

Post-Extrusion Solid-State Polymerization of Fully Drawn Polyester Yarns

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ABSTRACT: Post-extrusion solid-state polymerization (SSP) of a commercial fully drawn filament yarn (FDY) of poly(ethylene terephthalate) was carried out at 220°C, 230°C, and 240°C for a duration of 30 min to 2 h under inert atmosphere. Molecular weight of the solid-state polymerized polyester filaments was increased from 1.67×10^4 gm/mol to a maximum of 2.61×10^4 gm/mole for the sample subjected to 240°C for 2 h. The kinetics of the SSP in the highly oriented crystalline FDY polyester filaments was investigated using an empirical relation between initial molecular weight and time of SSP and was found to be greatly enhanced, compared to amorphous unoriented

polyester chips. Though the free annealing (i.e., under no tension) of samples at high temperature during solid-state polymerization had a detrimental effect on the orientation of the FDY yarn, the simultaneous increase in the molecular weight compensated the loss in mechanical properties to a great extent. Application of tension during SSP was found to improve the mechanical properties of the SSP yarn by a small value. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5113–5122, 2006

Key words: solid-state polymerization; polyester yarns; high-performance fibers

INTRODUCTION

It is well known that many properties of polymeric material can be improved with an increase in molecular weight and one of the routes to high molecular weight is through solid-state polymerization (SSP). SSP is a viable process for step-growth polymers such as nylons and polyesters.¹

Solid-state polymerization is carried out by heating the solid, low-molecular-weight PET below its crystalline melting point but above its glass transition temperature. The process is carried out at approximately 200–240°C. Under these conditions, polymer end groups are sufficiently mobilized for the reaction to take place. The main polycondensation reaction is an equilibrium reaction; therefore, the by-product ethylene glycol must be removed in order to make the reaction go forward. The reaction by-product is removed by allowing a flow of inert gas or by maintaining reduced pressure.

For the synthesis of high-molecular-weight PET, solid-state polymerization is an important industrial process which has wide application for soft-drink and beverage bottles, tire cord filaments, and industrial fibers. For each of the applications mentioned above, a certain average molecular weight is needed: $[\eta] = 0.60 - 0.70$ for films destined for audio or video

tapes, photographic films, food-packaging films, and insulating material for capacitors; $[\eta] = 0.40-0.70$ for synthetic fibers; $[\eta] = 0.70-0.85$ for carbonated soft-drink bottles and carbonated alcoholic-drink bottles (e.g., beer); and $M_n > 25,000$ or $[\eta] = 0.72-0.98$ for technical textile applications such as industrial tire cords where high mechanical strength is needed.²

Solid-state polymerization in the form of chips or powder, pre-extrusion SSP, is a common approach in the production of high-molecular-weight polymers for molded products. SSP may also be carried out after initial shaping operation has been accomplished (i.e., in the form of a fiber or thin films). This is termed as post-extrusion SSP. This process is still at the development stage, but potentially offers several advantages over the traditional pre-extrusion step. There is a limit to the molecular weight that can be achieved through pre-extrusion SSP. Also, the rate of reactions is slow. This is due to the slow diffusion of the by-product, ethylene glycol, in relatively larger particles, which makes the polycondensation reaction diffusion controlled in pre-extrusion SSP.³ The condensation product can be removed more effectively in post-extrusion SSP because extruded geometries such as fibers and films have at least one dimension that is much smaller than chips.⁴ This helps in driving the reaction at a faster rate and to a higher molecular weight than pre-extrusion SSP.

The second major concern associated with pre-extrusion SSP is the subsequent processing of high-molecular-weight polymers because they require high pressure and can undergo thermo-mechanical degradation, melt fracture, and filament breakage.

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TABLE I
Material Specification of Fully Drawn Polyester Yarn

Intrinsic viscosity (dL/gm)	0.61
Molecular weight (gm/mol)	1.67×10^4
Linear density (denier)	50
No of filaments	48
Tenacity (gpd)	4.65
Elongation (%)	39.36
Birefringence	0.19
Melting point (°C)	249

Although several studies^{5–19} have been reported on the pre-extrusion SSP of polyester/nylon chips, only a few attempts have been made to study and understand the SSP of polyester/nylon in fiber/filament form. Increase in intrinsic viscosity from 0.6 to 0.8 dL/gm has been reported in a patent²⁰ on SSP of freshly extruded filaments of 220/34 denier, which were re-melted immediately to obtain high-molecular-weight material. In another patent,²¹ fibers from a prepolymer of PET having intrinsic viscosity of 0.25 dl/g were compacted into porous pellets and solid-state polymerized to give intrinsic viscosity of 0.893 dL/g at 236°C in short reaction time. Recently,^{22–24} freshly extruded thick monofilaments of nylon 6 and nylon 66 were solid-state polymerized to high molecular weight. These studies indicate that SSP in filament form is an interesting proposition, as very high molecular weights may be obtained in relatively short reaction time as compared to chips. The present study is an attempt to investigate the kinetics of SSP in fully drawn (FDY) polyester filament yarns. This study also aims at investigating the effect of SSP on the structure and properties of these fibers.

EXPERIMENTAL SECTION

Materials

Fully drawn polyester yarns were obtained from Modipon Fibers Company (Modinagar, U.P., India). The detail of the FDY material is given in Table I.

Solid-state polymerization of FDY PET

A schematic diagram of the apparatus used for the solid-state polymerization of the FDY polyester is shown in Figure 1. The setup consisted of a quartz furnace of 100 cm length, wherein a polyester filament bundle of length 40 cm, containing 200×48 filaments, was placed inside the heated quartz tube. The sample was held from the two sides with the help of a Kanthal wire. One end was fixed, while to the other end tension was applied by hanging a calculated weight to the wire, which was placed over a pulley. The heating cycle with multiple steps was controlled using a PID controller.

Nitrogen was used as an inert gas to carry away the by-products formed during the condensation reaction. The gas was preheated in a heat exchanger placed immediately before the quartz furnace. The temperature of the inert gas inside the furnace was maintained with an accuracy of $\pm 1.5^\circ\text{C}$. The sample was placed at the room temperature inside the furnace and nitrogen flow rate of 3 l/min was maintained throughout the experiment. The heating cycle used for the experiment is shown in Figure 2.

Characterization of filaments

All the filaments within the bundle were found to have uniform properties after solid-state polymeriza-

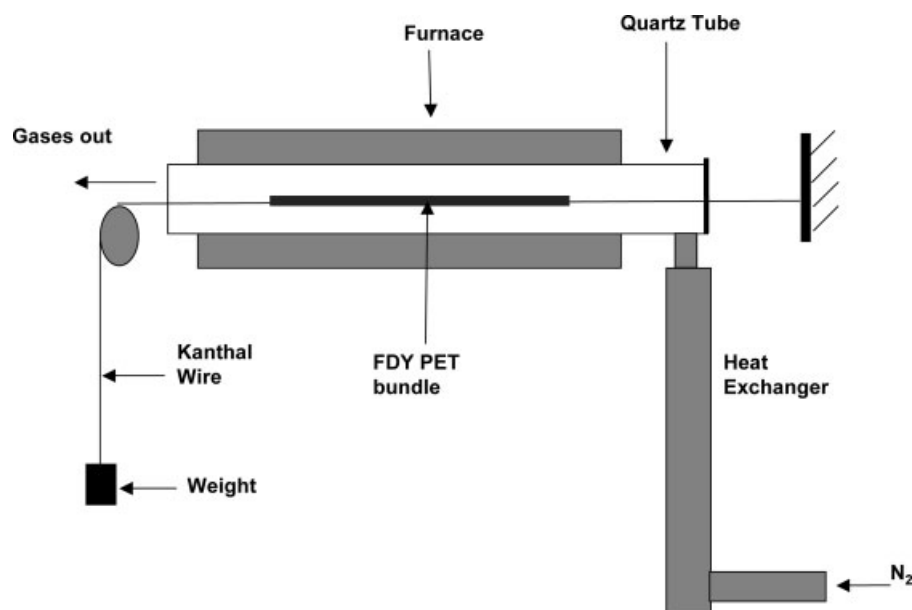


Figure 1 Schematic diagram of the apparatus used for the solid-state polymerization of FDY polyester.

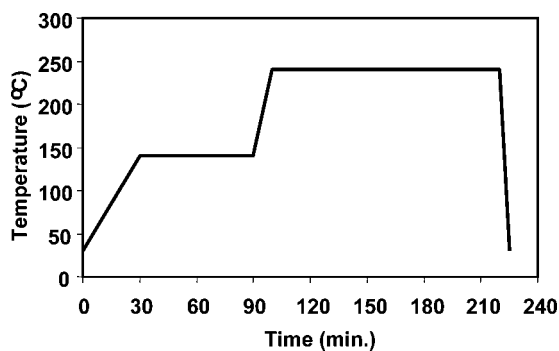


Figure 2 Time-temperature profile for solid-state polymerization of FDY PET at 240 °C for 2 h.

tion. The ends where the fiber was attached to the Kanthal wire were discarded while testing the samples.

Intrinsic viscosity

Intrinsic viscosity was determined by using an Ubbelohde viscometer with phenol : tetrachloroethane 50 : 50 (V/V) mixture as a solvent at 25°C.

Molecular weight was determined using the Mark-Houwink relation given by eq. (1).

$$\eta = kM_n^\alpha \quad (1)$$

where η is the intrinsic viscosity, dL/g, M_n is the number average molecular weight, and values of $k = 2.1 \times 10^{-4} \text{ dl g}^{-1}$ and $\alpha = 0.82$ for the above conditions were taken from the literature.¹

Density

Density measurement was carried out on a Devenport Density Gradient Column. The column was prepared using *n*-heptane (with specific density of 0.682 g/cc) and carbon tetrachloride (with specific density 1.595 g/cc). The mass fraction crystallinity (β) was calculated using eq. (2).

$$\beta = \frac{\rho_c(\rho - \rho_a)}{\rho(\rho_c - \rho_a)} \quad (2)$$

where ρ_a , ρ_c , and ρ are the densities of the amorphous, crystalline, and given samples, respectively. The standard values were used for crystalline ($\rho_c = 1.455 \text{ gm/cc}$) and amorphous ($\rho_a = 1.33 \text{ gm/cc}$) PET.

Wide-angle X-ray diffraction measurement

The yarn was cut into fine powder and compressed into a small rectangular orifice in a glass holder of the rotating stage of the Philips X-ray powder diffractometer (θ). The sample was scanned at 2°C/min for 2θ in the reflection from 10° to 35°.

Crystallinity

The Ferrow and Preston method²⁵ was used to evaluate the crystallinity. In this method, a radial scan of the randomized sample and the amorphous sample was done. The amorphous scattering curve was constructed below the scattering curve of the sample after appropriate scaling.

$$\text{Crystallinity} = \frac{\int s^2 I_c(s) ds}{\int s^2 I(s) ds} \quad (3)$$

where $s = 2 \sin\theta/\lambda$, $I_c(s)$ is the intensity of crystalline reflection, and $I(s)$ is the intensity of total reflection.

Crystallite size

The radial diffraction scan of the powdered sample was used for the measurement of the crystallite size.²⁵ The half-width values of the (100), (-110), and (010) reflections were measured and the crystallite size was calculated using the Scherrer equation given by eq. (4).

$$t = \frac{0.89\lambda}{B_{hkl} \cos \theta_{hkl}} \quad (4)$$

where λ is the wavelength of the radiation, θ_{hkl} is the Braggs angle for the (*hkl*) plane, $B(hkl)$ is the observed half-width of the peak and t is the thickness of the crystallite perpendicular to (*hkl*) plane.

Birefringence

Birefringence was measured using a Leitz tilting compensator and Leitz polarizing microscope (Wetzler, Germany). The diameter of the sample was also measured simultaneously.

Sonic modulus

Sonic velocity through the yarn was measured on a propagation meter PPM-5R (Norwood, MA) operated at 5 kHz at the room temperature.

Thermal characteristics

A Perkin Elmer DSC-7 thermal analyzer (Norwalk, CT) was used for the thermal characterization. Heating and cooling rate of 10°C/min was used in a nitrogen gas environment.

Tensile properties

Tensile testing of the PET multifilament yarn samples were carried out on a Statimat ME instrument (Monchengladback, Germany).

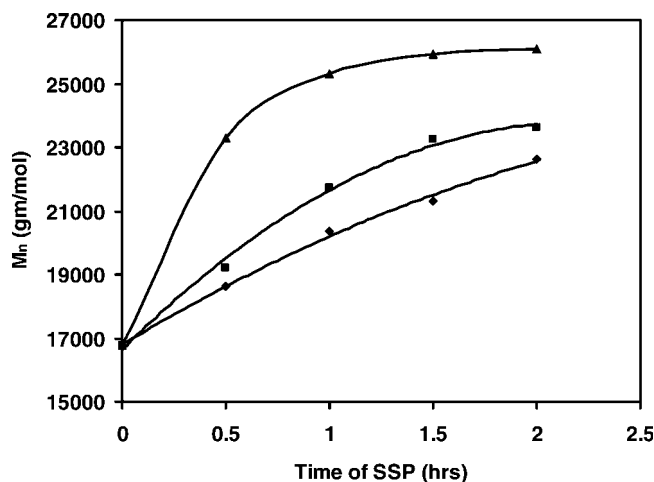


Figure 3 Effect of time and temperature of SSP on the molecular weight of solid-state polymerized FDY PET filaments: (▲) 240°C; (■) 230°C; (◆) 220°C.

RESULTS AND DISCUSSION

Kinetics of SSP in FDY polyester

The fully drawn polyester yarn samples were first dried to ensure that the samples do not undergo hydrolysis. Both drying and solid-state polymerization were carried out under nitrogen atmosphere. The heated nitrogen gas was allowed to flow through the tube so as to maintain inert atmosphere and to drive away by-products of SSP, which diffuse out of the sample. The drying time and nitrogen flow rate were optimized by conducting initial experiments of SSP at a predetermined temperature and for a fixed time. A low value of tension of about 0.1 gpd was applied to keep the filament bundle straight and simulate nearly free annealing conditions.

The samples were polymerized at 220°C, 230°C, and 240°C for different time intervals. Figure 3 shows the change in molecular weight with time of polymerization for all the three temperatures. From the figure, it is clearly seen that the increase in the molecular weight is significant at all temperatures. A maximum molecular weight of about 2.61×10^4 g/mol was achieved by SSP of polyester FDY filaments at 240°C for 2 h from the starting molecular weight of 1.67×10^4 g/mol. The rates of reaction were faster in the fiber compared to that observed in polymer chips. The reaction reached a saturating value of molecular weight within much shorter time of about 2 h (at 240°C), compared to the time taken by chips.⁵⁻¹⁹

Temperature had significant effect on the rate of SSP. The increase in the rate of SSP at higher temperatures was due to the increased mobility of the molecular chains. The increased mobility of chains allows functional groups to approach each other easily. However, prolonged exposure of the filament at high temperature 240°C resulted in a comparatively

lower increase in molecular weight at longer times and the molecular weight appeared to hit a saturation value. This may be the result of limited availability of the reactive end groups as the reaction proceeds.

It has been shown⁵⁻⁷ that the degree of polymerization can be expressed empirically to the square root of time of the reaction. Therefore, the change in molecular weight may be expressed as a function of time by a relation given as

$$M_n = M_{n0} + Ae^{-\Delta E/RT} \sqrt{t} \quad (5)$$

where M_n is the number average molecular weight at time t , M_{n0} is the initial number average molecular weight of precursor, A is the collision frequency factor for propagation, ΔE is the energy of activation for propagation (cal/mol), R is the gas constant, 1.987 cal/mol K, and T is the Temperature of reaction.

The reaction rate constant k at temperature T may be evaluated from the above relation by plotting the molecular weight versus under root of time. Figure 4 plots the relationship for all the three temperatures. As can be seen from the figure, the data points for the SSP reaction carried out at 220°C and 230°C follow nearly a straight-line relationship. However, for the reaction carried out at 240°C, the linear relationship is valid only for the first three points. The graph deviates from linearity due to the saturation effect as discussed above and, therefore, the last point has been ignored for this analysis.

Equation 6 can be solved to give the equilibrium rate constant k for solid-state polymerization at each condition.

$$k = \frac{M_n - M_{n0}}{\sqrt{t}} \quad (6)$$

At each solid-state temperature, value of k was obtained using the slope of the lines from Figure 4. The natural log of this value ($\ln k$) is plotted against inverse of temperature [$1/T$ (K)] to obtain an Arrhe-

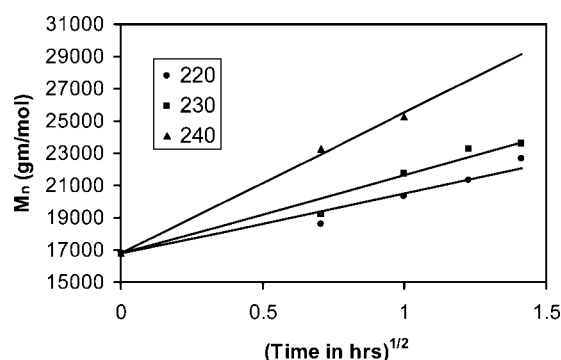


Figure 4 Plot for molecular weight as a function of the square root of SSP time at various SSP temperatures: (▲) 240°C; (■) 230°C; (●) 220°C.

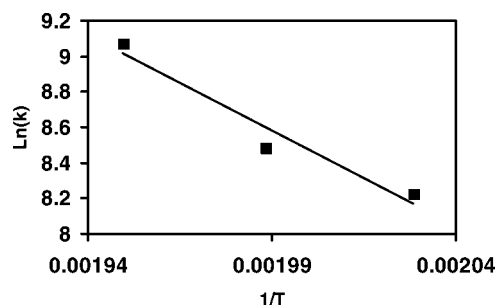


Figure 5 Arrhenius plot of $\ln(\text{rate constant})$ as a function of inverse of reaction temperature.

nius plot, as shown in Figure 5. Values for activation energy ΔE and frequency factor A were calculated from this plot.

The activation energy ΔE was found to be 21.3 kcal/mol, while the frequency factor A was 9.30×10^{12} . The kinetic rate constant for solid-state polymerization of polyester in fully drawn filament form may therefore be written as

$$K = 9.30 \times 10^{12} e^{(-21.3 \times 10^3 / RT)} \quad (7)$$

and the kinetic rate equation describing empirical relation between solid-state polymerization time, temperature, and molecular weight is given by

$$M_n = M_{n0} + 9.30 \times 10^{12} e^{-21.3 \times 10^3 / RT} \sqrt{t} \quad (8)$$

This indeed is an interesting result. For high-temperature SSP reactions (i.e., above 200°C), the A and E values for solid-state polymerization of polyester chips are reported^{5,6} to be $\sim 10^{10}$ g/mol/min^{1/2} and ~ 15 –16 Kcal/mol, respectively. In the case of post extrusion SSP of the FDY filaments, these values increased significantly to $\sim 10^{13}$ g/mol/min^{1/2} and ~ 21 Kcal/mol, respectively. This implies that the apparent activation energy ΔE of SSP in fully drawn and heat-set fiber is higher by $\sim 30\%$ as compared to that in randomly oriented amorphous chips. This higher barrier of activation may be due to the fact that the molecular network in an oriented and crystalline fiber is highly restricted and rigid. On the other hand, the same fact may significantly enhance the collision frequency (indicated by higher apparent frequency factor A by three orders of magnitude) of the two reactive groups when they come close and are not able to easily move away from the vicinity of each other. However, the apparent rate constant, which represents the combined effect of the above two changes, for SSP of FDY PET calculated using eq. (4) at temperatures between 220°C and 240°C are higher (by three to four times) than the values reported in the literature^{5,6} for PET chips.

This indicates that the reactivity of the available end groups in an oriented and crystalline FDY poly-

ester filament is significantly higher; however, due to the limited availability of reactive ends, the molecular weight hits a limiting value in a relatively much shorter period of reaction time (~ 1.5 h).

Physical appearance of the SSP samples

It was observed that solid-state polymerization at lower temperature (220°C) does not impart color to the fibers. However, the samples that were solid-state polymerized at higher temperature showed a slightly yellowish tint.

The behavior of the filaments during solid-state polymerization plays an important role in the course of the reaction. Fusion or sticking of the sample during solid-state polymerization is one of the limitations in the SSP of chips. In the SSP of multifilament yarn, this may create a considerable concern. However, in the case of FDY PET filament, sticking or fusion was not observed for the reaction temperatures up to 240°C. This may be due to the high glass transition temperature of the FDY, which has high degree of orientation and crystallinity.

Morphology and properties of solid-state polymerized FDY PET

Solid-state polymerization increases molecular weight to a considerable extent in FDY polyester. This increase in molecular weight is expected to bring about significant changes in the structure and properties of the yarn.

Figures 6 and 7 show the effect of both SSP temperature and time on the mechanical properties of SSP PET fibers. Tenacity was found to decrease though molecular weight increased with increasing time of SSP at all temperatures. This may be attributed to the fact that both high molecular weight and high orientation are necessary for the strength of the fiber.

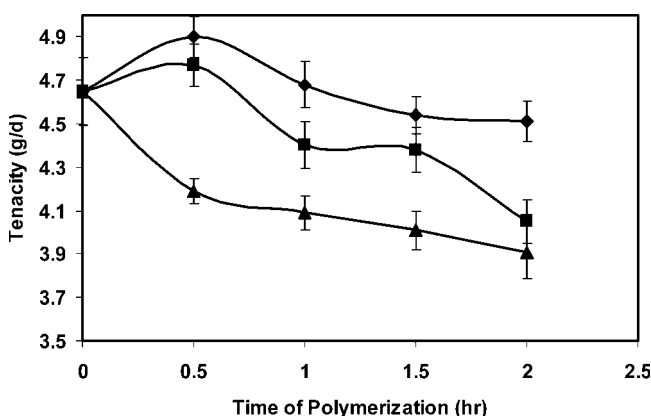


Figure 6 Effect of reaction time and temperature on the tenacity of solid-state polymerized FDY-PET: (▲) 240°C; (■) 230°C; (◆) 220°C.

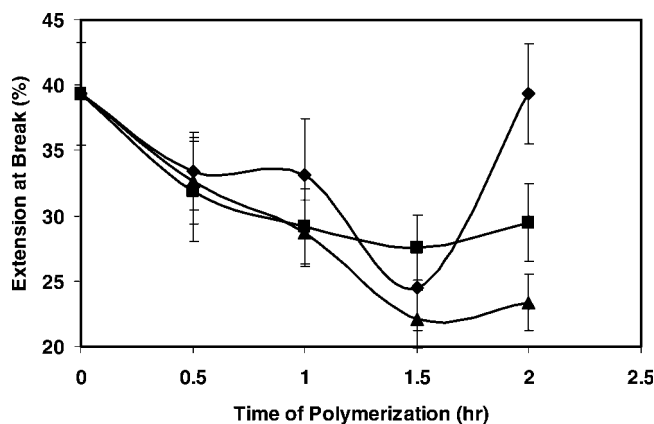


Figure 7 Effect of reaction time and temperature on the extensibility of solid-state polymerized FDY-PET: (▲) 240°C; (■) 230°C; (◆) 220°C.

With the increase in temperature and time of the SSP, the orientation of the fiber decreases, resulting in lower tenacity. At 220°C the decrease in strength is smaller, as compared to that at 240°C. At low temperatures the mobility of molecular chains is expected to be lower. Because of less mobility, relaxation and coiling of chains become difficult, and loss of orientation is less pronounced at lower temperature.

However, a small improvement in tenacity was observed for the reactions at 220°C and 230°C for 30 min. This is an indication that increase in molecular weight due to solid-state polymerization is trying to compensate the loss of properties due to disorientation on heating. Therefore, one can expect that even at other temperatures the loss of tenacity would have been more severe had there been no polymerization.

The positive effect of solid-state polymerization is more evident when the properties of the SSP yarn are compared to those that are simply heat set for short times (5–10 min.) at the above temperatures under slack condition (free annealing). In such cases, the polymer loses tenacity by about half at 220°C in 5 min.^{25–28}

On heating for short times (5–10 min), polymer chains disorient and fold into crystals, leading to low tenacity because of fewer tie points between any two crystals. On the other hand, the samples when solid-state polymerized at 220°C for 30 min to 1 h actually show a small increase in tenacity, and samples polymerized for 2 h show a decrease of only 15%. This indicates that the polymerization might be occurring between the end groups of oriented chains along the axis of the fiber, giving rise to extended chains of higher molecular weight. Also, reaction may be taking place among the amorphous ends of two crystals in the fiber, leading to extended order and connectivity.

It is also known that on heat-setting in slack conditions, the folding of chains into crystals also results

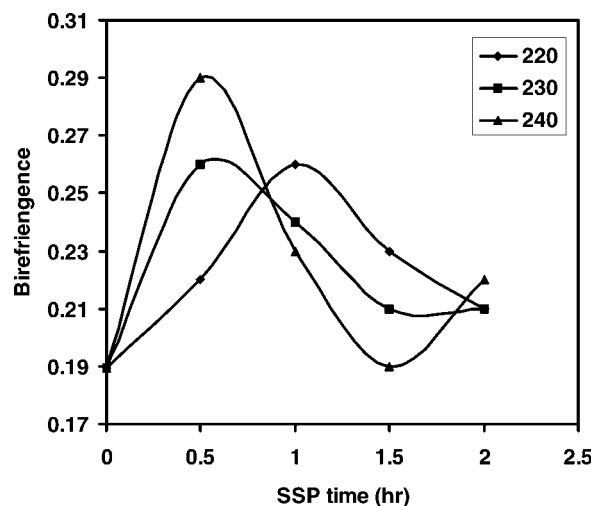


Figure 8 Effect of reaction time and temperature on the birefringence of solid-state polymerized FDY-PET: (▲) 240°C; (■) 230°C; (◆) 220°C.

in significant decrease in extensibility of the fibers; however, in our samples, only a small decrease was found in extensibility. This further indicates that an extended chain structure is being created which tries to retain extensibility, even after heating the fibers for the long time of 2 h. All solid-state polymerized samples showed a sharp decrease in extensibility when polymerized for shorter durations of up to 1 h; thereafter, the extensibility did not drop further and rather showed a marginal improvement. This is supported by the crystallinity of the samples, which did not increase after 1 h of SSP. In the sample polymerized for 2 h at 240°C, the improvement in extensibility was rather significant, possibly due to formation of better molecular network at higher rates of polymerization.

Figure 8 depicts the changes in birefringence of the SSP samples. Birefringence is indicative of the

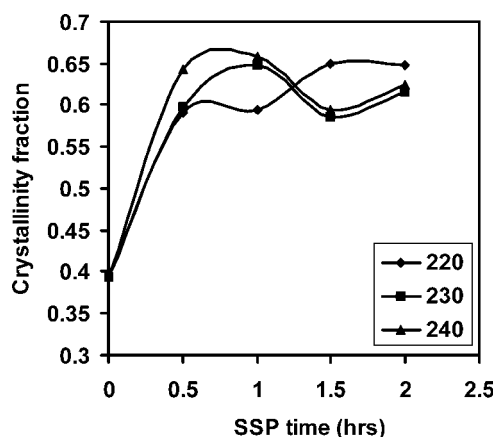


Figure 9 Effect of reaction time and temperature on the crystallinity of solid-state polymerized FDY-PET: (▲) 240°C; (■) 230°C; (◆) 220°C.

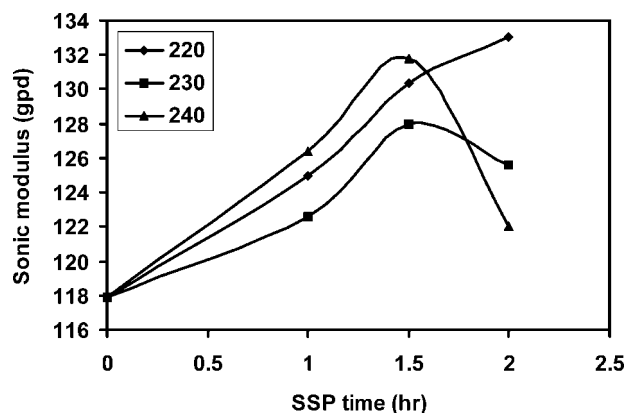


Figure 10 Effect of reaction time and temperature on the sonic modulus of solid-state polymerized FDY-PET: (▲) 240°C; (■) 230°C; (◆) 220°C.

overall orientation of the sample with a higher contribution from the oriented crystalline part. Since the overall orientation of the sample is expected to decrease with heat treatment, the increase in birefringence in all cases at 0.5 h is indicative of a substantial rise in oriented crystalline regions at the expense of oriented amorphous regions (Fig. 9). Both the crystallinity and birefringence were found to first increase and then decrease with an increasing time of SSP for all cases. The peak values occurred earlier for samples polymerized at 230–240°C than those at 220°C. Decrease in birefringence after the peak value may be due to the disorientation of crystalline regions when kept at longer times. However, it may also be partly due to a decrease in crystallinity at long reaction times. This decrease in crystallinity indicates the appearance of defects in the crystalline regions.

The rate of both the increase and decrease of birefringence is greater at higher temperatures. At 240°C birefringence value increases sharply at 0.5 h time followed by a sharp decrease, while at 230°C and 220°C rates are moderate and slow, respectively, as compared to 240°C.

The values of the sonic modulus of the polyester fiber after solid-state polymerization are summarized

TABLE II
Changes in the Crystal Dimensions After Solid-State Polymerization of FDY PET Filaments Under Various Conditions

Sample (temp./time)	Crystal thickness (Å)		
	100	-110	010
FDY	19.83	8.86	14.72
220/1.0	34.9	24.31	35.84
220/1.5	30.09	19.79	48.49
220/2	32.32	16.69	45.79
230/2	43.63	25.03	41.21
240/2	36.36	19.79	24.98

in Figure 10, which shows the effect of time and temperature. The sonic modulus increases with increasing reaction time of up to 1.5 h for all reaction temperatures. Except for samples polymerized at 220°C, the values drop sharply thereafter, indicating disoriented morphology at very long reaction times.

Crystal dimensions were found to increase initially with SSP. The results are summarized in Table II for a particular reaction condition. It is clear that the crystal thickness for all the three planes increases on heating. The perfection of crystals is also evident from the DSC curves (Fig. 11), which show a small

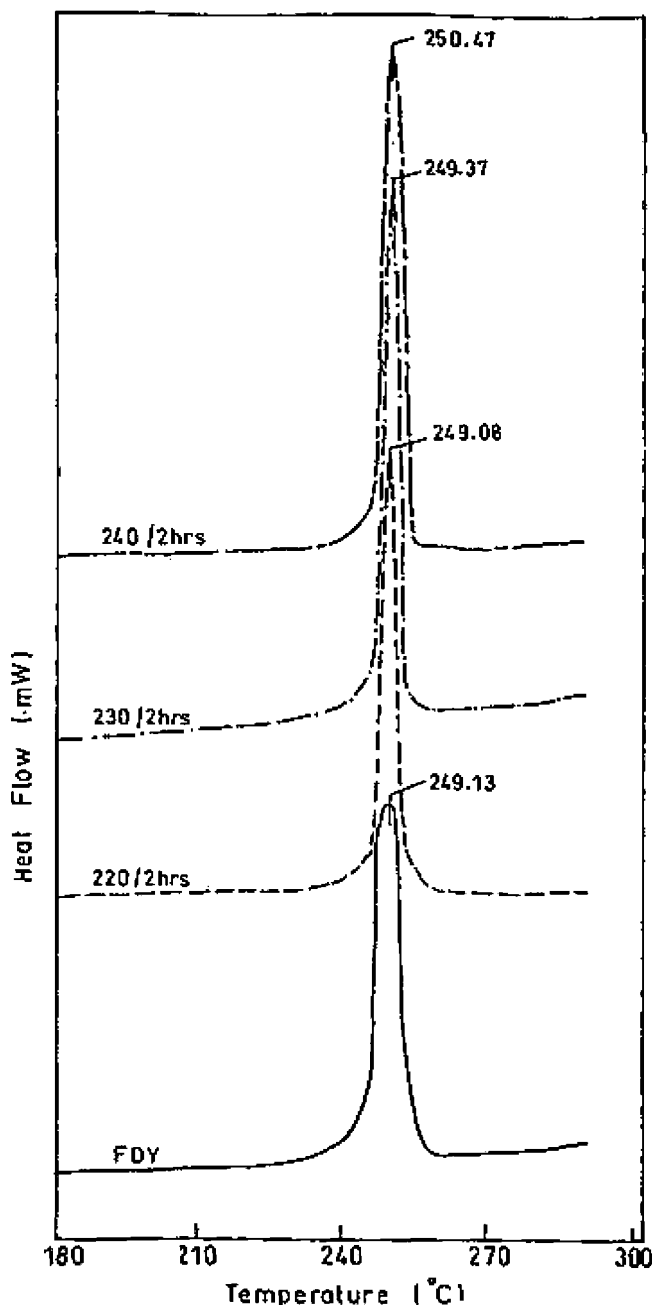


Figure 11 Thermal transitions in solid-state polymerized FDY-PET samples (heating cycle).

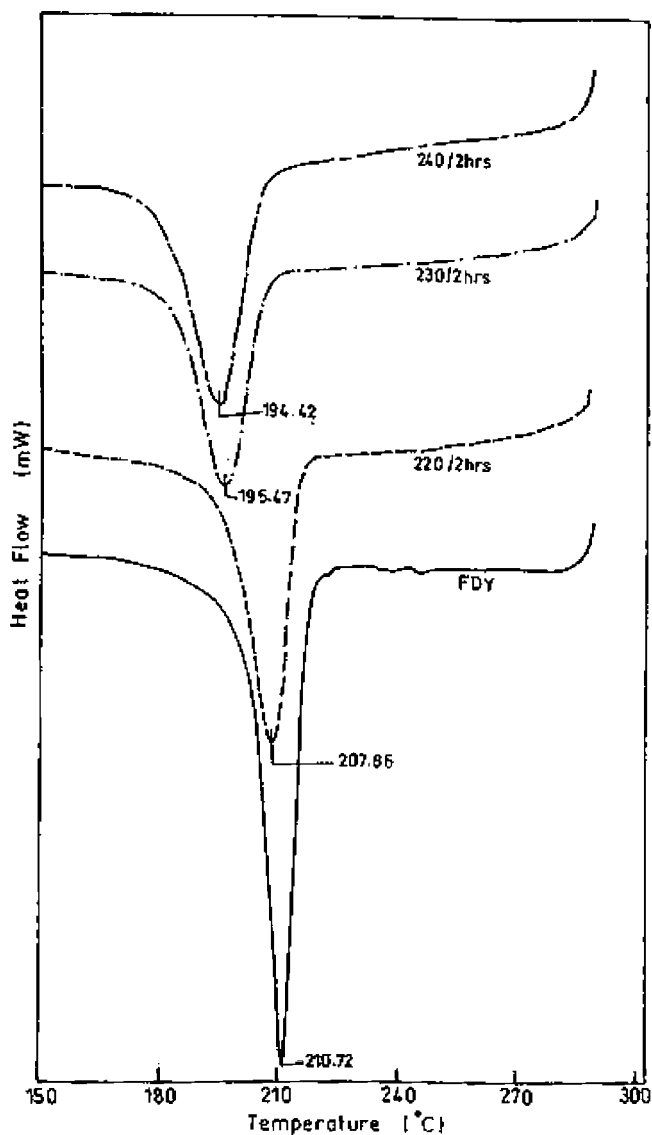


Figure 12 Thermal transitions in solid-state polymerized FDY-PET samples (cooling cycle).

increase in the melting point of the samples after solid-state polymerization. Also, the increased sharpness of the melting peaks in SSP samples indicates that the crystal perfection has increased. However, it appears that the crystalline structure starts to change a little due to thermal degradation when the fibers are kept for a long time at high temperature.

Upon cooling from the molten stage, an interesting feature, shown in Figure 12, is observed for the SSP samples. The rate of crystallization was slower (broader peaks) for samples polymerized at higher temperature and for longer reaction time. In addition, the temperature at which melt crystallization initiates is lower (i.e., more supercooling is required) for the solid-state polymerized fibers as compared to the control (original) sample. This delay in crystallization is attributed to the increase of the molecular

weight of the polymer. Because of higher molecular weight, the rearrangement of chains to form order may be relatively difficult, resulting in the above observations.

SSP fibers show no shrinkage in boiling water. This was expected because the fibers were subjected to prolonged heat-treatment during SSP, which allows them to attain the state of minimum energy configuration. The diameter of the fiber did not change significantly after SSP.

Effect of tension on SSP of FDY PET

PET FDY filaments were solid-state polymerized at 220°C for 1 h under different levels of tension. At temperatures higher than 220°C the sample could not sustain tension higher than 0.33 gpd, so the study was conducted only at 220°C. However, the sample was not able to sustain the tension above 0.5 gpd even at 220°C. Therefore, the effect of tension during polymerization could be studied only in a narrow range of applied force. Figures 13 and 14 summarize the results of the mechanical properties of the solid-state polymerized fibers under tension. Tenacity was found to increase marginally from 4.68 to 4.88 gpd and elongation decreased to 25.37% from 39.36% with an increase in tension from 0.1 to 0.5 gpd.

During SSP, tension is expected to play an important role on the morphology and properties of the fiber. As the fiber is under constraint, the disorientation is expected to lessen (to some extent), giving rise to better networking of chains and subsequent properties. This increase in strength at higher tension is attributed to the increase in orientation and overlapping of molecular chains within the fiber.

The change in dimension (extension or contraction) of the filament bundle during solid-state polymerization was studied as a function of the applied tension. At very low tension (0.1 gpd, equivalent to

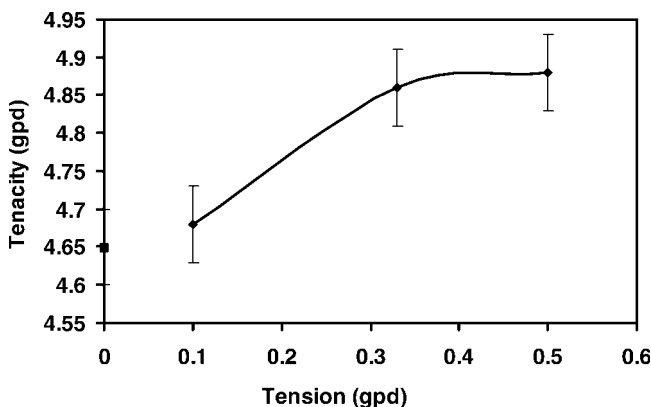


Figure 13 Effect of applied tension on the tenacity of FDY PET solid-state polymerized at 220°C for 1 h.

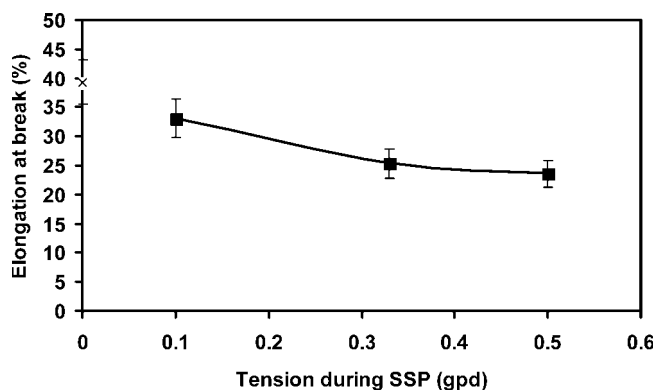


Figure 14 Effect of applied tension on the elongation of FDY PET solid-state polymerized at 220 °C for 1 h.

free annealed), the sample showed contraction when the temperature was increased to a drying temperature of 140°C. A total contraction of around 1.25% was observed. On further increase of temperature to the reaction temperature, a further contraction was observed, though it was not significant. As the temperature was maintained at the reaction temperature, the sample slowly extended but never attained its original length. This indicated folding of the molecular chains as a result of disorientation during solid-state polymerization under free (i.e., low tension) conditions.

However, when solid-state polymerization was carried out under higher tension, the abovementioned contraction was not observed during the entire cycle of polymerization. Rather, the extension of the yarn was observed during polymerization conditions and the extension was more at higher tension. For 0.33 gpd tension, net extension was around 2.73%, while for 0.5 gpd it was around 4.4%, which results in an improvement of the mechanical properties.

The mechanical properties of the SSP fibers could not be improved significantly compared to the control sample. It is likely that if the sample is subjected to a control drawing during solid-state polymerization, better properties will be obtained. Further studies are being conducted in this direction so that high-performance fibers may be obtained directly using the approach of post-extrusion SSP.

CONCLUSIONS

High-molecular-weight PET is industrially obtained by solid-state polymerization of polyester chips (pre-extrusion form) for various industrial applications, including production of high-performance fibers. SSP may also be carried out post-extrusion after initial shaping operation in the form of fiber or thin films. This process potentially offers several advantages over traditional pre-extrusion step in terms of

enhanced rates of reaction, avoidance of processing difficulties, and so forth.

The FDY PET samples were solid-state polymerized at 220°C, 230°C, and 240°C for different time intervals from 0.5–2.0 h. The molecular weight was found to increase significantly at all temperatures. A maximum molecular weight of about 2.61×10^4 g/mol was achieved by SSP of polyester FDY filaments at 240°C for 2 h from the starting molecular weight of 1.67×10^4 g/mol. The rates of reaction were much faster due to oriented crystalline structure in the FDY fiber form in contrast to that observed in polymer chips. The kinetic parameters such as apparent activation energy ($\Delta E = 21.3$ kcal/mol) and frequency factor ($A = 9.30 \times 10^{12}$) were found to be significantly higher to those found for polyester chips.

The properties and morphology of the polymerized fibers were studied and found to undergo substantial changes. The crystallinity of the sample increased significantly, whereas the orientation of the sample was found to decrease with increasing reaction time and temperature. Increase in molecular weight during SSP was found to significantly compensate the decrease in mechanical properties expected due to chain folding and crystallization under slack conditions. The tenacity was found to increase marginally with increase in tension from 0.1 to 0.5 gpd during polymerization. These results indicate that the post-extrusion SSP is an interesting approach; however, it warrants further studies in order to make it useful for developing high-performance fibers.

References

- McIntyre, J. E. Polyester Fibers in Handbook of Fiber Chemistry, Lewin, M.; Pearce, E. M., Eds.; 2nd ed.; Marcel Dekker: New York, 1998.
- Gupta, V. B.; Bashir, Z. In Handbook of Thermoplastic Polyesters; Fakirov, S., Ed.; Wiley-VCH Verlag: Weinheim, 2002; Vol. 1.
- Vouyiouka, S. N.; Karakatsani, E. K.; Papaspyrides, C. D. Solid-State Polymerization, Progress Polym Sci 2005, 30, 10.
- Almonacil, C.; Desai, P.; Abhiraman, A. S. Macromolecules 2001, 34, 4186.
- Kim, T. Y.; Lofgren, E. A.; Jabarin, S. A. J Appl Polym Sci 2003, 89, 197.
- Kim, T. Y.; Jabarin, S. A. J Appl Polym Sci 2003, 89, 213.
- Duh, B. J Appl Polym Sci 2002, 84, 857.
- Ma, Y.; Agarwal, U. S.; Sikkema, D. J.; Lemstra, P. J. Polym 2003, 44, 4085.
- Boiko, Y. M.; Marikhin, V. A.; Milagin, M. F. J Macromolecular Sci Phys 2002, B41, 1007.
- McGehee, J. F.; Witt, A. R. Presented at the American Institute of Chemical Engineers Spring National Meeting, New Orleans, LA, Mar. 30-Apr. 3, 2003, p 1518.
- Schiavone, Robert J. J Appl Polym Sci 2002, 86, 230.
- James, N. R.; Ramesh, C.; Sivaram, S. Macromolecular Chem Phys 2001, 202, 1200.
- Rovaglio, M.; Algeri, C.; Manca, D. Industrial Eng Chem Res 2004, 43, 4267.

14. Medellin-Rodriguez, F. J.; Lopez-Guillen, R.; Waldo-Mendoza, M. A. *J Appl Polym Sci* 2000, 75, 78.
15. Mallon, F. K.; Ray, W. Harmon. *J Appl Polym Sci* 1998, 69, 1233.
16. Mallon, F. K.; Ray, W. *J Appl Polym Sci* 1998, 69, 1203.
17. Kang, C.-K. *J Appl Polym Sci* 1998, 68, 837.
18. Wu, D.; Chen, F.; Li, R.; Shi, Y. *Macromolecules* 1997, 30, 6737.
19. Chen, S. A.; Chen, F. L. *J Appl Polym Sci Part A: Polym Chem* 1987, 25, 533.
20. Trayon, S., Del, C. (to FMC Corporation). U.S. Pat. 3,634,356 (1972).
21. Scannapieco, S. N. U.S. Pat. 4849497 (1989).
22. Abhiraman, A. S., *Macromolecules* 1998, 31, 6813.
23. Srinivasan, R.; Desai, P.; Abhiraman, A. S. *Polymeric Mater Sci Eng* 1994, 71, 137.
24. Srinivasan, R.; Desai, P.; Abhiraman, A. S.; Knorr, R. S. *J Appl Polym Sci* 1994, 53, 1731.
25. Gupta V. B. *J Text Inst* 1995, 86, 299.
26. Gupta, V. B. *J Appl Polym Sci* 2002, 83, 586.
27. Ramesh, C.; Gupta, V. B.; Radhakrishnan, J. *J Macromolecular Sci Phys* 1997, B36, 281.
28. Gupta, V. B.; Kumar, S. *J Appl Polym Sci* 1981, 26, 1897.