

Solid-State Polymerization of Melt-Spun Poly(ethylene terephthalate) Fibers and Their Tensile Properties

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ABSTRACT: The production of high modulus and high strength poly(ethylene terephthalate) fibers was examined by using commercially available melt-spun fibers with normal molecular weight (intrinsic viscosity = 0.6 dL/g). First, molecular weight of as-spun fibers was increased up to 2.20 dL/g by a solid-state polymerization, keeping the original shape of as-spun fibers. Second, the polymerized as-spun fibers were drawn by a conventional tensile drawing. The achieved tensile modulus and strength of as-drawn fibers (without heat setting) were 20.0 and

1.1 GPa, respectively. A heat setting was carried out for the as-drawn fibers. Tensile properties of the treated fibers were greatly affected by the condition of the heat setting. This was related to the increase of sample crystallinity and molecular degradation during the treatments. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1791–1797, 2007

Key words: fibers; drawing; solid-state polymerization; modulus; strength

INTRODUCTION

Poly(ethylene terephthalate) (PET) has received considerable attention in the manufacture of fibers and films. All of these applications make use of PET in the drawn state to enhance the tensile properties. Thus, there is an extensive literature on the drawing behavior of PET.

It has been reported for some semicrystalline polymers that a molecular weight has a remarkable effect on the tensile properties of the resultant drawn samples. The larger the molecular weight, the higher the tensile properties can be achieved.^{1–3} PET also follows this relation. That is, the tensile modulus and strength of drawn films at a given draw ratio (DR) increased with increasing molecular weight.² For PET, such molecular weight dependences were explained by the suppressions of disentanglement and relaxation of oriented molecular chains during deformation, which are important in the development of structural anisotropy and continuity along the draw direction.²

The melt viscosity of high molecular weight materials is usually extremely high, which restricts the melt process for the production of fibers and films. Several techniques have been examined to overcome this problem.^{4,5} For high molecular weight PET, a solution-spinning method has been reported.⁶ The

tensile modulus and strength of the resultant highly drawn fibers (DR ~16.4) from solution spinning of high molecular weight material (intrinsic viscosity, IV ~2.6 dL/g) reached 39.0 and 2.3 GPa, respectively.⁶ However, a serious problem for the process is a high production cost due to the utilization of expensive organic solvent.

An idea to reduce the cost is the utilization of commercially available melt-spun PET fibers with normal molecular weight as a starting material. It is expected that the molecular weight of as-spun fibers can be increased by a solid-state polymerization (SSP). If the SSP can be done keeping the fiber in the original shape, we can get as-spun fibers with high molecular weight, which can be drawn directly by a conventionally drawn technique.

In this study, we examined the SSP for the melt-spun PET fibers with normal molecular weight. Then, a preliminary test of tensile drawing was carried out for the polymerized fibers.

EXPERIMENTAL

Material and solid-state polymerization

Commercially available melt-spun poly(ethylene terephthalate) (PET) fibers (intrinsic viscosity, IV = 0.6 dL/g, diameter ~ 400 μm) were used as a starting material. The as-received fibers were dried at 100°C for 3 h under vacuum. Wide-angle X-ray diffraction patterns of the dry fibers confirmed that the as-received fibers were amorphous with no chain orientation.

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When the dry fibers were heated up directly to the solid-state polymerization (SSP) temperature of 240°C, the fibers became sticky, which made it difficult to keep the fibers in the original shape. To overcome the problem, the dry fibers were crystallized at 220°C for 2 h, followed by the SSP at 240°C for constant time in the range of 1–3 h under an Ar gas flow.

Drawing

The solid-state polymerized fibers (SSP-F) were drawn by a home-built tensile machine at a constant temperature in the range of 130–265°C under a constant tension in the range of 1.6–2.7 kg/mm². Details of the tensile machine were described elsewhere.⁷ The drawn fibers were heat-treated at a constant temperature in the range of 230–250°C under a constant load in the range of 25–50 kg/mm². After the heat treatment, all samples were cooled to room temperature under a constant load.

The draw ratio (DR) was determined by measuring the separation between lateral ink marks on the sample before and after drawing.

Measurements

The tensile modulus and strength of drawn fibers along the fiber axis were measured at room temperature and at a strain rate of $1 \times 10^{-3} \text{ s}^{-1}$ and $1 \times 10^{-2} \text{ s}^{-1}$, respectively. The modulus was determined from the initial slope of stress–strain curve at a low strain (<0.1%). Sample density was determined at 30°C by a density gradient column prepared from *n*-heptane and carbon tetrachloride. Weight percent crystallinity was calculated from the observed density on the basis of a two-phase model. The amorphous and crystalline densities for PET were taken to be 1.335 and 1.455 g/cm³, respectively.⁸ The IV of the sample was measured in a mixed solvent of trifluoro acetic acid and dichloromethane (50/50, v/v).

RESULTS AND DISCUSSION

Solid-state polymerization

Extensive works have been devoted to increase the molecular weight of PET by the utilization of chain extender⁹ and by the improvement of SSP.^{10,11} Cohn reports that the utilization of porous and fibrous aggregates is a key point to increase the efficiency of SSP since such structures are suitable to remove the by-products produced during the SSP. He obtained PET with an extremely high molecular weight of IV = 5.49 dL/g by this method.¹¹ We also examined the preparation of high molecular weight PET by the SSP from commercially available PET.¹² According

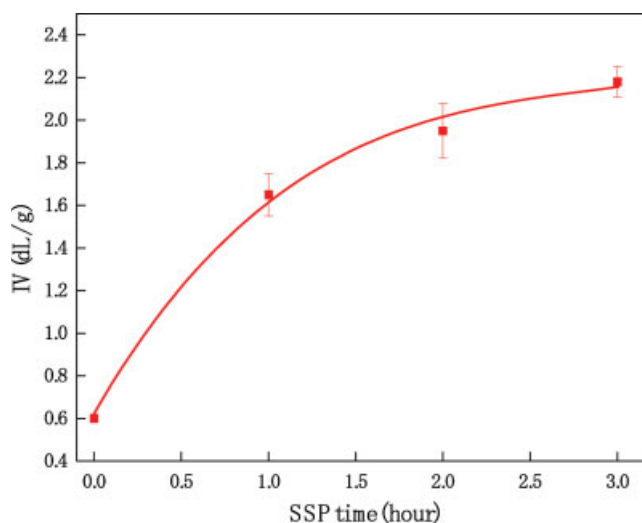


Figure 1 Relation between intrinsic viscosity and SSP time at 240°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

to Cohn's idea, as-received chips were converted into porous and fibrous aggregates. The SSP was carried out under a reduced pressure. The molecular weight achieved was affected by the competition between efficiency of SSP and degradation of PET molecules during the process. In general, efficiency of SSP depends on the by-product removal at a given temperature. The polymerization time is a dependent parameter and depends on many factors like temperature, particle size, and gas flow. In fact, the efficiency was greatly affected by the SSP temperature and time. At a given time, the efficiency increased with increasing the SSP temperature up to 240°C, and then the efficiency began to decrease with further increase of temperature. At a given SSP temperature, the IV increased with increasing the SSP time, followed by saturation around 10 h. In this work, thus, the SSP temperature was set to be 240°C.

Figure 1 shows the relation between SSP time and IV achieved at 240°C. Up to 2 h, the IV steadily increased with time followed by a gradual increase with further increase of SSP time. As stated in the Experimental section, the SSP was carried out under an Ar gas flow. The polymerization efficiency was dependent on the flow rate of Ar gas. Fast gas flow, in general, gives better SSP rates as the vapor pressure of the by-products will be high and diffuse out the material quickly. However, too high gas flow induced cool down the samples leading to the decrease in the efficiency of SSP. In this study, volume of polymerization chamber was around 0.3 L. In that case, a slow flow rate of 2 L/min was enough to get high efficiency of polymerization. After 1 h of SSP, the increase of IV with time was small when compared with the previous results.¹²

The fibers used for the SSP was as-spun fibers produced by the melt spinning. Thus, the surface of the fibers was quite smooth when compared with the previous one. The rate of SSP depends on the by-product removal. By-product removal depends on the effective surface area. Rough surface will have more surface area to facilitate faster removal of the by-products than a smooth surface. The achieved IV obtained at 240°C for 3 h of SSP was 2.20 dL/g. However, this value is more than twice for commercially available PET.

The diameter of the fibers used for the SSP was as large as 400 μm . Thus, we measured IVs of surface and central part of fiber independently to check the gradient of molecular weight between them. However, the difference of IV between them was negligibly less of about 2%. In this work, we did not determine the molecular weight dispersion of the SSP-F. Our previous work revealed that the molecular weight dispersion (M_w/M_n) of solid-state polymerized PET chips was around 2.3.¹² In this work, similar value was expected since the conditions for the SSP were similar to the previous one.

Drawing behavior

Extensive investigations have been performed on the drawing of PET for obtaining high performance fibers and films. However, most of them were the deformation studies of amorphous PET around its T_g followed by the heat setting at high temperatures. In this study, the SSP-F, which had a high crystallinity (60 wt %), were utilized for the drawing. Thus, the deformation behaviors of SSP-F were quite different from those of amorphous PET. The lowest temperature possible to draw was around 130°C. Below the temperature, we could not get drawn fibers with macroscopically homogeneous deformation ratio. The strain rate possible to draw increased with increasing draw temperature (T_d) and initial stress on draw (σ_d), which was calculated by using a cross-sectional area of SSP-F. For example, at a given σ_d of 2.4 kg/mm², the rate increased from 14 to 18/min with increasing the T_d from 190 to 250°C. At a given T_d of 190°C, the rate also increased from 6 to 14/min with increasing the σ_d from 1.6 to 2.4 kg/mm².

We report the effects of initial morphology on the deformation behavior and the structure of the resultant drawn films.^{13,14} For the drawn samples from initially amorphous state, the crystallinity increases with increasing the DR due to the strain-induced crystallization. However, the crystallinity from initially highly crystalline material decreases with DR. During the drawing, the crystals existed in the pre-drawn material are destroyed, and simultaneously strain-induced crystallization happens but the degree of crystallization is not high enough to reach the

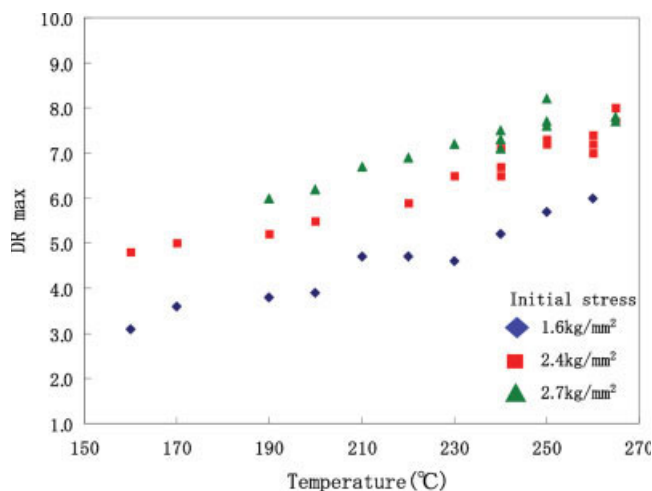


Figure 2 Relation between DR_{\max} and draw temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

original crystallinity. In this work, a similar decrease in the crystallinity by the drawing was observed. The initial crystallinity of 60% decreased to $\sim 50\%$ after the drawing.

In Figure 2, the achieved draw ratio (DR_{\max}) for the SSP-F with the IV of 2.20 dL/g is plotted as a function of T_d at different σ_d . At a given σ_d , the DR_{\max} increased steadily with the increase in T_d . It should be noted that the SSP-F could be drawn even around the melting temperature ($\sim 260^\circ\text{C}$) of PET crystals. The melt viscosity of SSP-F was extremely high due to high IV of 2.20 dL/g, which might make it possible to draw around the melting temperature of PET crystals.

As seen, the highest DR_{\max} was around 8.0 at T_d of 250°C and σ_d of 2.7 kg/mm². The minimum draw ratio (DR_{\min}) necessary for full chain extension is dependent on the chain length between the entanglements of macromolecules.

In this work, melt-spun amorphous fibers were utilized for the SSP. If the entanglement densities of the fiber were not affected by the SSP, the molecular weight between neighboring entanglements in SSP-F corresponds to that of PET melt, which is assumed to be about 3500. In that case, the DR_{\min} is estimated to be 3.4.² This value is quite low when compared with the experimental result of 8.0. The results suggest that the disentanglements and/or chain slippage might happen during the drawing at high temperature. This means that, we must consider the efficiency of draw, which can be evaluated from the tensile properties of drawn samples.

Mechanical properties of drawn fibers

Tensile modulus and strength of drawn samples were affected by several factors including DR, draw

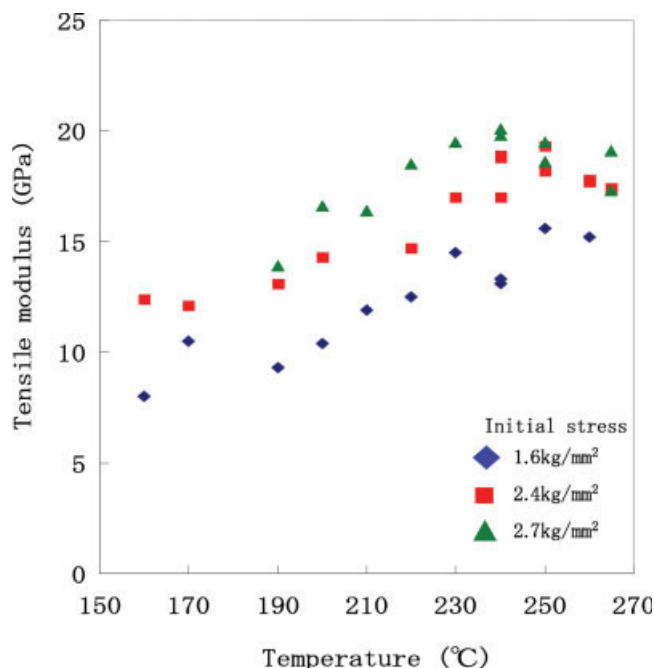


Figure 3 Relation between tensile modulus and draw temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

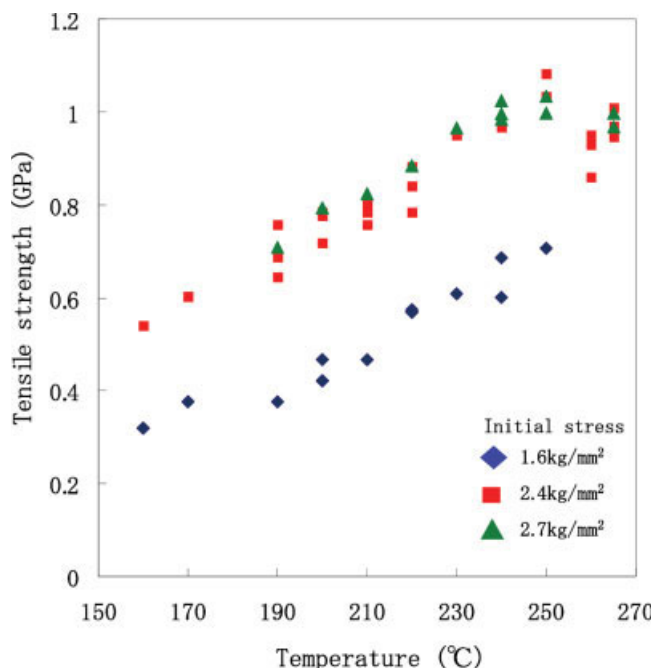


Figure 4 Relation between tensile strength and draw temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

temperature, and tension applied to the sample during drawing and cooling from draw temperature to room temperature.

Figure 3 shows tensile modulus of drawn fibers with DR_{max} as a function of draw temperature obtained at different σ_d . Up to T_d of 240°C, the modulus increased gradually with the increasing T_d followed by a saturation with a further increase of T_d . At a given T_d , the modulus increased with the increasing σ_d .

In Figure 4, the tensile strength of drawn fibers with DR_{max} are plotted as a function of T_d at different σ_d . The strength increased gradually with the increasing T_d and σ_d , similar to the case of modulus versus T_d and σ_d . For both Figures 3 and 4, modulus and strength value were for drawn samples with different DR_{max} , which was dependent on the T_d and σ_d (Fig. 2). Thus, the modulus and strength value are plotted as a function of DR, which corresponds to DR_{max} of the sample in Figures 5 and 6. It is clearly seen that both tensile modulus and strength increased with the DR independent of T_d and σ_d . The achieved tensile modulus and strength of the resultant drawn fibers appeared around DR 8 were 20.0 and 1.1 GPa, respectively. It should be noted that both tensile modulus and strength simply depend on the DR independent of T_d and σ_d . The results suggest that all drawn samples have similar efficiency of draw. For drawn films and fibers from amorphous PET, the tensile properties were much

affected by draw temperature.¹⁵ At a given DR, the higher the draw temperature, the lower the tensile properties of drawn samples that were observed. The results were explained by the disentanglement and/or chain slippage during tensile drawing. Such

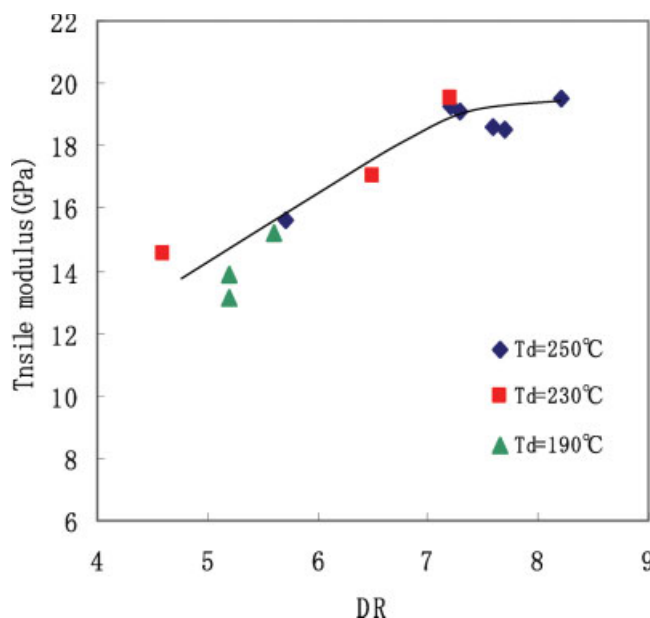


Figure 5 Relation between tensile modulus and draw ratio. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

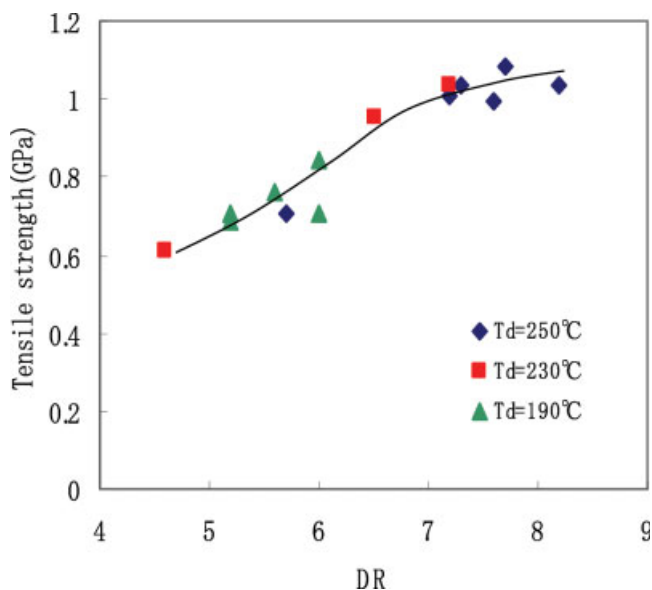


Figure 6 Relation between tensile strength and draw ratio. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

effects were greatly suppressed by the utilization of high molecular weight materials and an introduction of crystalline phase in the predrawn samples. The SSP-F utilized for the drawing had high crystallinity and high molecular weight, leading to an effective chain extension and orientation even at a high draw temperature.

As stated, the minimum DR necessary for the full extension of macromolecules between the chain entanglements existed in the amorphous PET was estimated to be 3.4.² As seen in Figures 5 and 6, the tensile properties continued to increase even above DR of 5. The results suggest that the drawing might be accompanied by the chain slippage. However, the slippage proceeds under a high friction, which might minimize the drop in the efficiency of draw.

It is well-known that a heat setting is an effective process to increase the tensile properties of drawn PET. By the heat setting, we can expect an increase of sample crystallinity induced by the crystallization of highly oriented noncrystalline molecules. Thus, the annealing was carried out for the drawn fibers. Figure 7 shows the tensile modulus and strength of heat-treated drawn fibers as a function of annealing time at 230°C. The drawn fibers used for the annealing were obtained at 190°C, which had tensile modulus and strength values of 14.6 and 0.8 GPa. After the short time of annealing (5 min), both tensile modulus and strength increased remarkably. Then, the modulus increased gradually with the further increase in annealing time. After 30 min of annealing, the modulus reached 23.0 GPa. On the other hand, the strength dropped from 1.0 GPa attained

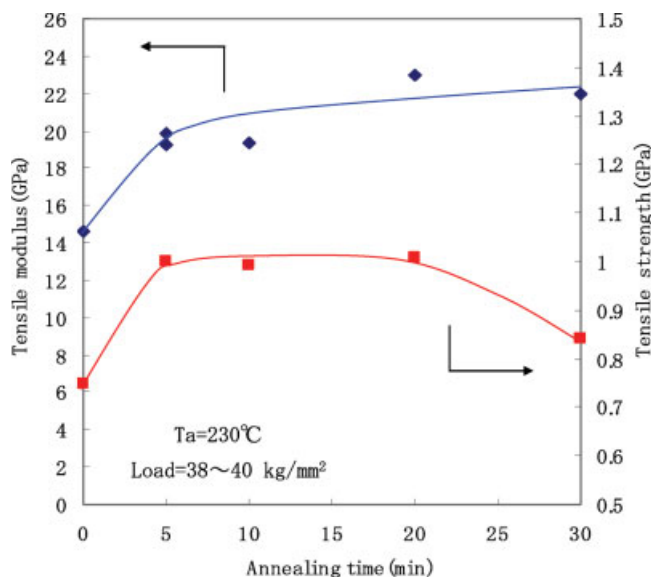


Figure 7 Relation between tensile properties and annealing time under a load of 38–40 kg/mm². [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

by the 5 min of annealing to 0.8 GPa at a prolonged annealing time of 30 min.

In Figure 8, sample crystallinity and birefringence of the heat-treated fibers are plotted as a function of heat-treatment time. The data were for the same samples as for Figure 7. At an initial stage of heat setting, both crystallinity and birefringence increased respectively, from 50 to 60% and 0.15 to 0.20 followed by saturation with further increase of annealing time. These structural changes by the heat treatments could be well correlated to the tensile modulus-treatment time relation shown in Figure 7. That

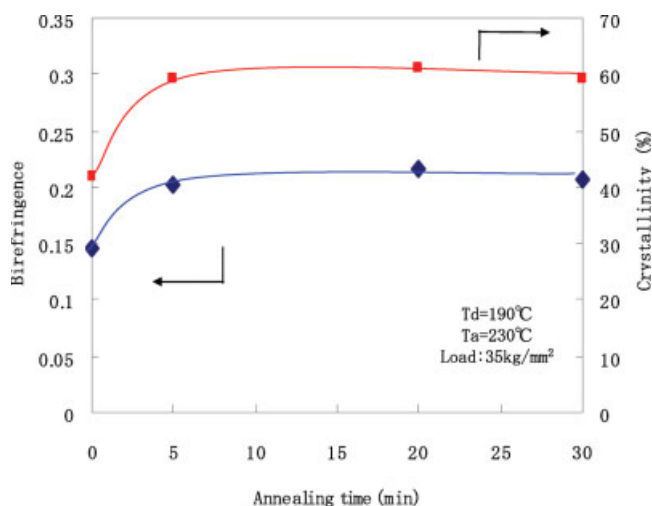


Figure 8 Crystallinity and birefringence as a function of annealing time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

is, oriented noncrystalline polymer chains were transformed into crystalline bridges, which induced the increase of sample crystallinity and birefringence, leading to the increase of tensile modulus.

Figure 9 shows the relation between IV and heat-treatment time for the same samples as of Figure 7. Within a short time of annealing, the IV dropped abruptly from 2.20 to 1.95 dL/g followed by a gradual decrease of IV with the further increase of treatment time. Around 30 min, the IV drop was remarkable. Long-heat treatment enhanced the molecular degradation, which might induce the decrease in the tensile strength.

Both tensile modulus and strength increased gradually with increasing the load applied to the drawn fibers during the heat treatment. However, the maximum load applied to the sample decreased with increasing the treatment time. Figure 10 shows the relation between tensile properties and load applied to the samples during annealing at 230°C for 5 min. The samples used were drawn at 190°C up to DR_{max} . The heat treatment at 230°C under a load of 45 kg/mm² for 5 min produced the fibers with tensile modulus of 22.0 GPa and strength of 1.1 GPa. Under a higher load of heat treatment, the relaxations of oriented polymer chains are severely restricted, which might induce the increase in the content of crystalline bridges.

We report that the tensile strength of drawn PET fibers were affected by molecular weight and fiber diameter.¹⁶ At a given molecular weight, and at a given DR, the smaller the diameter, the higher the tensile strength could be achieved. In this work, we used as-spun fibers with a large diameter of 400 μm,

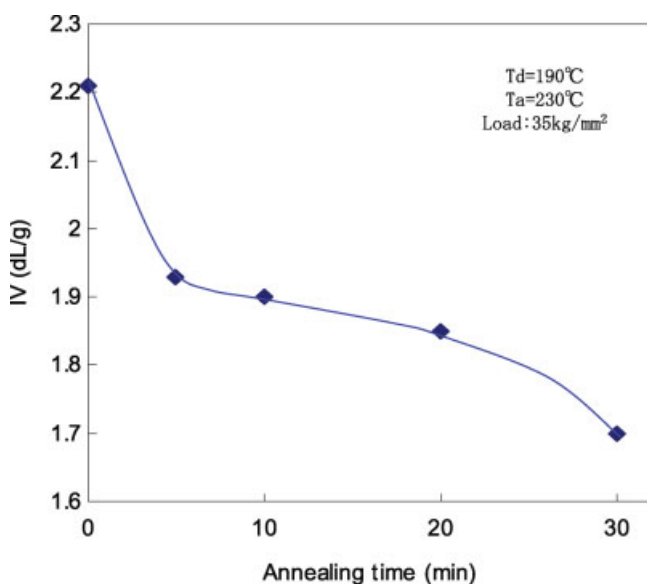


Figure 9 Relation between intrinsic viscosity and annealing time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

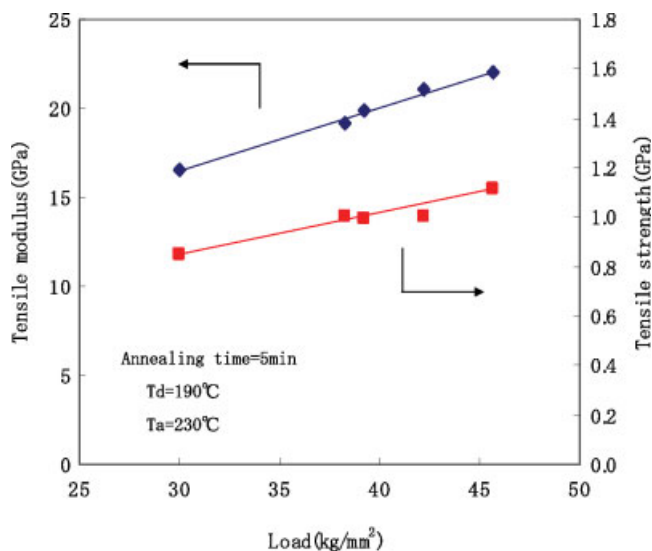


Figure 10 Relation between tensile properties and load applied to the sample during annealing. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

which was about four times bigger than the previous one,⁶ which showed the strength value of 2.3 GPa. Thus, we can expect a further increase of tensile strength by using a narrow fiber. These are currently studied.

CONCLUSIONS

The production of high modulus and high strength fibers was examined by using melt-spun PET fibers with a normal molecular weight ($IV = 0.6$ dL/g). The molecular weight of the fibers could be increased up to IV of 2.20 dL/g by a SSP without changing the fiber geometry. The fibers obtained by the SSP could be drawn above 130°C. The achieved tensile modulus and strength of the drawn fibers were 20.0 and 1.1 GPa, respectively. A heat treatment was carried out for the drawn fibers to increase the tensile properties. Drawn fibers at 190°C were heat-treated at 230°C under a constant load. Under an appropriate treatment condition, the tensile modulus and strength achieved were 23.0 and 1.1 GPa, respectively. The increase of tensile modulus by the heat treatment could be explained by the increased crystallinity. On the other hand, the improvement of tensile strength was minor due to the molecular degradation during the treatment.

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