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Swollen-state polymerization of poly(ethylene terephthalate) in fibre form

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The swollen-state polymerization of poly(ethylene terephthalate) in fibre form was performed in hydrogenated terphenyl as the swelling solvent. Ultra-high-molecular-weight poly(ethylene terephthalate) (UHMW-PET) fibre with an intrinsic viscosity of 3–4 dl g^{-1} ($M_n = 2-3 \times 10^5$) was obtained. The polymerization rate of as-spun PET fibres in the swollen state was greater than that of PET granules in the swollen state. It was clarified that the polymerization rate was related to the chain mobility of the starting materials. The chain mobility was influenced by various conditions, such as changing rigidity of the segments during copolymerization, the chain orientation of the starting fibre before swollen-state polymerization and the temperature of pretreatment with the solvent. Pretreatment with solvent before polymerization was effective in increasing the chain mobility. The relation between chain mobility and polymerization rate was examined by wide-angle X-ray diffraction, density, differential scanning calorimetry, solvent content and viscoelastic measurements. Undrawn UHMW-PET fibres could be drawn 10 times or more by the zone drawing technique in spite of their high crystallinity, and the drawn fibre showed high tensile strength (12 g d^{-1}) and high modulus (240 g d^{-1}).

(Keywords: poly(ethylene terephthalate); UHMW fibre; swollen-state polymerization)

INTRODUCTION

There has been much work to obtain high-performance fibres from special polymers. Owing to the success of gel-spun polyethylene in high-performance fibres, many attempts to make new high-performance fibres from other conventional polymers were studied via gel spinning using ultra-high-molecular-weight polymer. Ultra-high-molecular-weight poly(ethylene terephthalate) (UHMW-PET)[1–7] was also studied. High-tensile-strength and high-modulus fibres from solution spinning[8–11] of UHMW-PET with intrinsic viscosity (IV) = 3.6 dl g^{-1} were reported.

In previous articles[12,13], we reported a new polymerization technique for UHMW-PET, that is, swollen-state polymerization in a specific solvent, and discussed the effects of the solvent and the kinetics of swollen-state polymerization. However, swollen-state polymerization in granule form needed a longer reaction time. Additionally, the processing of UHMW-PET may be difficult because of the high melt viscosity. Such difficulties might be avoided by processing into fibre or film form prior to swollen-state polymerization. In this paper, we report the swollen-state polymerization in fibre form in order to study the polymerization rate and the polymerization mechanism of swollen-state polymerization.

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EXPERIMENTAL

Preparation of samples

The PET homopolymer was obtained in the same manner as that of previous work[12]. The PET copolymers were prepared from one of the aromatic dicarboxylic acid dimethyl esters and dimethyl terephthalate by ester interchange reaction, followed by melt-phase polymerization.

The as-spun PET fibres with $IV = 0.86$ dl g^{-1} were obtained by melt spinning from conventional solid-state polymerized PET with $IV = 1.0$ dl g^{-1}. The diameter of an as-spun fibre was about 70 μm (57 denier) and the birefringence of an as-spun fibre was 2.1×10^{-3}.

Swollen-state polymerization

The details of the swollen-state polymerization were described in the previous paper[12]. In the case of fibre form, sample fibres were wound on a stainless-steel frame. Typical conditions for the swollen-state polymerization were as follows: As-spun PET fibres (0.5–1 g) wound on the frame were dipped in a bath filled with hydrogenated terphenyl (400 ml) as the swelling solvent. The dipped fibres were pretreated by dry nitrogen gas bubbling into the solvent through a porous glass tube with stirring at 220°C for 20 h prior to the swollen-state polymerization. Then, the temperature of the solvent was raised to 236°C, and held at that temperature with nitrogen bubbling (2 l min^{-1}).

The IV, content of solvent, relative density of the polymer and differential scanning calorimetry (d.s.c.) were measured in the same manner as in the previous

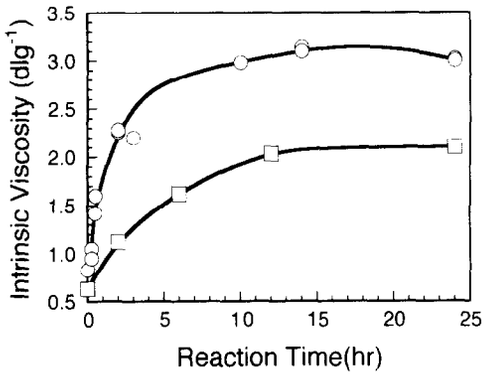

Figure 1 Reaction-time dependence on intrinsic viscosity of the PET formed by polymerization at 236°C: (○) as-spun PET fibre; (□) PET granules (3 mm diameter)

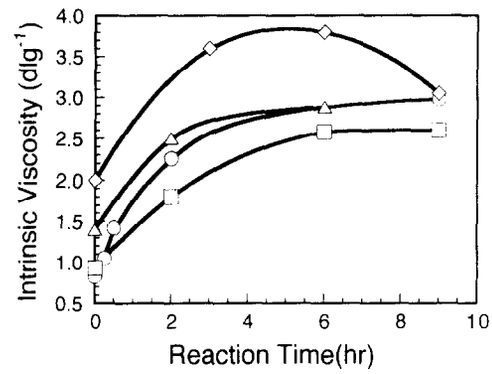

Figure 2 Effects of pretreatment temperature and reaction time on intrinsic viscosity of the PET formed by polymerization at 236°C. Pretreatment: (□) 150°C, 20 h; (△) 200°C, 20 h; (◇) 220°C, 20 h; (○) none

study[12,14]. Dynamic viscoelasticity was measured by a Reovibron® (Toyo Baldwin Co. Ltd, Rheo-2000) at 110 Hz at a heating rate of 2°C min^{-1}.

Zone drawing of UHMW-PET fibre

UHMW-PET fibres after swollen-state polymerization were drawn by two-step drawing. The first step of drawing was conducted at room temperature and the draw ratio was about five times. The second drawing was carried out by the zone drawing technique[15] where the draw ratio of swollen fibre was twice or more. The upper end of the fibre (50 mm) was fixed, and the weight of the lower end was gradually increased for suitable tension. The zone drawing temperature was 185°C. The tensile strength of drawn fibre was measured at a strain rate of 10 cm min^{-1} by using a Tensilon (Toyo Baldwin Co. Ltd, UTM-III). The tensile modulus was determined from the initial slope of the stress–strain curve.

RESULTS AND DISCUSSION

Effect of form of starting material

The fibre form as a starting material for the swollen-state polymerization was expected to increase the polymerization rate because of the faster impregnation of the solvent into the PET. The influence of particle size was examined in the previous work[14]. *Figure 1* shows a comparison of the form of the starting material. As-spun

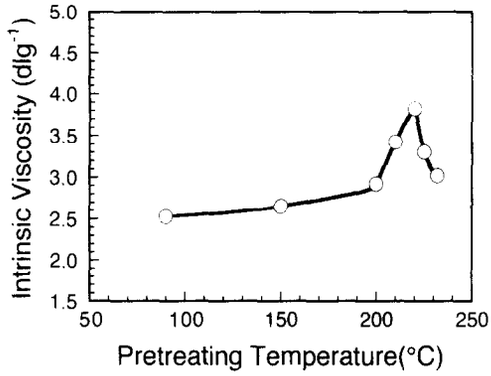

Figure 3 Effect of pretreatment temperature on ultimate intrinsic viscosity of the PET formed by polymerization at 236°C for 20 h

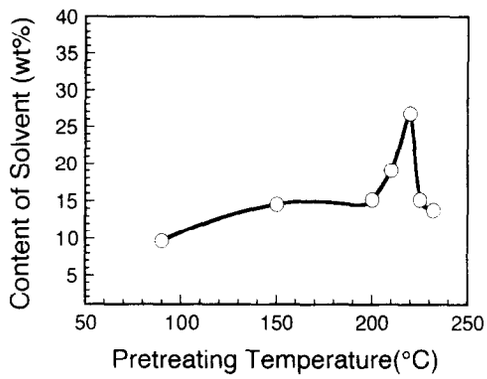

Figure 4 Effect of pretreatment temperature on content of impregnated solvent in the PET fibre

PET fibres as the starting material attained $IV = 3.1$ dl g^{-1} ($M_n = 2.1 \times 10^5$) after 14 h polymerization. The content of solvent after polymerization was 15 wt% in the PET fibre, whereas the PET granules showed 10 wt% of solvent and gave IV of 2.0 dl g^{-1}. As a result, the polymerization time to obtain IV of 2 dl g^{-1} could be reduced to about 2 h by use of the fibre form in contrast to granules.

Effect of pretreatment

Furthermore, it was clarified that the reaction could be accelerated by using the technique of solvent pretreatment, where the starting fibre was kept at a specific temperature for a specific time in the solvent prior to the swollen-state polymerization. *Figure 2* shows the intrinsic viscosity build-up of fibres that were pretreated at various temperatures in the solvent. The highest IV of 3.8 dl g^{-1} by the swollen-state polymerization of fibre was obtained by pretreatment at 220°C for 20 h followed by 6 h polymerization. *Figure 3* shows the effect of pretreatment temperature on the ultimate IV of the PET fibre polymerized at 236°C. *Figure 4* also shows the dependence of pretreatment temperature on content of impregnated solvent in the PET fibre. According to these results, one can conclude that higher molecular weight can be attained by higher impregnation of the solvent and that the optimum temperature of pretreatment is 220°C.

The pretreatment in the solvent was accompanied by the crystallization of PET. *Figure 5* shows that the relative density of PET fibre increased with increase of

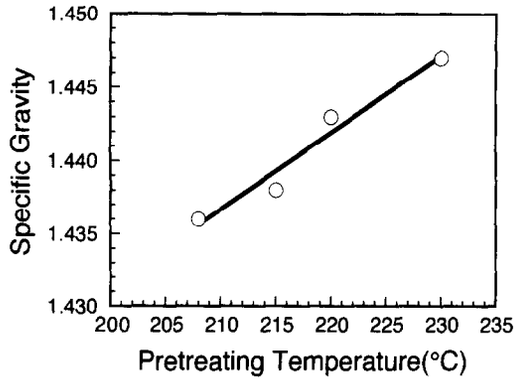

Figure 5 Relative density (specific gravity) change of the PET fibre as a function of pretreatment temperature in the solvent

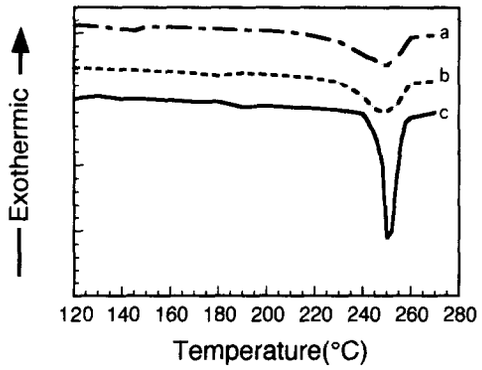

Figure 6 Differential scanning calorimetry profile of the PET fibre after pretreatment for 20 h in the solvent: (a) 90°C, (b) 150°C, (c) 220°C

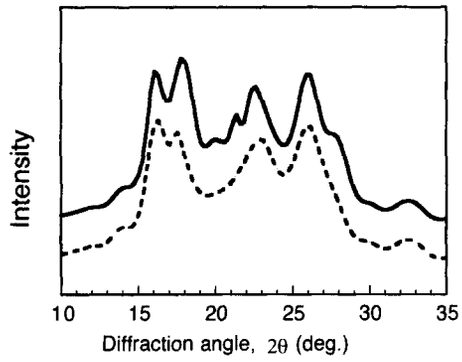

Figure 7 Wide-angle X-ray diffraction patterns for UHMW-PET fibre polymerized in the swollen state (full curve) at 236°C and PET fibre polymerized in the solid state (broken curve) at 220°C

pretreatment (swelling) temperature. *Figure 6* shows that the endothermic peak in d.s.c. became larger and was sharpened with the increase of swelling temperature. The wide-angle X-ray diffraction pattern in *Figure 7* also shows the larger crystal size of UHMW-PET fibre from the swollen-state polymerization than that of PET fibre from conventional solid-state polymerization. It was thought that such high crystallinity restricted the molecular motion of PET and depressed the polymerization rate.

The mobility of polymer chains can be evaluated by the mechanical loss tangent ($\tan\delta$). *Figure 8* represents the $\tan\delta$ vs. T curves of the fibres after solvent

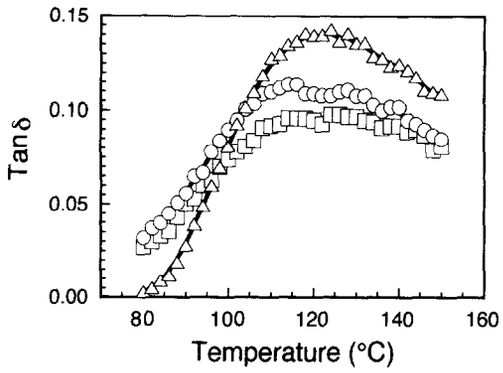

Figure 8 Tan δ of PET fibre after pretreatment at various temperatures for 20 h: (□) 236°C, (○) 220°C, (△) 150°C

Table 1 Peak temperature of tan δ after pretreatment for 20 h in the solvent

Pretreatment temperature (°C)	Peak temperature of tan δ (°C)
90	125
150	122
200	124
220	115
236	126

pretreatment at various temperatures. The relation of the peak temperature of tan δ and the pretreatment temperature of the fibres in the solvent is summarized in *Table 1*. The swollen PET fibres obtained by pretreating at 220°C had the lowest peak temperature of tan δ. As mentioned above, 220°C is the optimum pretreatment temperature for the swollen-state polymerization and the impregnation of solvent.

Illers[16] and Mutsuishi[17] reported that the peak temperature of tan δ rose with the increase of temperature of heat treatment for PET fibre. Also, they pointed out that PET fibres pretreated at 210–220°C have lower peak temperature of tan δ. These results were interpreted by the correlation of PET crystal size and crystallinity. That is, heat treatment at lower temperature gives fine crystals in the PET fibre and these fine crystals prevent their molecular motion in the amorphous phase by crosslinking with each other. However, the crystals grow in size with treatment at higher temperature, leading to a decrease in the number of crosslinks of each crystal and yielding a looser packing. Thus, the molecular motion of the polymer chain is easier. However, when the temperature of heat treatment exceeds 220°C, the crystallization proceeds more rapidly and the molecular motion is restricted again. We expected the same phenomenon to occur in the swollen-state polymerization of PET in fibre form. That is, the fibre treatment at 220°C balanced the crystal size and the crystallinity for easy molecular motion.

Effect of copolymerization

Figure 9 shows that the fibre from the copolymer of PET with isophthalic acid (2.5 mol%) had larger polymerization rate than homo-PET fibre and achieved $IV = 4.8\,\mathrm{dl\,g^{-1}}$. But, the fibre of copolymerized PET with 2,6-naphthalenedicarboxylic acid (2.5 mol%) had a

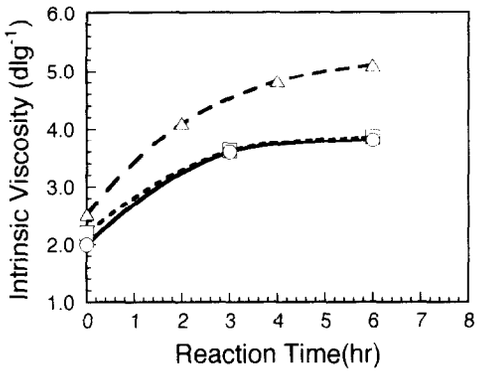

Figure 9 Reaction-time dependence on intrinsic viscosity of the copolymerized PET fibre: (○) as-spun homo-PET fibre; (△) as-spun isophthalic acid (2.5 mol %) copolymerized PET fibre; (□) as-spun 2,6-naphthalenedicarboxylic acid (2.5 mol%) copolymerized PET fibre as the starting material

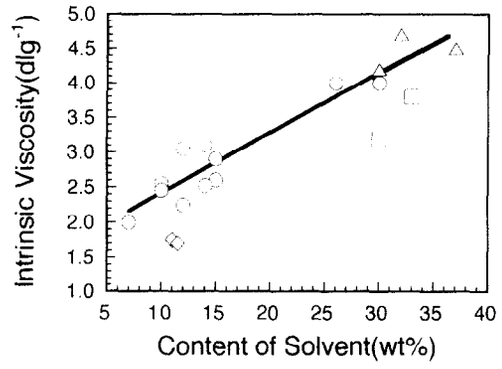

Figure 10 Relation of ultimate intrinsic viscosity and solvent content of the fibre after the swollen-state polymerization: (○) as-spun homo-PET fibre; (◇) drawn homo-PET fibre; (△) as-spun isophthalic acid (2.5 mol%) copolymerized PET fibre; (□) as-spun 2,6-naphthalenedicarboxylic acid (2.5 mol%) copolymerized PET fibre as the starting material

similar rate to that of homo-PET fibre, whereas drawn PET fibre attained only $IV = 1.8\,\mathrm{dl\,g^{-1}}$. *Figure 10* shows the relation of the ultimate intrinsic viscosity and solvent content after swollen-state polymerization. Drawn PET fibre showed apparently lower content of the solvent and ultimate IV compared with the undrawn amorphous PET fibre. The copolymer with isophthalic acid (2.5 mol%) had the same trend as homo-PET. That is, the fibre having the higher swelling (higher content of the solvent) was able to achieve higher ultimate intrinsic viscosity. On the other hand, the fibre from the copolymer with 2,6-naphthalenedicarboxylic acid (2.5 mol%) had a high content of solvent (high degree of swelling), but the fibre from the copolymer had similar IV to homo-PET fibre. Therefore, a stiff segment like 2,6-naphthalenedicarboxylic acid moiety impeded molecular motion during the swollen-state polymerization and depressed the polymerization rate. The copolymerized PET with isophthalic acid had higher degree of swelling and greater polymerization rate than that of homo-PET. These results substantiated the significance of molecular motion in swollen-state polymerization.

Drawing of swollen fibre

The crystallinity of UHMW-PET fibre with $IV = 3.8\,\mathrm{dl\,g^{-1}}$ was 94% calculated by relative density[14]. However, the fibre after swollen-state polymerization was able to draw about five times at room temperature. It is noted that UHMW-PET fibre from the swollen-state polymerization contained 25–30 wt% of solvent (hydrogenated terphenyl). The solvent exuded and vaporized during drawing. After the zone drawing, the amount of solvent in the drawn fibre decreased to 0.5 wt% or less. When the UHMW-PET fibres were washed thoroughly with acetone, these fibres could not be drawn because of their brittle and fragile characteristics. The fibre with $IV = 3.8\,\mathrm{dl\,g^{-1}}$ after the swollen-state polymerization was drawn about five times at room temperature prior to zone drawing. Then the fibre drawn twice or more by zone drawing at 185°C and the drawn fibre showed tensile strength of $12\,\mathrm{g\,d^{-1}}$ and modulus of $230\,\mathrm{g\,d^{-1}}$ (d = denier). Total draw ratio of the fibre was 10 times or more. It is expected that such high draw ratio of the swollen-state fibre was due to the impregnated solvent working as an agent to plasticize and disentangle the polymer chains.

CONCLUSIONS

The swollen-state polymerization of as-spun PET fibres was performed in hydrogenated terphenyl as the swelling solvent. UHMW-PET fibre with an IV of $3–4\,\mathrm{dl\,g^{-1}}$ ($M_n = 2–3 \times 10^5$) was obtained. The polymerization rate in swollen fibres was greater than that of granules in the swollen state. It was clarified that the mobility of the polymer chain influenced the rate of swollen-state polymerization. The fibre having the lower peak temperature of $\tan\delta$ after pretreatment in the solvent attained the higher ultimate IV. A fibre with highly impregnated solvent was obtained by treatment in the solvent under specific conditions. It was estimated that such fibre had large crystals and gave loose packing. The copolymer with isophthalic acid had a higher degree of swelling (the higher content of solvent in polymer) and higher polymerization rate. In conclusion, the high mobility of the polymer chain induced fast polymerization in the swollen-state fibre. The swollen-state polymerization was accompanied by the crystallization of the polymer. The fibres from the swollen-state polymerization had high crystallinity; however, the UHMW fibre in the swollen state could be drawn and showed high tensile strength and modulus.

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