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Melt viscosity reduction of poly(ethylene terephthalate) by solvent impregnation

Susumu Tate*, Shuji Chiba and Katsuya Tani
Toyobo Research Institute, Toyobo Co. Ltd, Katata, Ohtsu, Shiga 520-02, Japan
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The melt viscosity of poly(ethylene terephthalate) (PET) was decreased by the impregnation of an aromatic solvent, such as l-methyl naphthalene or diphenyl ether. Porous PET granules for impregnation of the solvent were prepared by swollen-state polymerization in hydrogenated terphenyl as the swelling solvent. The PET granules could take up 20% of the solvent by heating with the solvent. On the other hand, PET granules polymerized in the solid-state scarcely absorbed the solvent, except for l-methyl naphthalene. The apparent melt viscosity of PET decreased to 1/5 by the impregnation of l-methyl naphthalene (20%). The solvent-containing PET granules allowed extrusion at lower temperature (270°C), which led to a reduction of the degradation of PET and produced high tensile strength (2 GPa) and high modulus (30 GPa) fibres. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(ethylene terephthalate); solvent; melt viscosity)

Introduction

Many studies for obtaining high strength and high modulus poly(ethylene terephthalate) (PET) fibre have been performed. Kunugi *et al.*[1] reported the zone annealing method for making a high modulus PET fibre. Other approaches for obtaining high strength PET fibres were reported: heat drawing of PET fibre under microwaves[2], co-extrusion of gel PET fibre at low temperature[3] and solution spinning of ultra-high molecular weight PET[4,5]. High molecular weight PET with an intrinsic viscosity (IV) exceeding 1 dl g^{-1} is difficult to be spun into fibres because of its high melt viscosity. For example[6], the PET polymer with an IV of 2.1 dl g^{-1} reaches a melt viscosity of 8×10^5 P under zero shear at 300°C.

Hence, in order to reduce the melt viscosity, the melt processing of high molecular weight PET has to be conducted at a temperature over 300°C. Such high temperatures may cause serious thermal degradation of the polymer. A previous paper[7] showed some specific solvent swollen PETs, in which polymerization was accelerated by easier molecular motion of the polymer chain. A similar relationship can be expected to reduce the melt viscosity of PET by impregnation of a specific solvent.

We have studied the effect of the solvent on the melt viscosity of solvent-containing PET. As the results show, porous PET polymerized in the swollen state had high absorbability of the solvent, which was highly effective for reducing the melt viscosity. Solvent-containing PET polymers allowed extrusion at lower temperature and produced high tensile strength and high modulus fibres.

Experimental

Synthesis of porous PET granules. The porous PET with IV = 2.0 dl g^{-1} was prepared by swollen-state polymerization in hydrogenated terphenyl[8]. Starting materials for the swollen-state polymerization were commercial PET polymers with IV = 0.6 dl g^{-1} (Toyobo Co.). The porous PET granules after the swollen-state polymerization were washed thoroughly in acetone and dried overnight *in vacuo* at 150°C.

Solvents for impregnation. l-Methyl naphthalene and diphenyl ether were obtained commercially as reagent grade (Aldrich Chemical Co.). Ethyl biphenyl (Therm S-600$^{\mathrm{TM}}$) and hydrogenated terphenyl (Therm S-900$^{\mathrm{TM}}$) were also obtained commercially as heat transfer media (Nippon Steel Chemical Co.). All solvents were purified by distillation before use.

Measurement of apparent melt viscosity. The solvent-containing PET was prepared by impregnation of the solvent. The mixture of dry PET granules and l-methyl naphthalene (4/1 by wt) were charged into a rotary mixing apparatus and maintained at 70°C with stirring *in vacuo* (10 mm Hg). About 2–4 h later, the PET granules absorbed all the solvent and appeared to be just like dry particles. The content of the solvent in the PET granules was determined from the weight loss before and after extracting with acetone and drying *in vacuo*. Solvent-containing PET polymers were extruded through orifices with diameters of 0.5–7 and 2.5–31 mm. The apparent melt viscosity of the solvent-containing PET was determined by the relation of the mass flow rate and the pressure drop at the orifice using the Hagen–Poiseuille law. The IV of the PET after extrusion was measured in the

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*To whom correspondence should be addressed. Present address: Japan U-pica Technical Research Institute, Japan U-pica Co. Ltd, 5-3-3 Higashiyawata Hiratsuka, Kanagawa 254, Japan

same manner as that of the previous study[8], after removal of the solvent.

Spinning of solvent-containing PET. The solvent-containing PET was spun at 270°C through orifices with a diameter of 0.28 mm. The solvent in the filaments was evaporated by the cross flow air. As-spun fibres were taken up at 50 m min^{-1} and then drawn by the two-stage process in which the draw ratio of each stage was 2–3 times. The IV of as-spun fibres measured in the same manner as mentioned in the previous paper[7]. The content of the solvent in PET fibres was determined from the weight loss, which was measured by heating the samples from room temperature to 500°C at 20°C min^{-1} under an argon atmosphere in a thermobalance (TA-50, Shimadzu Co.). The tensile strength and modulus of the drawn fibre were measured by the same method of the previous[7].

Results and discussion

Impregnation of solvent. The previous work[7] clarified that some specific solvent could swell PET polymers and accelerated the polymerization by facilitating the molecular motion of the polymer chain. Similarly, it was expected that a certain solvent would act as a melt viscosity reducing agent for PET. The lower melt viscosity would be able to lower the processing temperature, which may reduce the degradation of the polymer. The solvent for melt viscosity reduction must be stable under high temperature and must evaporate after spinning. Aromatic solvents were selected for reason of their thermal stability, e.g. 1-methyl naphthalene, diphenyl ether, ethyl biphenyls and hydrogenated terphenyl. These solvents have high solubility of PET at >220°C, except hydrogenated terphenyl.

In order to estimate the melt viscosity reduction, at first we tried feeding the mixture of PET and solvent to the extruder. However, this method did not work well because of unstable mass flow caused by incomplete mixing of the solvent and PET. This result required the fine mixture of the solvent and PET granules. The PET granules prepared by swollen-state polymerization have a honey-comb structure which can be observed by a scanning electron microscope, as shown in the previous paper[8].

The porous structure seemed to be the preferable one to take up the solvent. Dry PET granules prepared by swollen-state polymerization were able to absorb the solvent only by heating with the solvent. *Table 1* shows the relation of the content of the solvent in PET granules and the temperature of heat treatment. Porous PET granules prepared by swollen-state polymerization were able to absorb about 15% of various solvents at 50°C. On the other hand, PET pellets prepared by conventional solid-state polymerization at 210°C absorbed less than 1% of the solvent after the same heat treatment. Additionally, the PET polymerized in the swollen state was able to take up >20% of the solvent at 150°C. However, the PET polymerized in the solid state absorbed less than 10% of the solvent, except in the case of 1-methyl naphthalene, which had high compatibility to PET. Thus, the content of the absorbed solvent was related to the compatibility of the PET and solvent as well as to the morphology of the PET granules. The content of solvent in swollen PET after swollen-state polymerization was about 20%, which varied with the swollen-state polymerization condition[7,9]. Hence, 20% of the solvent is presumably the maximum content of the solvent in PET granules.

Table 1 Content of the solvent in PET granules after heat treatment with various solvents

	Content of solvent (wt%)			
	SWP-PET[a]		SSP-PET[b]	
Solvent	50°C	150°C	50°C	150°C
1-Methyl naphthalene	15	22	0	10
Diphenyl ether	16	21	0	4
Ethyl biphenyl	15	21	0	6
Hydrogenated terphenyl	14	21	0	0

[a] Prepared by swollen-state polymerization (IV = 2.0 dl g^{-1})
[b] Prepared by solid-state polymerization (IV = 1.1 dl g^{-1})

Melt viscosity reduction by solvent. The relationship of the apparent melt viscosity (η) of solvent-containing PET and the content of the solvent was examined at various shear rates. *Figure 1* shows the differences of the apparent melt viscosity between the original PET and solvent-containing PET at 300°C. The melt viscosity of solvent-containing PET was decreased by about 1/5 of the original PET. It is noted that original PET polymers with IV = 2 dl g^{-1} could not extrude at 270°C because of their high melting point (272–278°C) and high melt viscosity. The IV of the original PET decreased to 1.2 from 2 dl g^{-1} after extruding at 300°C.

On the other hand, the solvent-containing PET with 1-methyl naphthalene (20%) was able to extrude at 270°C, and the IV of the solvent-containing PET after extruding was about 1.6 dl g^{-1}, as shown in *Figure 2*. Namely, the solvent in PET allowed extrusion at lower temperature (270°C), which led to retention of high IV by reducing degradation.

Figure 2 also shows that the IV of the PET after extruding did not depend on the nature or content of the solvent. The thermal degradation behaviour of PET exceeding IV = 2 dl g^{-1} has already been studied[6] and it was reported that the degradation rate, calculated from IV change, increased with degradation temperature, time and molecular weight of the PET itself.

Figure 3 shows the effect of the solvent species on the melt viscosity of solvent-containing PET at 270°C.

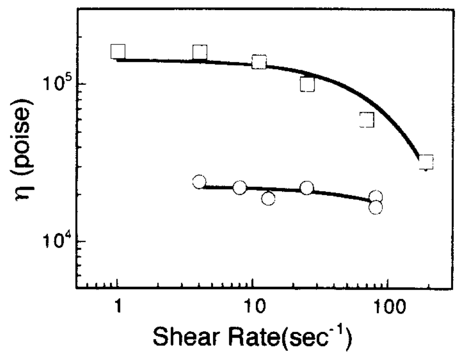

Figure 1 Apparent melt viscosity (η) of solvent-containing PET polymers at 300°C as a function of shear rate: (□) original PET; (○) 1-methyl naphthalene (20%)-containing PET

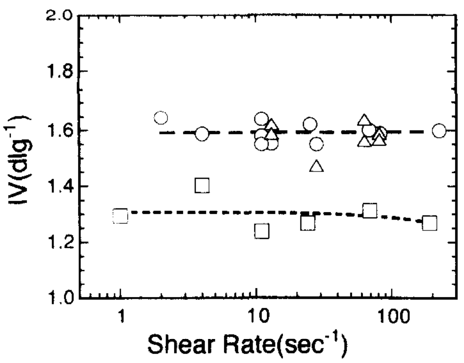

Figure 2 IV of solvent-containing PET, after extruding, as a function of shear rate: (○) l-methyl naphthalene (20%)-containing PET extruded at 270°C; (△) diphenyl ether (20%)-containing PET extruded at 270°C; (□) original PET extruded at 300°C

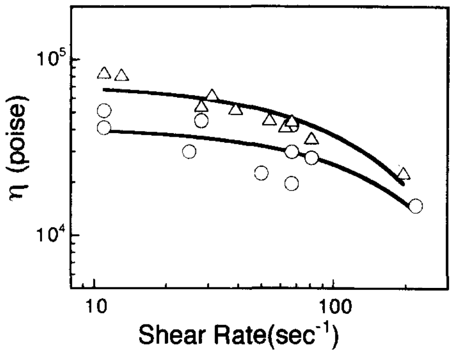

Figure 3 Effect of solvent on apparent melt viscosity (η) at 270°C: (○) PET containing l-methyl naphthalene (20%); (△) PET containing diphenyl ether (20 wt%)

l-Methyl naphthalene was a little more effective than diphenyl ether at lower shear rate. As mentioned above, l-methyl naphthalene had high compatibility with PET and reduced the melt viscosity by allowing an easier molecular motion. However, the relationship between the structure of the solvent and the melt viscosity was not clear in this study.

Figure 4 shows the relationship between the l-methyl naphthalene content in the PET and the melt viscosity. The melt viscosity decreased with an increase in the amount of solvent and shear thinning was observed in solvent-containing PET as well as in the original PET. The IV of the PET polymers after extruding was almost the same unless at the same extruding temperature, as shown in *Figure 2*.

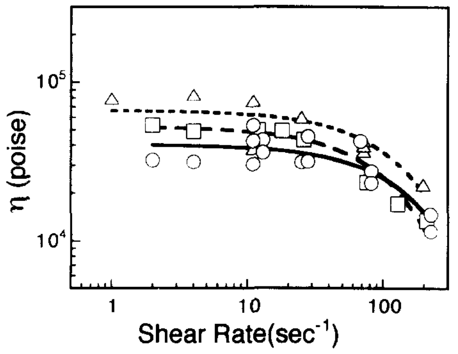

Figure 4 Apparent melt viscosity (η) of l-methyl naphthalene-containing PET at 270°C: (○) 20 wt%; (□) 14 wt%; (△) 7 wt%

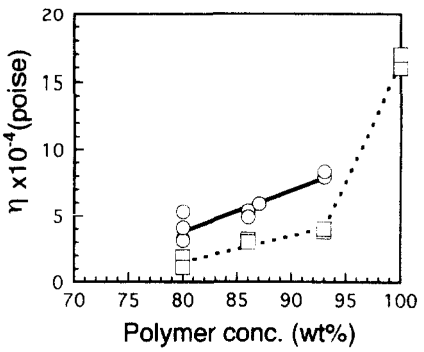

Figure 5 Apparent melt viscosity (η) of l-methyl naphthalene (20%)-containing PET under low shear rate (1–10 s^{-1}) as a function of polymer concentration: (○) 270°C; (□) 300°C

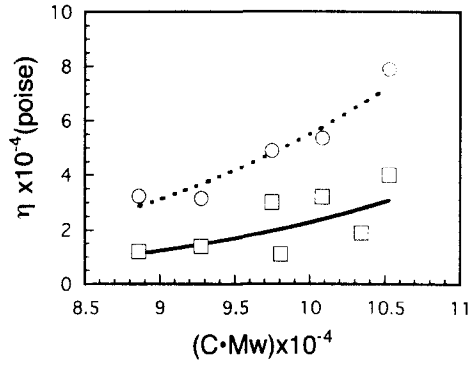

Figure 6 Relationship between the apparent melt viscosity (η) of l-methyl naphthalene-containing PET under low shear rate (1–10 s^{-1}) and the product of polymer concentration and weight average molecular weight: (○) 270°C; (□) 300°C

The apparent melt viscosity under low shear rate (1–10 s^{-1}) could be presumed to be the melt viscosity under zero shear and in which the melt viscosity decreased with increasing the amount of the solvent, as shown in *Figure 5*. The melt viscosity reduction by the impregnation of l-methyl naphthalene was highly effective for small amounts of the solvent. The melt viscosity of the polymer solution under zero shear is proportional to the concentration and the molecular weight of the polymer[10]. The melt viscosity of solvent-containing PET under low shear rate also increased with the product of the polymer concentration and the molecular weight, as shown *Figure 6*. The correlation analysis afforded the following equation, where C is the concentration of polymer in PET and M_W is the weight-average molecular weight, calculated in the same manner as that of the previous paper[6]:

$$\eta_0(270^\circ\mathrm{C}) = 2.14 \times 10^{-5}(C \times M_W)^{5.41} \qquad (1)$$

Spinning of solvent-containing PET. The spinning of solvent-containing PET was carried out by using l-methyl naphthalene as the melt viscosity reducing agent. l-Methyl naphthalene was selected from its melt viscosity reduction effect and its boiling point (242°C), which is lower than that of diphenyl ether (259°C). About 40% of l-methyl naphthalene in the PET granules vaporized during spinning, e.g. 20% of l-methyl naphthalene in the PET decreased to 12.6 wt% in undrawn fibre. The residual solvent in undrawn fibre was removed (to

0.1% or less) during the drawing. The IV of as-spun fibre at 270°C from solvent-containing PET was 1.5–1.7 $\mathrm{dl\,g^{-1}}$. As-spun fibres were taken up and then drawn in the same manner as described in the experimental section. The drawn fibres were of high tensile strength (2 GPa) and high modulus (30 GPa) owing to the higher molecular weight.

Conclusions

The melt viscosity of PET was decreased by the impregnation of an aromatic solvent such as l-methyl naphthalene on diphenyl ether. Porous PET granules for the impregnation of the solvent were prepared by swollen-state polymerization in hydrogenated terphenyl as the swelling solvent. The porous PET granules could absorb various solvents at higher concentration. On the other hand, PET polymerized in the solid-state scarcely absorbed the solvent, except for l-methyl naphthalene. The apparent melt viscosity of PET with 2 $\mathrm{dl\,g^{-1}}$ of IV could be reduced to about 1/5 by the impregnation of l-methyl naphthalene (20%).

Solvent-containing PET polymers allowed extrusion at lower temperature (270°C), which led to a reduction of the degradation of PET. The high tensile strength and high modulus PET fibres were obtained from the spinning of the PET containing l-methyl naphthalene.

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