Structure–Property Relationship in Fibers Spun from Poly(ethylene terephthalate) and Liquid Crystalline Polymer Blends. II. Effect of Spinning Temperature on Fiber Properties

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SYNOPSIS

A series of fibers based on neat poly(ethylene terephthalate) (PET) and PET/10% liquid crystalline polymer (LCP) blends were spun at various temperatures, ranging from 250 to 310°C, and the effect of spinning temperature on properties was studied. Improved tensile strengths and higher moduli of hot-drawn fibers were obtained with fibers spun at and above 300°C, which was explained by increased transesterification and the randomized structure of the PET/LCP blends. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In our previous article,[1] we discussed the effect of concentration of the dispersed phase and processing parameters, such as drawing temperature, on properties. Spinning temperature was kept constant. It is reasonable to suggest that the spinning temperature could have an important effect on fiber properties, especially those based on blends. In this article, we analyze the effect of spinning temperature on properties. We studied spinning in two temperature ranges: above melting points of both components, i.e., above 280°C, and below the melting point of poly(ethylene terephthalate) (PET) ($T_m \sim 175$°C). At the high end of processing temperatures, i.e., at 300°C and above, a higher degree of transesterification is possible. This produces a more random liquid crystalline polymer (LCP) structure and enhances the matrix–LCP miscibility. In the previous study,[1] we kept spinning temperature moderately high (at 290°C) to avoid breakup of rigid LCP blocks. In this work, we also wanted to examine the effect of increased transesterification on properties. By increasing processing temperature, the viscosity of the melt is reduced and heat-transfer properties during solidification are somewhat altered. The highest temperature that we could reach without visible degradation (gas formation) was 315°C. The first and second temperature zones of the extruder are set to below the melting point of PET. The melting takes place at the third zone, while the die (fourth) zone dictates temperature of the melt leaving the extruder. We first kept the temperatures of the three zones constant and varied the temperature of the die. Since the temperature of a particular zone is measured at the wall of that extruder section, the displayed value is not necessarily the true temperature of the melt in that zone. When the effect of temperature of the die was correlated with the properties of the fibers, the correlation was not very good, partly because the temperature of the melt in the die was affected by the temperature of the third zone. This was particularly true when the temperature difference between the third zone and the die was substantial. Thus, we simultaneously varied temperatures of the third zone and the die. The results that follow, therefore, reflect the effect of combined zone 3 and die zone temperature on fiber properties.

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EXPERIMENTAL

Materials

Fiber-grade PET was used as the matrix polymer. Main-chain LCP, designated as TR-4-*co*-PBT(2, 4, 7), was used as a reinforcing agent. The structure and properties of the LCP were described earlier.[2]

Methods

The experimental conditions for the preparation and testing of the fibers were described previously.[1,3] PET was ground to a powder and tumble-mixed with the LCP powder. The mixture was then compression-molded into a plate, which was subsequently crushed, ground, and sieved to obtain a particle size less than 1 mm. The zone 1 and zone 2 extruder temperatures were 220 and 240°C, respectively, while the zone 3 and die temperature were varied according to Table I.

The extruded fibers were wound on the spool at a take-up speed of 75 or 225 m/min. As-spun fibers were cold- and hot-drawn approximately six to seven times their original length to increase crystallinity and orientation and to improve properties. Two sets of results are presented: one on as-spun and the other on hot-drawn fibers.

RESULTS AND DISCUSSION

We were unable to find references explaining the effect of extruder temperatures on properties of fibers based on PET/LCP blends. It is known that PET undergoes transesterification in the melt, provided that the residence time in the extruder is sufficient. Since our LCP is also polyester, prolonged exposure to high temperature may lead to altering of molecular weight distribution, in addition to the formation of the PET–LCP copolymers. The residence time in our case was about 3–4 min, and some transesterification could not be avoided, especially at temperatures above 300°C. Miley and Runt studied transesterification in polybutylene terephthalate/polyarylate blends[4] at temperatures between 260 and 320°C. Transesterification was confirmed by a reduced degree of crystallinity, melting point depression, and structural changes, as observed by NMR. We will first discuss properties of as-spun fibers extruded at different temperatures and, then, properties of the hot-drawn fibers spun at the same temperatures. Comparisons will be made between properties of fibers prepared at two take-up speeds, as well as those of neat PET fibers and fibers containing 10% LCP.

Table I Combinations of Temperature Used in This Work

Die Temperature	Zone 3
250	260
260	260
260	270
270	270
270	280
280	280
280	290
290	290
300	300
310	300

Figure 1 illustrates the dependence of the modulus of as-spun PET fibers on spinning temperature, prepared at a lower take-up speed of 75 m/min. As expected, at low spinning temperatures, the modulus is higher due to the increased orientation. The lower value of the modulus of the fiber spun at 250/260°C is obtained on the sample which was made under critical conditions, which were reflected in a uneven fiber diameter. It is not clear why the increased modulus is obtained at high spinning temperatures. A similar trend was observed with fibers spun at a 225 m/min take-up speed, as shown in Figure 2.

Figures 3 and 4 show the effect of spinning temperature on the modulus of as-spun PET/10% LCP fibers spun at two take-up speeds. Both diagrams show a decrease in modulus with increasing extrusion temperature. Variations above 280°C were small, reflecting a lower orientation at higher temperature, a fact attributed to the altered kinetics of cooling.

The modulus of hot-drawn PET fibers was found to increase with increasing spinning temperature, as they allowed a higher draw ratio. Whereas fibers spun at 75 m/min take-up speed display fairly regular behavior, as shown in Figure 5, much greater variations were observed with thinner fibers prepared at 225 m/min take-up speed, as observed in Figure 6. These results are used as a standard for comparison with fibers based on PET/10% LCP blends, shown in Figures 7 and 8. Figure 7 reveals the same trend of modulus change with temperature as with PET fibers, but also a very high moduli of fibers spun at high temperatures. Most of the moduli of PET fibers spun under optimal conditions are

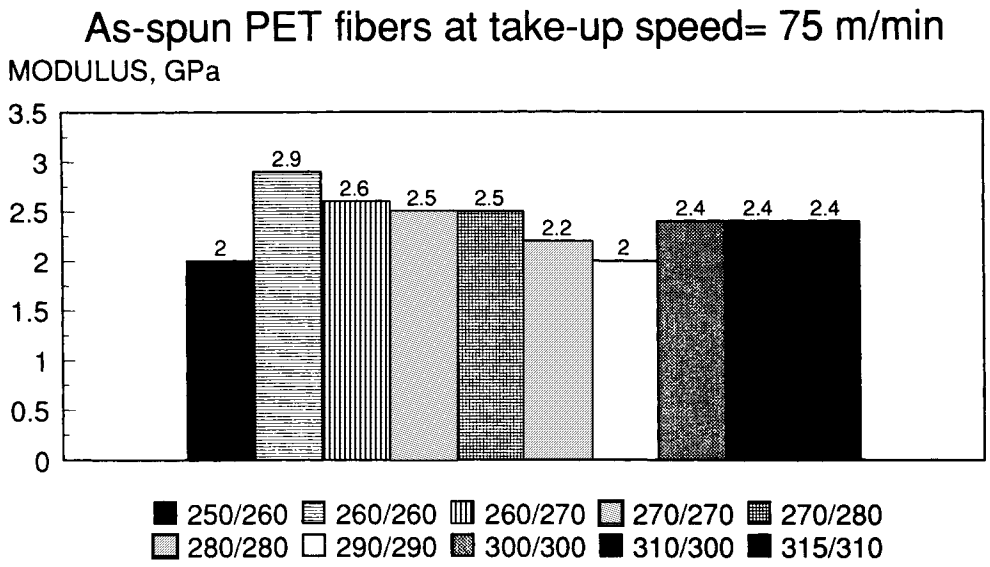

Figure 1 Dependence of modulus of as-spun fibers at take-up speed of 75 m/min on spinning temperature. First figure indicates die zone temperature, and the second, zone 3 temperature.

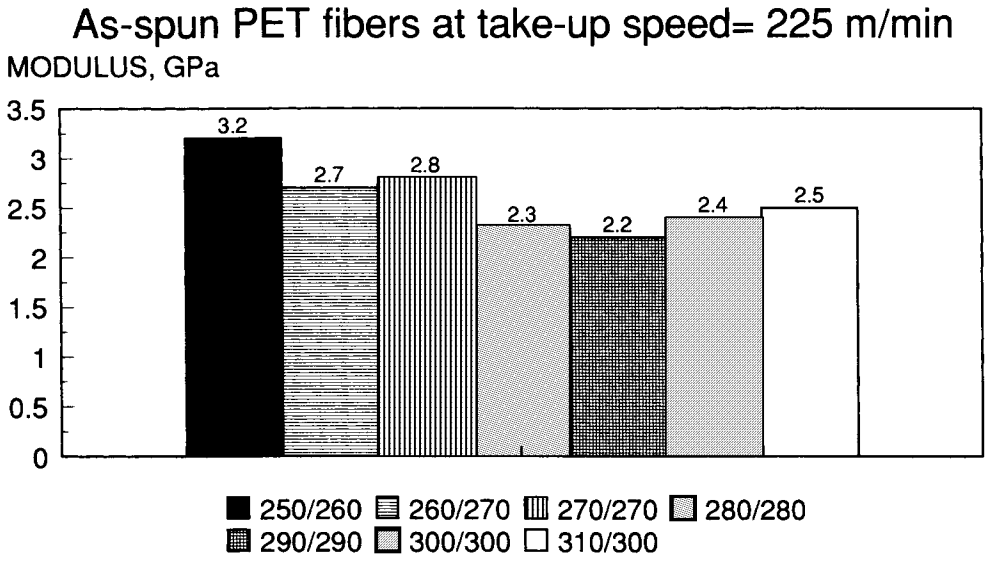

Figure 2 Dependence of modulus of as-spun fibers at take-up speed of 225 m/min on spinning (die/zone 3) temperature.

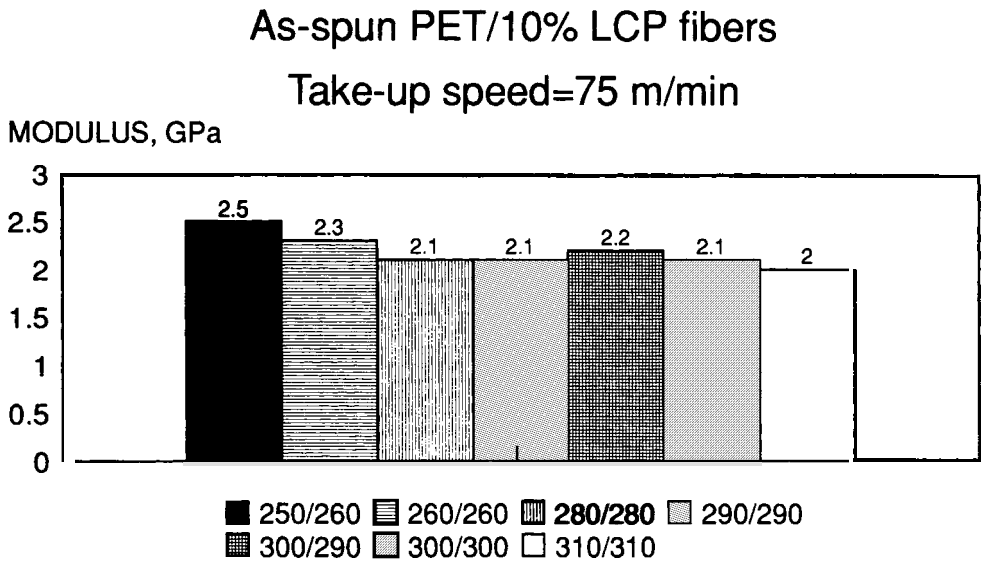

Figure 3 Dependence of modulus of as-spun fibers at the take-up speed of 75 m/min on spinning temperature.

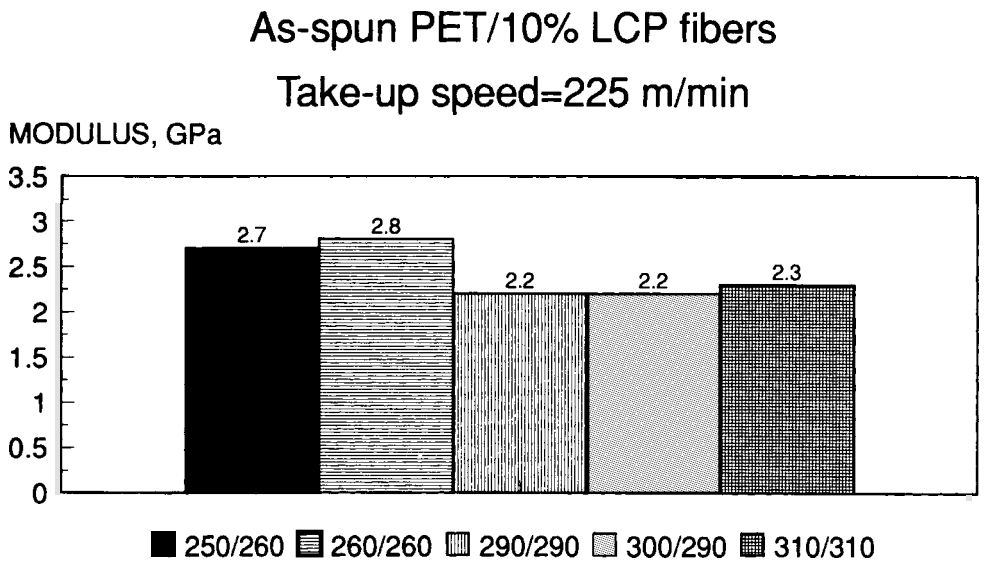

Figure 4 Dependence of modulus of as-spun fibers at the take-up speed of 225 m/min on spinning temperature.

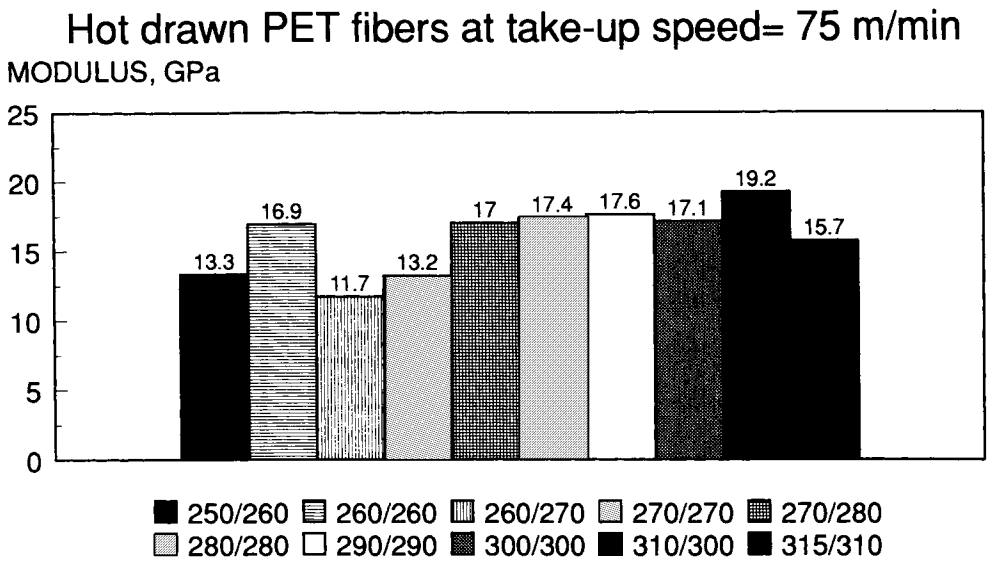

Figure 5 Dependence of modulus of hot-drawn PET fibers prepared at take-up speed of 75 m/min, on spinning temperature.

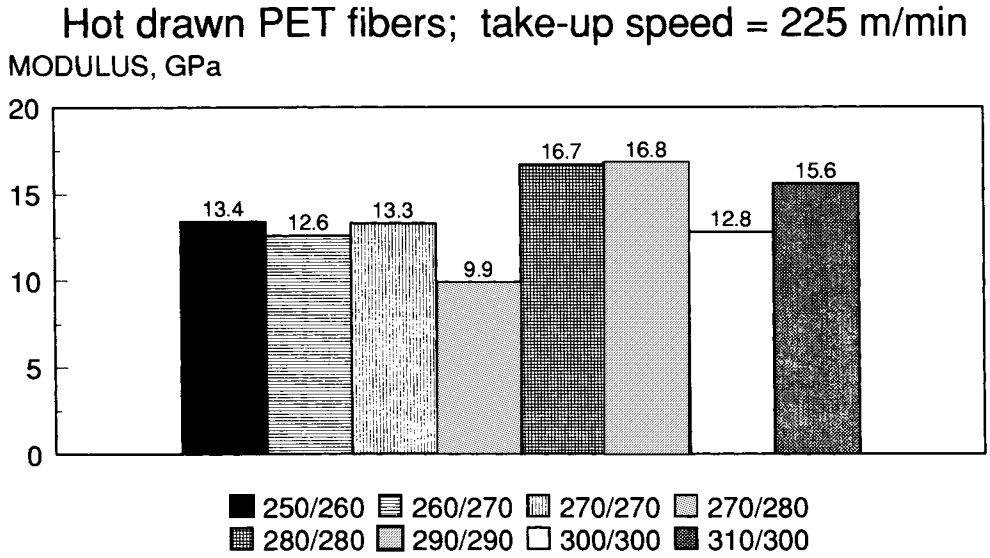

Figure 6 Dependence of modulus of hot-drawn PET fibers prepared at take-up speed of 225 m/min, on spinning temperature.

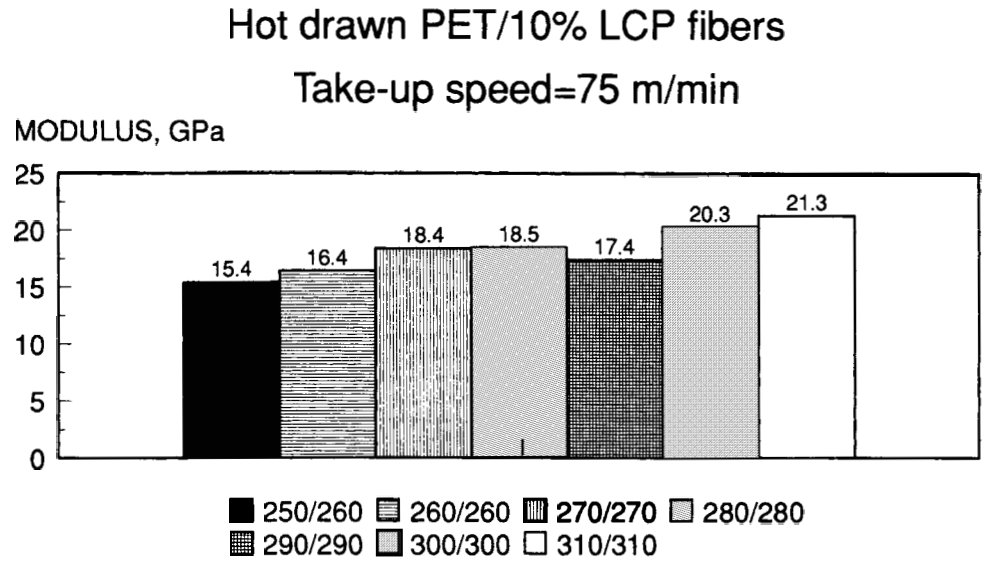

Figure 7 Dependence of modulus of hot-drawn PET/10% LCP fibers prepared at take-up speed of 75 m/min, on spinning temperature.

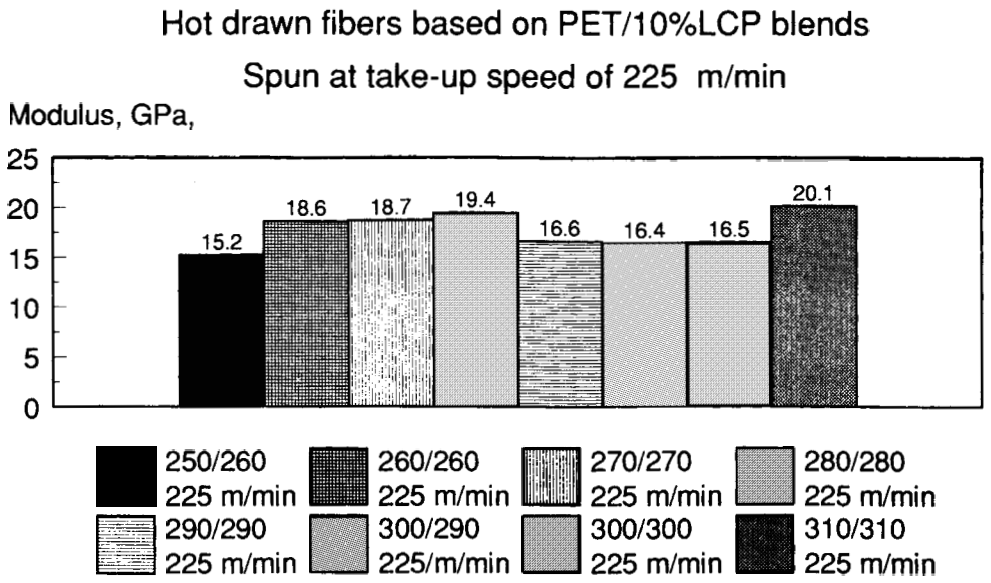

Figure 8 Dependence of modulus of hot-drawn PET/10% LCP fibers, prepared at take-up speed of 225 m/min, on spinning temperature.

between 17 and 18 GPa, while here we have 20 and 21 GPa, unattainable with neat PET. Unlike pure PET fibers, fibers containing 10% LCP, spun at 225 m/min, show high moduli even at low spinning temperatures. This suggests that the addition of LCP improves processability at these temperatures. The increase in modulus at high spinning temperatures could be explained by the randomization effect of the LCP structure due to transesterification. It has been suggested that in some cases more random LCP structure may have a more favorable effect on blend properties than does the blocky structure of LCP.[5]

The dependence of engineering tensile strength on spinning temperature of as-spun PET fibers, prepared at take-up speeds of 75 and 225 m/min, is displayed in Figures 9 and 10. The fibers prepared at 75 m/min show an expected increase in strength with decreasing temperature, paralleling the change in modulus, due to probable increased orientation at low temperatures. Spinning at 225 m/min did not follow such a trend.

In the case of as-spun PET/10% LCP fibers, a slight decrease in tensile strength with increasing spinning temperature was observed. Figures 11 and 12 illustrate the change in engineering tensile strength of as-spun fibers containing 10% LCP. Mechanical properties of these fibers are fairly regular but not so strongly dependent on spinning temperature.

More dependent on spinning temperature is the change of the tensile strength of hot-drawn fibers. As expected, increased spinning temperature allows better drawing and thus higher strengths, as seen from Figures 13 and 14. High strengths are obtained with spinning temperatures above 280°C. The change of tensile strengths of hot-drawn PET/10% LCP fibers with temperature is shown in Figures 15 and 16. Again, the same effect of spinning temperature on properties is observed, although not as strong. It appears that the addition of LCP allows better drawing at low spinning temperatures which leads to relatively high strengths. Tensile strengths of PET/LCP fibers are generally lower than those of corresponding pure PET fibers. Maximum values obtained with 10% LCP in the blend were on the order of 1050 MPa as compared with 1200 MPa for neat PET.

Figure 17 illustrates a steady increase of elongation at break of as-spun PET fibers at 75 m/min, with increasing spinning temperature. The same trend, but much less pronounced, was observed with as-spun PET fibers at 225 m/min, as shown in Figure 18.

As Figures 19 and 20 show, the trend of change of elongation at break with PET/10% LCP fibers was not so clear. In the case of the fiber spun at 225 m/min at 300/290°C, a fragile sample was formed upon standing, so that only small elongations were measurable. The same fiber was cold- and hot-drawn immediately after spinning to a high draw ratio. It

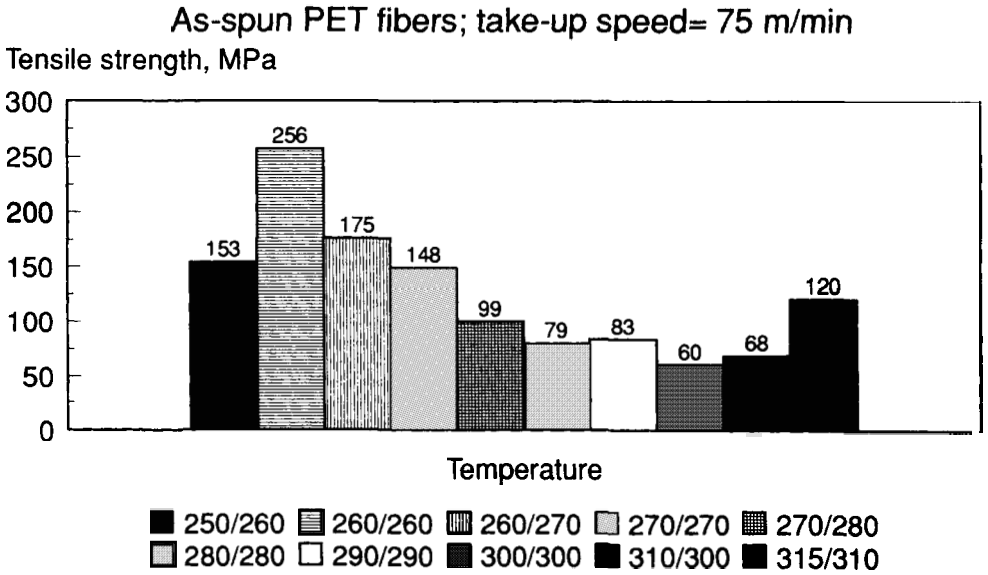

Figure 9 Dependence of tensile strength of PET fibers, spun at 75 m/min, on spinning temperature.

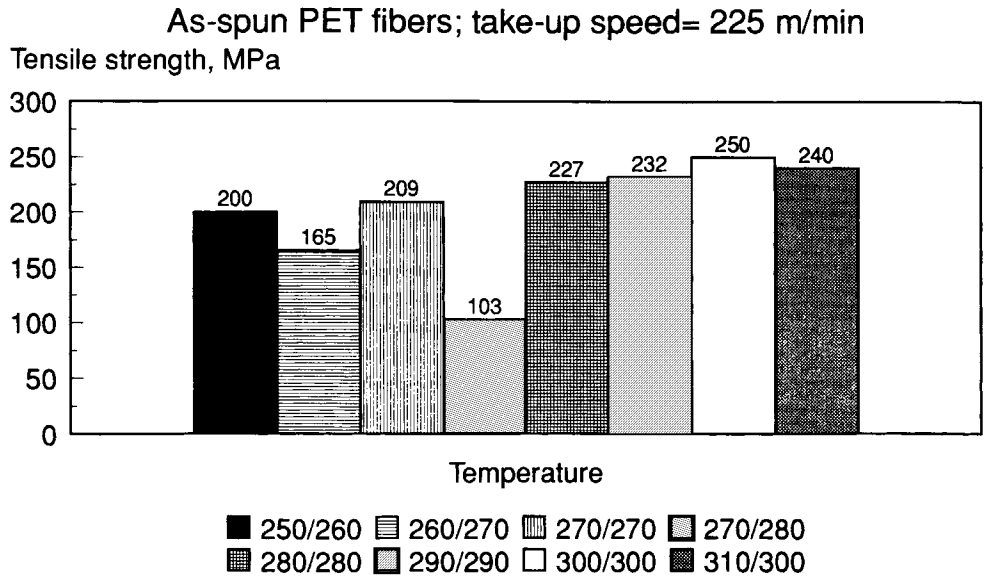

Figure 10 Dependence of tensile strength of PET fibers, spun at 225 m/min, on spinning temperature.

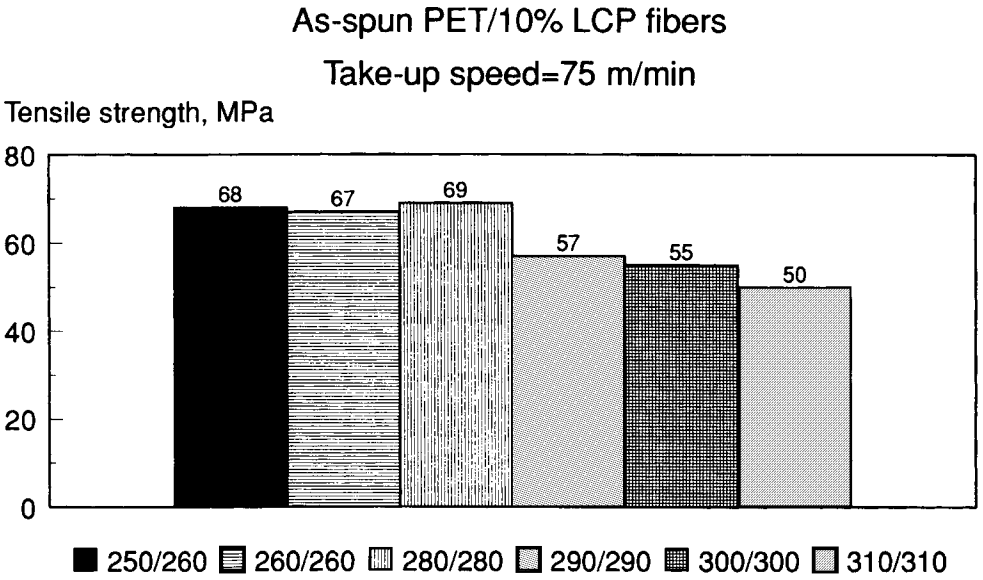

Figure 11 Effect of spinning temperature on tensile strength of as-spun PET/10% LCP fibers, spun at 75 m/min.

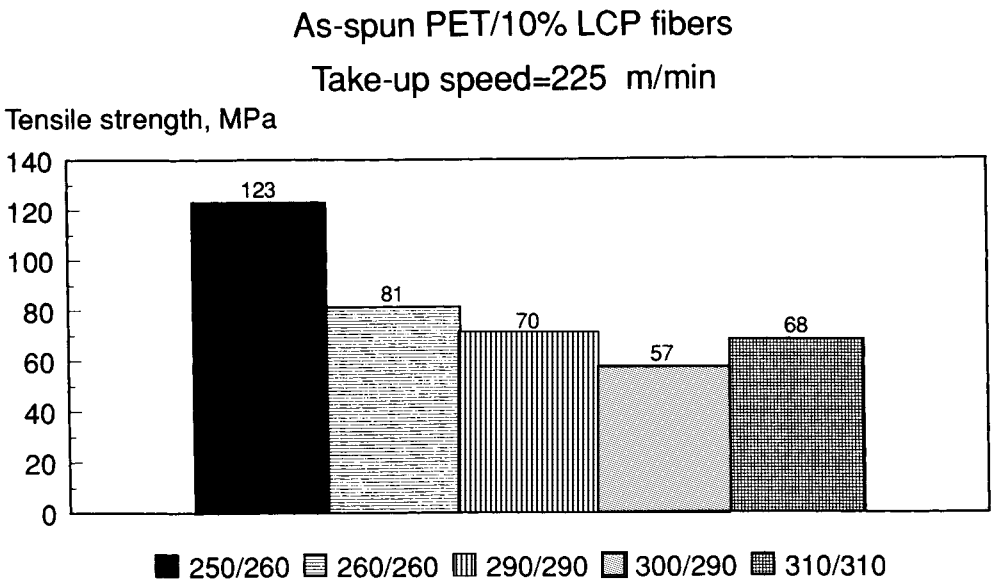

Figure 12 Effect of spinning temperature on tensile strength of as-spun PET/10% LCP fibers, spun at 225 m/min.

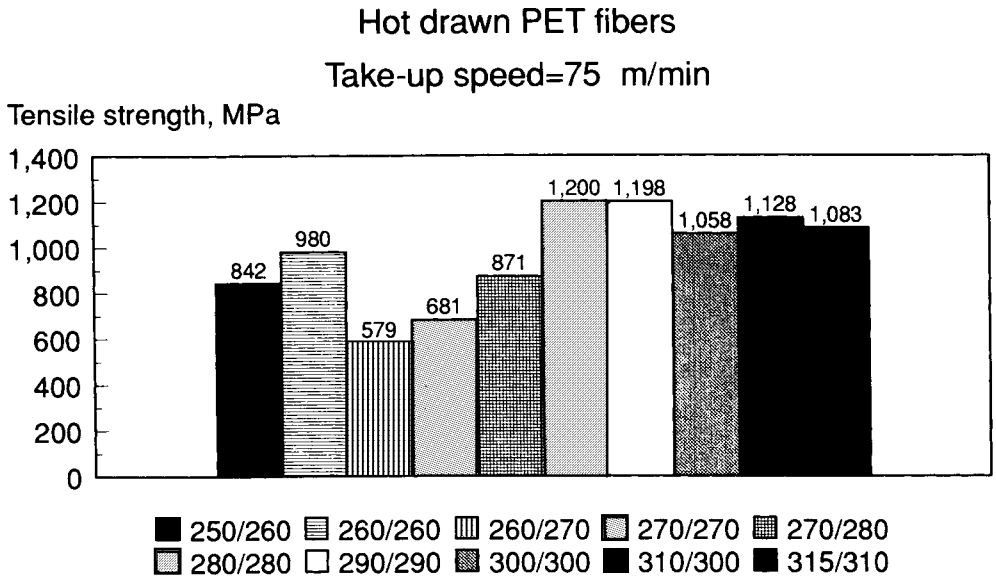

Figure 13 Effect of spinning temperature on tensile strength of hot-drawn PET fibers, spun at 75 m/min.

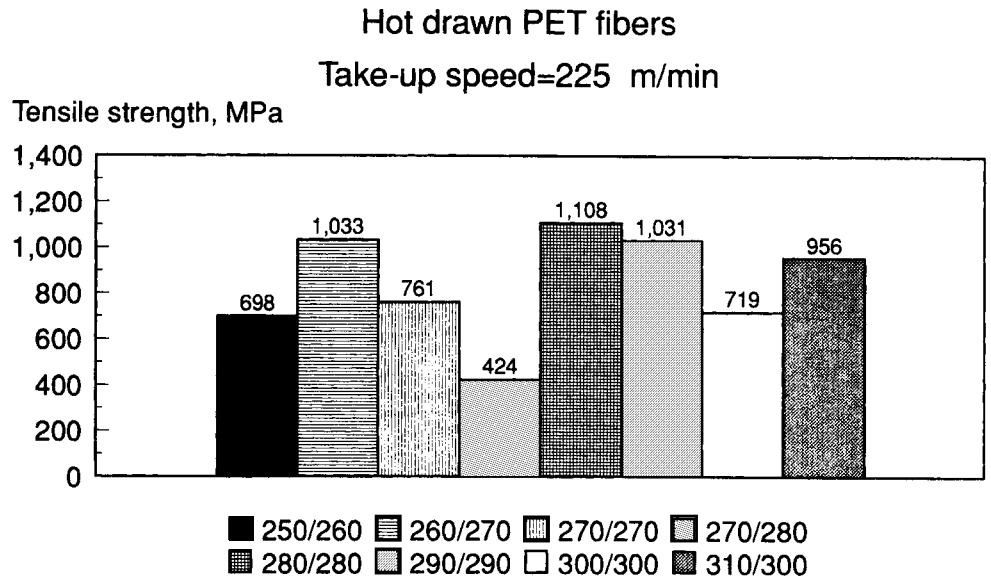

Figure 14 Effect of spinning temperature on tensile strength of hot-drawn PET fibers, spun at 225 m/min.

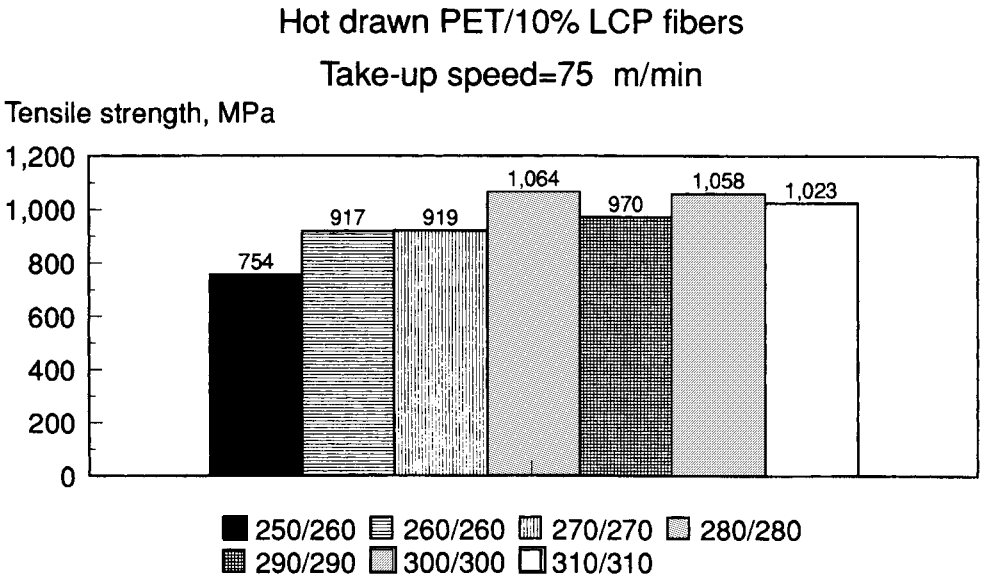

Figure 15 Effect of spinning temperature on tensile strength of hot-drawn PET/10% LCP fibers, spun at 75 m/min.

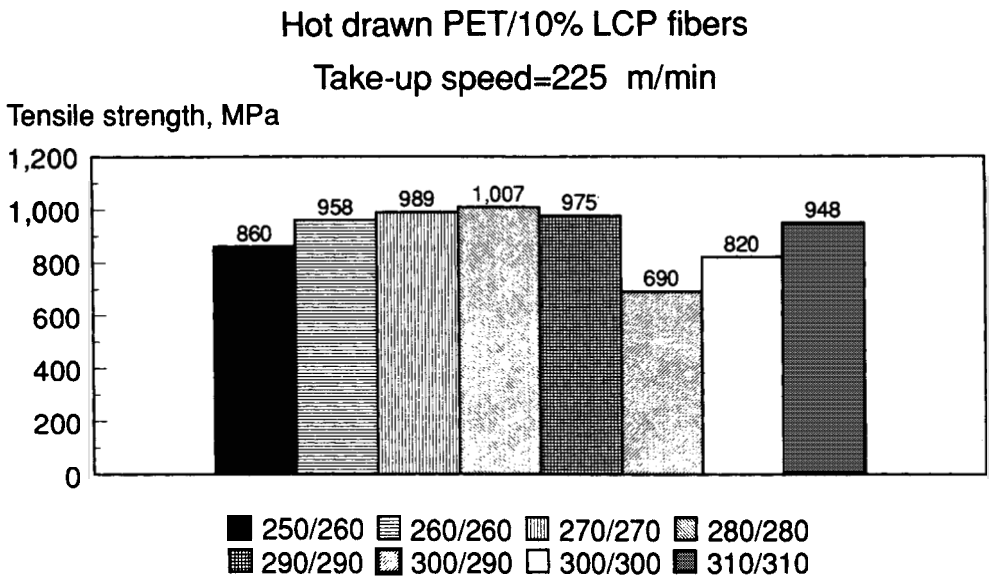

Figure 16 **Effect of spinning** temperature on tensile strength of hot-drawn PET/10% LCP fibers, spun at 225 m/min.

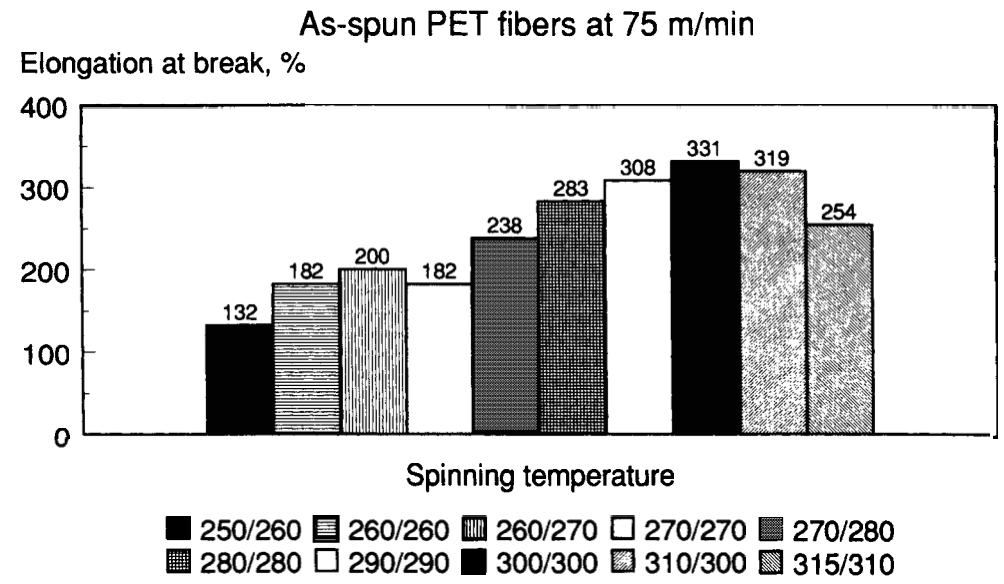

Figure 17 **Effect** of spinning temperature on elongation at break of as-spun PET fibers, spun at 75 m/min.

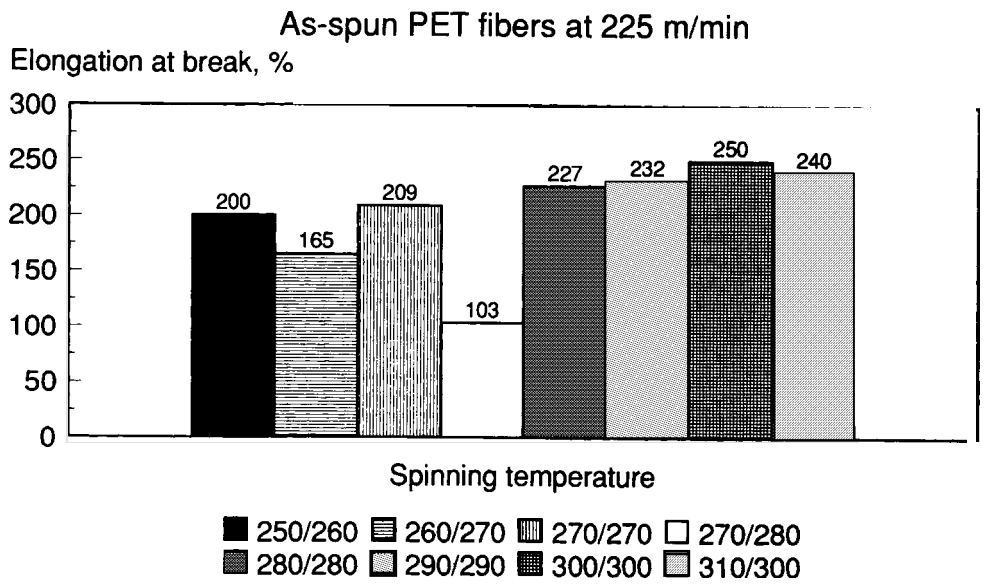

Figure 18 Effect of spinning temperature on elongation at break of as-spun PET fibers, spun at 225 m/min.

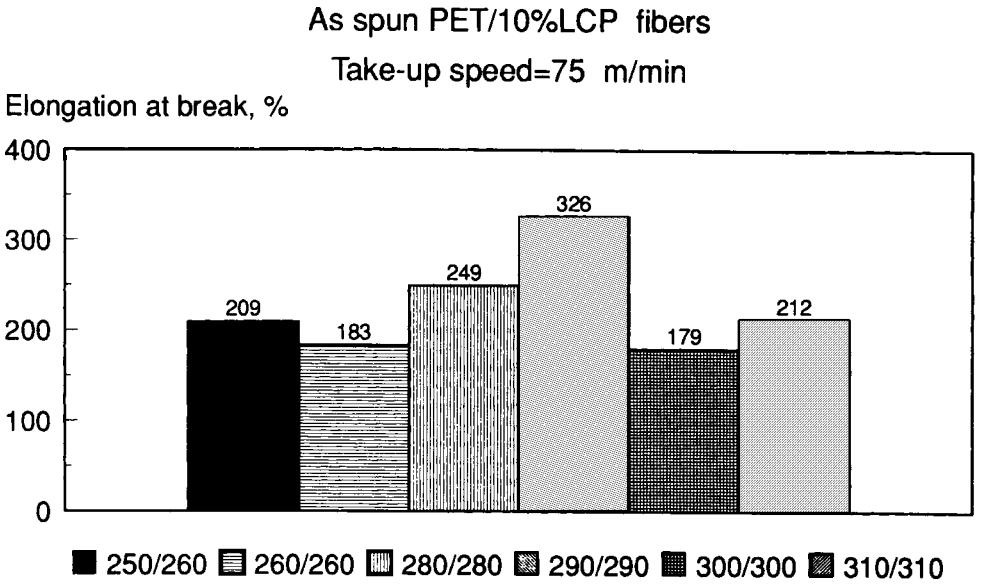

Figure 19 Effect of spinning temperature on elongation at break of as-spun PET/10% LCP fibers, spun at 75 m/min.

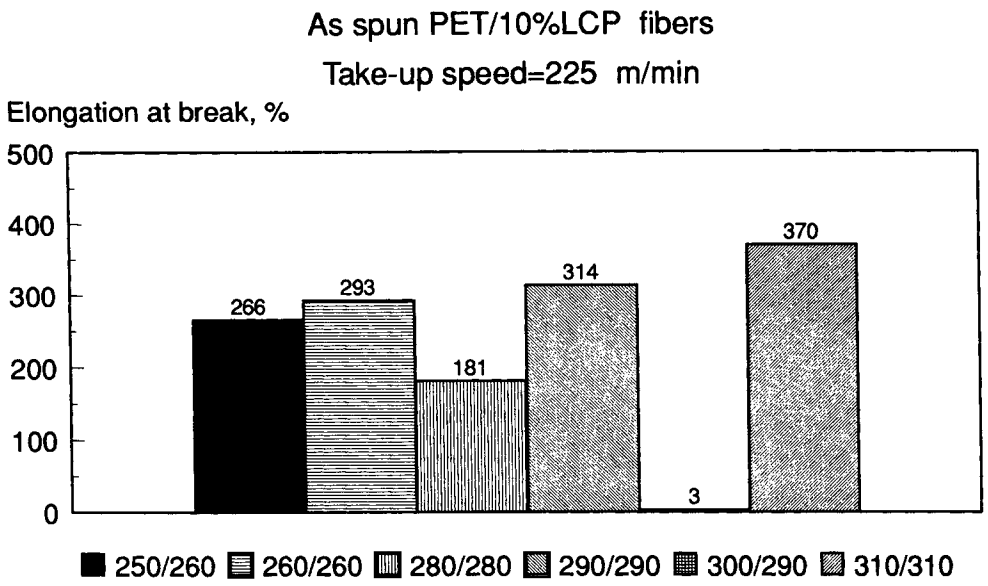

Figure 20 Effect of spinning temperature on elongation at break of as-spun PET/10% LCP fibers, spun at 225 m/min.

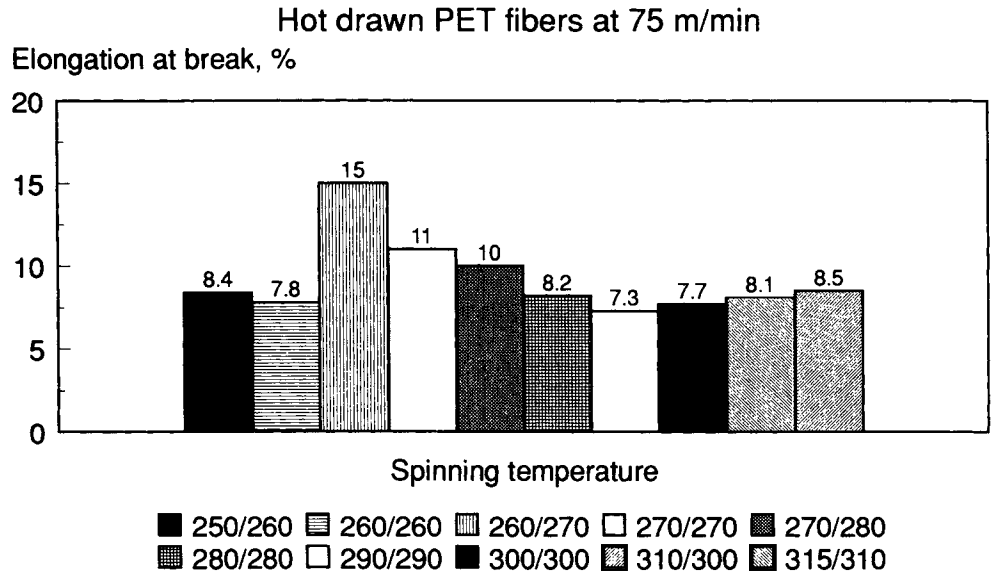

Figure 21 Effect of spinning temperature on elongation at break of hot-drawn PET fibers, spun at 75 m/min.

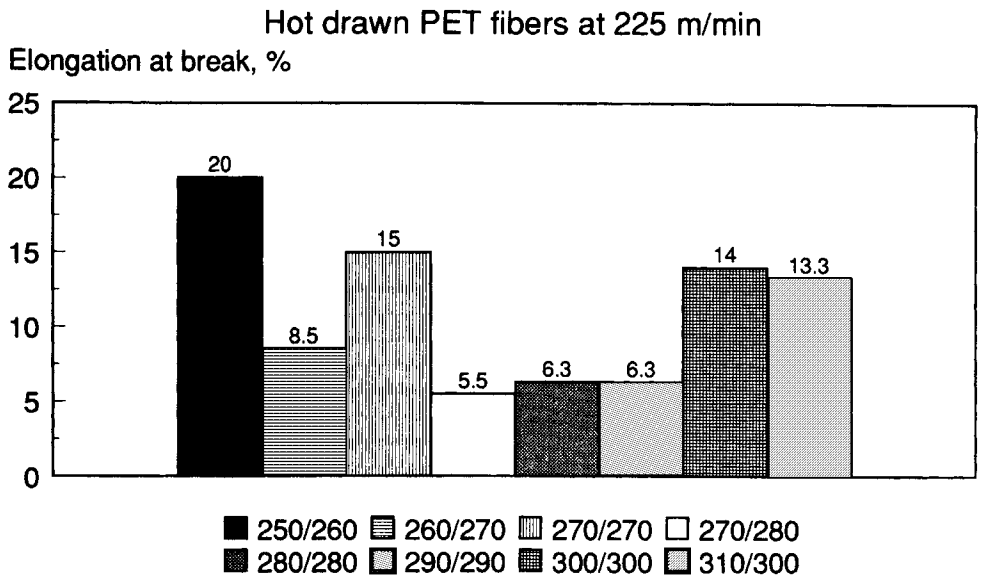

Figure 22 Effect of spinning temperature on elongation at break of hot-drawn PET fibers, spun at 225 m/min.

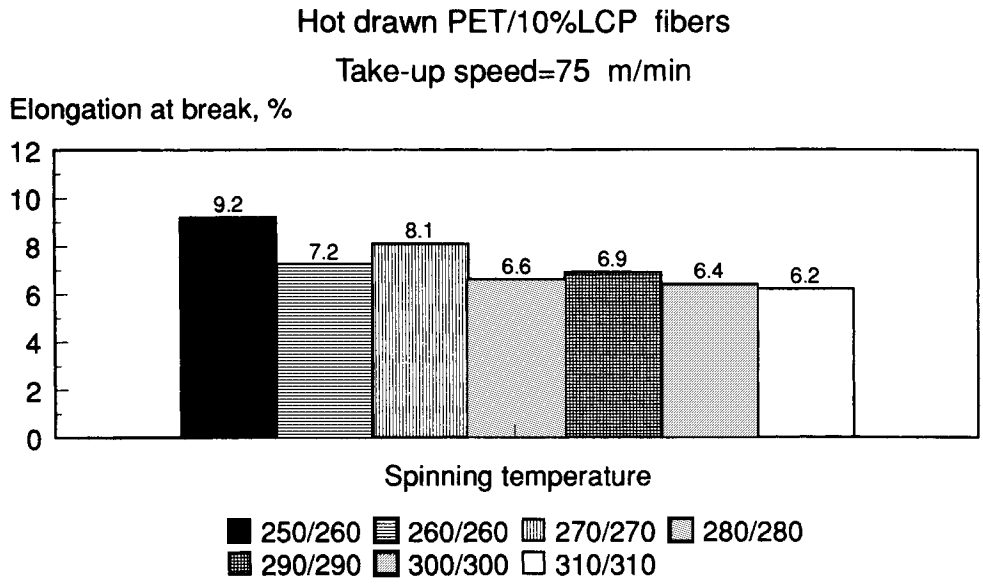

Figure 23 Effect of spinning temperature on elongation at break of hot-drawn PET/10% LCP fibers, spun at 75 m/min.

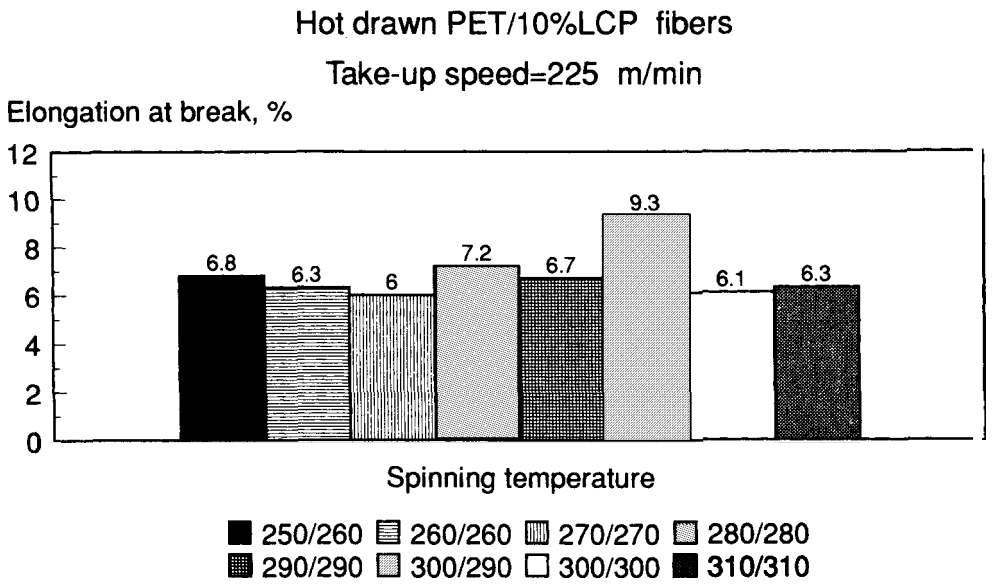

Figure 24 Effect of spinning temperature on elongation at break of hot-drawn PET/10% LCP fibers, spun at 75 m/min.

may have been that LCP acted as a nucleant, although the same effect was not observed with other fibers.

As discussed earlier, elongation at break of hot-drawn fibers is a good indicator of the draw ratio, being about 6–7% for optimum drawing. Elongation at break of the hot-drawn PET fibers are shown in Figures 21 and 22. The erratic values, some of them very high, with the change of spinning temperatures, show that in many cases optimal draw ratio was not attained. This was particularly true when a take-up speed of 225 m/min was used. On the other hand, elongation at break of fibers containing 10% LCP are uniform and close to optimal values. Figures 23 and 24 display the dependence of elongation at break on spinning temperature of hot-drawn PET/10% LCP fibers, at two take-up speeds.

These results show that the LCP used in this work does improve the drawing properties and the modulus of hot-drawn fibers. They also demonstrate that the optimal properties are obtained at spinning temperatures above 300°C, probably due to randomization of the LCP structure. The mechanism of reinforcement by LCP involves in some way the modification of the PET matrix.

CONCLUSIONS

The effect of spinning temperature on properties of the as-spun and hot-drawn fibers was examined on neat PET fibers and fibers based on PET/10% LCP blends. The results suggest that the modulus of as-spun fibers decreases with increasing spinning temperature as a consequence of higher orientation produced at lower temperatures. This is true both for fibers based on neat PET and PET/10% LCP blends. However, hot-drawn fibers spun at temperatures above 300°C had moduli of about 21 Gpa, indicating that randomization of the LCP structure and perhaps some transesterification exchange between the PET and the LCP had a favorable effect on orientation. Tensile strengths of fibers containing LCP, spun at high temperatures, were generally better than in those spun at lower temperatures, but lower than in corresponding neat PET fibers.

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