fig. 9. Load–elongation curves of PET yarns treated in perchloroethylene at different temperatures: (—) slack; (---) at constant length.

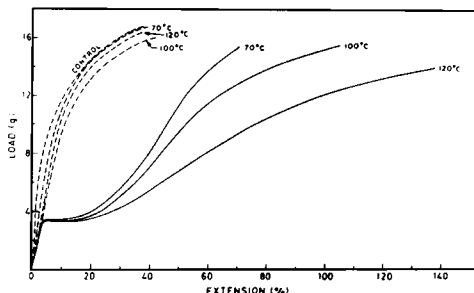


Fig. 10. Load-elongation curves of PET yarns shrunk in tetrachloroethane over a wide range of temperature: (—) treated in slack; (---) treated at constant length.

treatment in the slack condition is seen to result in lowering, to a small extent, of the value of breaking tenacity (Table III), especially at the highest temperature of treatment. The probable reasons for this reduction will be discussed later. The treatment at constant length, on the other hand, results in only minor reduction in the initial modulus and yield stress, and practically no change in the breaking extension. The tenacity at break is marginally increased as compared with the tenacity of the control.

The samples treated with DMF (Fig. 11) and nitrobenzene (Fig. 12) show load-elongation behavior similar to those shown by the samples treated in TCE at comparable treatment temperatures. It should be pointed out, however, that the samples treated in nitrobenzene especially at 100 and 120°C show very high extensibility (Table IV).

The yield stress of PET yarn is considerably reduced on slack treatment in methylene chloride (Fig. 13) even at as low a temperature as 5°C. The reduction in the yield stress of the samples treated in slack at 5°C and above is comparable to that of the samples treated in TCE at 70°C and above. This indicates that methylene chloride molecules have high mobility even at 5°C and diffuse rapidly into the fibers. As a consequence of this chemical energy input, the segmental mobility in the polymer becomes sufficient to permit the relaxation of strains introduced into the fiber structure during the spinning and drawing processes.

It is interesting to point out that the extensibility of the fiber (slack treated) is considerably high depending on the treatment temperature and the nature of the solvent. On the other hand, the range in the yield stress of the treated samples, is rather limited. The yield stress for the sample treated at 120°C in perchloroethylene with the least plasticizing capability is 3.6 g, while for the sample treated at 120°C in the strongest plasticizing agent, namely, tetrachloroethane, it is 3.3 g. The lowest value of the yield stress is observed for the sample treated at 120°C in nitrobenzene. Incidentally this sample shows the highest extension at break.

Stress at 10% Extension

The fabric is normally often subjected to small stresses and strains during its use and the fiber is expected to be able to withstand these impacts. The load required to produce small extensions, say of the order of 10% of the breaking extension, appears to be a useful parameter for characterizing its performance

TABLE III
Mechanical Properties of PET Filaments Treated with Solvents

Solvent	Temperature of treatment (°C)	Free shrinkage (%)	Samples treated in slack			Samples treated at constant length		
			Breaking strength (g/denier)	Breaking extension (%)	Work of rupture (g cm)	Breaking strength (g/denier)	Breaking extension (%)	Work of rupture (g cm)
Control	—	—	4.9	37	4.3	—	—	—
Perchloroethylene	70	0.8	4.9	38	4.3	4.8	39	5.3
	85	2.1	4.7	51	5.7	5.1	41	5.3
	100	2.8	4.9	50	5.5	5.0	42	5.0
	120	10.1	4.8	63	6.8	5.1	40	5.5
<i>s</i> -Tetrachloroethane	70	18.3	4.9	64	7.5	5.2	35	4.7
	85	24.4	4.9	97	8.8	5.1	40	5.1
	100	30.3	4.9	102	9.9	5.0	39	5.1
	120	38.0	4.6	131	11.5	5.1	36	4.4
Nitrobenzene	70	11.5	5.0	80	7.6	4.9	37	4.4
	85	18.5	4.9	99	9.2	5.0	35	4.9
	100	22.7	4.9	126	15.1	4.9	42	4.3
	120	26.3	4.5	186	17.2	4.9	33	3.9
Dimethylformamide	70	11.0	4.9	72	7.2	5.1	39	5.3
	85	15.0	4.9	76	8.2	4.9	43	5.3
	100	19.0	4.9	86	9.3	5.2	37	5.0
	120	22.7	4.6	107	10.0	5.0	41	5.4

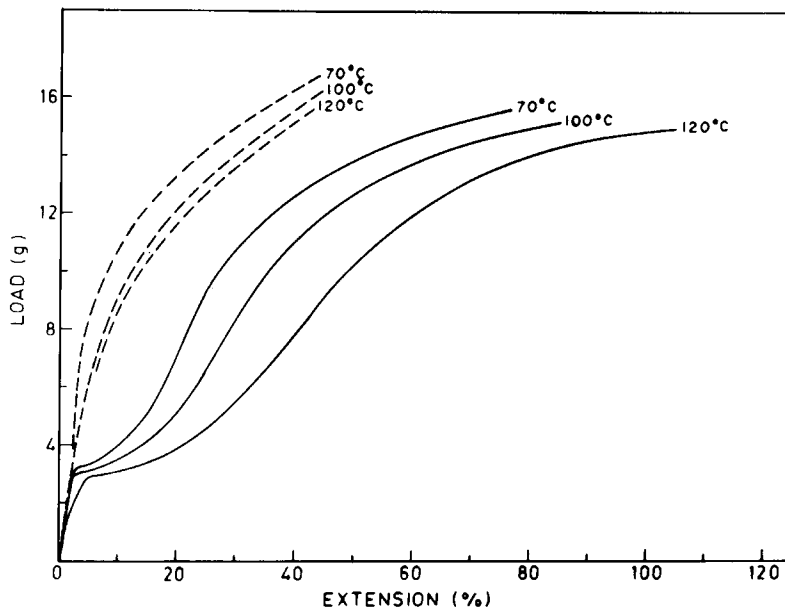


Fig. 11. Load-elongation curves of PET yarns treated at different temperatures in dimethylformamide: (—) treated in slack; (---) treated at constant length.

during actual use. It is desirable that this load should remain high as a result of any treatment designed to improve its dimensional stability.

The load required to produce a 10% extension in the control is 11.8 g. This is drastically reduced on treatment in the slack condition in any of the solvents. The temperature of treatment has, on the other hand, a smaller effect on the subsequent load-bearing capacity of the fiber. For example, the load at 10% extension is about 4 and 3.4 g, respectively, for PET treated with PCE at 120°C and with TCE, DMF, or nitrobenzene at 70°C; and it is about 3.1 g for samples treated at 120°C. These observations suggest that the samples treated in the slack conditions or by allowing fairly high shrinkage to occur during the treat-

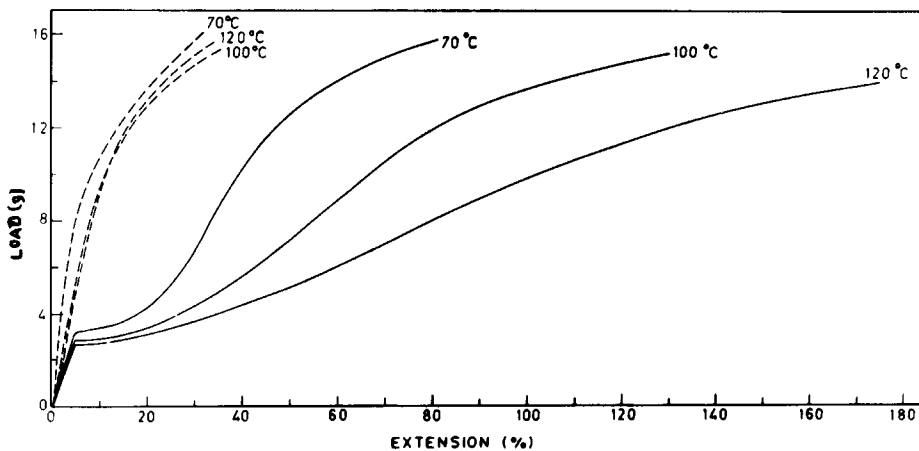


Fig. 12. Load-elongation curves of PET yarns treated in nitrobenzene: (—) treated in slack; (---) treated at constant length.

TABLE IV
Dry Crease Recovery Angles of PET Filaments with *s*-Tetrachloroethane

Temperature (°C)	Crease recovery angles (deg)	
	Treated (slack)	Treated (constant length)
Control		97
50	130	129
70	146	143
85	158	141

ment, may not exhibit satisfactory dimensional stability for all considerations, namely, (1) low residual shrinkage during washing, and (2) capacity to withstand sudden impacts during wear. In that case, the solvent-setting treatment at room temperature in mixtures of methylene chloride and TCE, PCE, or trichloroethylene cannot be employed. However, it should be mentioned once again that the treated fibers harden quickly under the impact of stress and thereafter behave like normal fibers. Further, the treated fibers exhibit improved crease recovery angles compared to the control (Table IV). However, it is desirable to carry out the study on fabric in order to determine whether or not the solvent treatment at room temperature, with allowance made for high shrinkage during the treatment, can impart satisfactory dimensional stability. This study is in progress in our laboratories.

From the results given in Table III it is clear that the changes in the breaking tenacity of the filament yarns as a result of the treatment in various solvents, either in the slack condition or at constant length, are small. These results are contrary to the observations of Buchanan and Dumbleton,²⁰ Dumbleton,²¹ and Dismore and Station.²² The tenacity of PET samples with a draw ratio of 5 has been found to decrease, from about 7 g/denier to about 3.7 and 2.0 g/denier, on a heat setting at 225°C in the slack condition in air for 10 min and in silicone oil

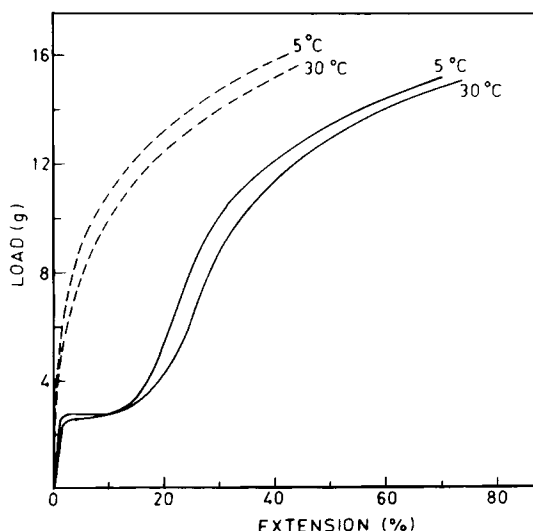


Fig. 13. Effect of temperature of treatment of PET yarns in methylene chloride on their subsequent mechanical properties: (—) treated in slack; (---) treated at constant length.

for 1 min, respectively. On the other hand, Ribnick et al.⁵ have not observed any drop in tenacity of PET yarns determined after a 16-hr conditioning at room temperature (21°C) in a number of solvents. It should be pointed out that the tenacity at break as reported here was not corrected for the increase in denier on heat setting. On heat setting in the slack condition, the diameter of the fiber increases by as much as 10% (Table V). The density is also known^{4,9,23} to increase significantly as a result of heat setting, either in the slack condition or at constant length. The combined effect is a net increase in the denier of the sample by not more than 20% (assuming additivity) for the slack-treated samples and by about 10% for the samples treated at constant length. It is debatable whether the increase in denier arising purely from an increase in density (i.e., crystallinity) and without actually increasing the area of cross section of the fiber should be considered while computing the tenacity at break. Further, assuming that the volume of the fiber remains constant during the breaking test, the area of cross section of the control fiber, as well as that of the slack treated samples, just at the time of the breaking are about the same (Table V). Even when the tenacity values reported in Table III are corrected for the increase in denier arising from the shrinkage, as well as for the density, the drop in tenacity is not as significant as that reported by the previous workers.^{21,22}

Figure 14 shows the load-elongation curves for the PET filaments treated with tetrachloroethane at 50 and 70°C for 3 hr in the slack condition. For comparison the load-elongation curves of the samples treated at 70 and 100°C for 2 min in the same solvent in the slack condition are also shown. The curves of the samples treated for long periods are very similar to those treated for 2 min. It has been shown earlier that the sample treated at 50°C for 2 min exhibits mechanical properties more or less identical to those of the control. This is mainly due to very little interaction between the solvent and PET in such a short time at 50°C. It is clear from the shrinkage data and also from the load-elongation curves (Fig. 14) that if enough time is allowed, the solvent will penetrate the fiber more effectively, causing higher shrinkage. The net effect is that the samples treated for longer periods in the slack condition exhibit higher extension at break than the samples treated for shorter intervals. The behavior of the samples treated in the solvent for longer intervals is similar to that of the samples subjected to dry heat for longer durations up to about 200°C.^{15,16}

Above 200°C, the samples subjected to dry heat for longer durations exhibit lower extension at break than the samples treated for shorter durations because of the development of much higher crystallinity.

Another aspect which has an important bearing on the dimensional stability

TABLE V
Effect of Shrinkage on Denier of PET Filament

Sample	Free shrinkage (%)	Diameter of filament (μm)	Ratio of diameters	Ratio of areas of cross section
Untreated control	—	20.8	1	0.70
Slack treated in air at 230°C	23.0	22.4	1.077	0.62
Slack treated in oil at 230°C	47.9	23.0	1.106	0.63
Slack treated in TCE ^a at 100°C	30.3	23.1	1.106	0.61

^a *s*-Tetrachloroethane.

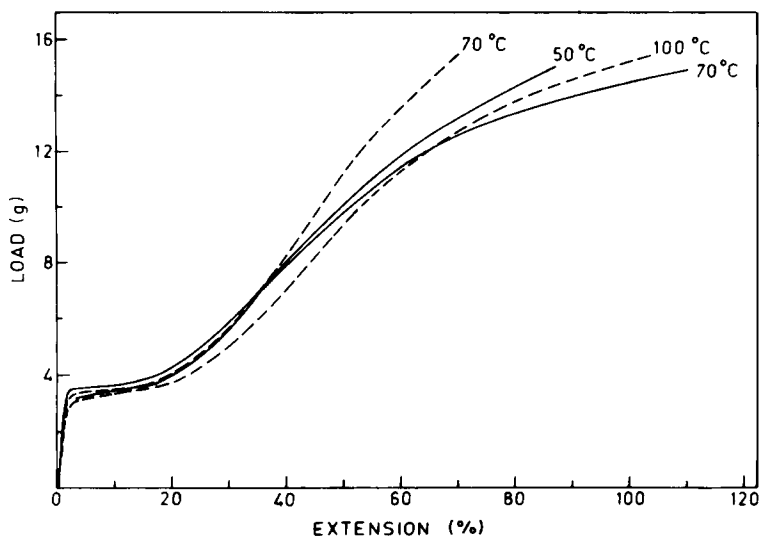


Fig. 14. Effect of time of treatment of PET yarns in TCE on their load-elongation curves: (---) 2-min data; (—) 3-hr data.

of the solvent-treated PET is the improvement in crystallinity as a consequence of the treatment in various solvents. The structural changes accompanying heat (in air as well as in silicone oil) and solvent-induced shrinkage are currently being studied in detail and will be published shortly.

CONCLUSIONS

The free shrinkage of PET filament yarn is largely a function of temperature as well as time of treatment. The equilibrium shrinkage depends to a very great extent on the time of treatment in the case of solvents particularly at lower temperatures of treatment.

The treatment in the slack condition results in satisfactory dimensional stability in the treated material. On the other hand, the treatment at constant length hardly stabilizes the structure, yielding the result that the treated material exhibits large residual shrinkage in boiling water.

The samples treated in the slack condition exhibit significantly reduced yield stress followed by an extended flow region. However, the filaments harden quickly on extension and thereafter behave like normal fibers. The tenacity at break is not significantly affected by the solvent treatment for short times at temperatures up to 120°C, either in slack or constant length conditions.

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