two monomer units and relaxation of such a bulky structure by main chain bond rotation would be expected to be similar to the relaxation time for backbone bond rotation, that is approximately 5 ns. It may be that the relaxation process for the co-operative motion resulting in spatial re-orientation of the excimer is sterically unfavourable.

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Preparation of high-modulus nylon-6 fibre by an improved zone-annealing method

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We have prepared high modulus, high strength nylon-6 fibres from crystalline polymers by an annealing method called 'zone-annealing'. In this study the zone-drawing was repeated 4 times (heater temperature 80°C; heater moving speed 40 mm $\min^{-1}$; under tension of 1.6 kg mm^{-2}). Zone-annealing conditions were decided after numerous preliminary experiments. It was thought that the amorphous molecular chains become selectively loose when the tension is removed after zone-annealing and relaxation leads to a decrease in macro-modulus. This was prevented by heat-setting on the zone-drawn and zone-annealed nylon-6 fibre.

Keywords Heat treatment; mechanical properties; nylon-6 fibre; annealing; stability; modulus

Introduction

We have succeeded in preparing high-modulus and high-strength fibres from crystalline polymers, already widely used, by a new annealing method called the 'Zone-annealing Method'. So far this method has been applied to poly(ethylene terephthalate)[1-6], polyethylene[1-3,7], and nylon-6[1-4,8,9]. In spite of very simple apparatus and easy procedure, the resulting fibres exhibited excellent mechanical properties and high dimensional stabilities at elevated temperatures.

In the case of nylon-6, however, the extent of approach of the maximum modulus to the crystal modulus (6.5%) is markedly low compared with those of poly(ethylene terephthalate) (19.8%) and polyethylene (23.0%). This indicates that there is room for further improvement of the mechanical properties. With the intention of investigating this point, we have attempted an improved zone-annealing method and a subsequent heat-setting. Consequently, we could obtain a fibre with a remarkably high modulus.

Experimental

The original material used in this study is as-spun nylon-6 fibre of diameter, 0.41 mm, supplied by Toray Research Center, Inc. The fibre has a birefringence of 9.5×10^{-4}, a crystallinity of 29.4% and $\bar{M}_n = 2.86 \times 10^4$, $\bar{M}_w = 1.18 \times 10^5$. The apparatus used for zone-drawing and zone-annealing is identical to that used in the previous studies[1-9]. The procedure consists of two stages: namely zone-drawing and zone-annealing. The zone-drawing was repeated 4 times increasing the tension applied to the fibre from 0.90 to 18.4 kg mm^{-2} at a band-heater temperature of 80°C with a heater moving speed of 40 mm $\min^{-1}$. The zone-annealing was carried out 6 times under a tension of 21.5 kg mm^{-2} at a band-heater temperature of 180°C with a moving speed of 300 mm $\min^{-1}$. Subsequently the zone-drawn and zone-annealed fibre was heat-set. Heat-setting was carried out at 190°–200°C for 5 min under a nitrogen gas atmosphere. The dynamic viscoelastic properties, E', E'', tan δ were measured at 110 Hz over a temperature range from room temperature to 190°C at a heating rate of 1.5°C $\min^{-1}$.

Results and Discussion

As nylon-6 crystallizes easily on cooling from the molten state and during storage in atmospheric moisture, even as-spun fibre has a large number of lamellae. In order to further increase the modulus, it is necessary to more effectively unfold the lamellae and to form a more-extended chain structure. The zone-drawing in the previous studies[8,9] was carried out only once at a band-heater temperature of 80°C with a heater moving speed of 40 mm $\min^{-1}$ under a tension of 1.6 kg mm^{-2}. However, in the present study the zone-drawing was repeated 4 times under the conditions described above. The conditions for zone-annealing were also decided after numerous preliminary experiments. It is considered that the amorphous molecular chains become selectively loose when the tension is removed after zone-annealing and the relaxation leads to a decrease in macro-modulus. To prevent the unfavourable relaxation of amorphous molecular chains, heat-setting was subsequently attempted on the zone-drawn and zone-annealed fibre.

Figure 1 shows the temperature dependence of dynamic storage modulus for the three kinds of the fibres. It is clear from the figure that the fibre prepared by the improved zone-annealing method is far superior to one by

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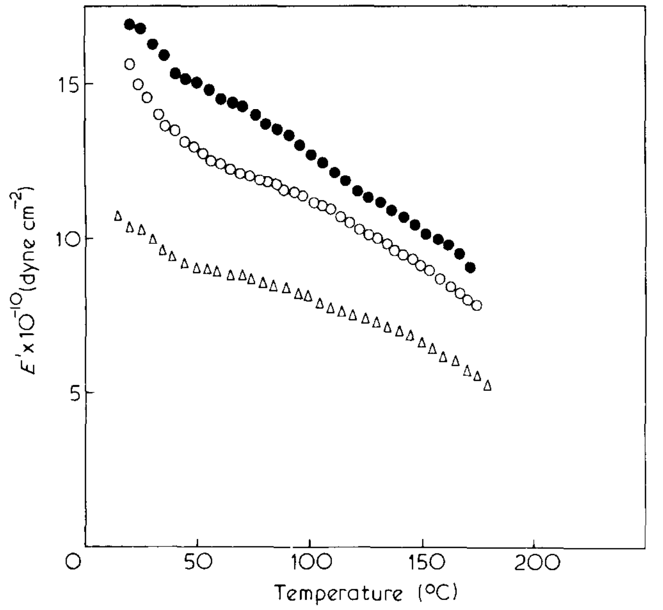

Figure 1 Temperature dependence of dynamic storage modulus E' for the fibre prepared by the previous zone-annealing method (△), the fibre prepared by the improved zone-annealing method (○), and the fibre prepared by the improved zone-annealing method and heat-setting (●)

the previous zone-annealing method and the addition of heat-setting is effective for further improvement of the mechanical properties.

The E' value at room temperature reached 16.9×10^{10} dyne cm^{-2}, which corresponds to 3.4–6.3 times that of the high-tenacity fibre available commercially. Also, the value is much higher than the highest value available in the literature (14×10^{10} dyne cm^{-2} by Acierno *et al.*). It was found that the superstructure of the amorphous region plays an important role in improvement of the mechanical properties. These detailed results will be reported in the near future.

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