

Effect of Copolymer Mixing on Elongation Property of As-Spun PET Fibers

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ABSTRACT: The change of elongation property in the melt spinning process of polyethylene terephthalate (PET) fibers, mixed with small amount of additive copolymer less than 5% by weight, was studied. The additive polymer was synthesized to improve the extensibility of matrix PET in the spinning process. The amount, molecular weight of additive polymer, and spinning conditions were changed to investigate the extensibility of as-spun fibers. Experimental results show that the blend of copolymer improves the extensibility

of as-spun PET fibers. The elongation at break of as-spun fibers increases with molecular weight and amount of additive polymer. The additive polymer prevents the fiber orientation and this causes the increase of extensibility of as-spun fibers. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1426–1431, 2006

Key words: melt spinning; additive polymer; matrix PET; extensibility; elongation at break

INTRODUCTION

Melt spinning process is a continuous deformation process and the most widely used method for manufacturing commercial synthetic fibers. It has been developed progressively in the field of spinning process and used to obtain new fibers with special functions.^{1–5} Productivity is the main concern of fiber manufacturers and studies on improving productivity have been made in many fields. Attempts to increase the productivity have been mainly done by means of increasing spinning speed or boosting the capacity of polymerization process. Studies on high speed spinning up to 10,000 m/min were done and commercialized up to 6000 m/min and are still being done to commercialize the high speed spinning.^{6–11}

Elongation at break, one of the tensile properties of filament, is the important characteristic in the drawing and texturing process of undrawn yarn (UDY) and partially oriented yarn (POY), and varies with the fiber orientation related to spin-draw ratio and take-up speed. If the elongation at break of filament could be controlled, the increasing of take-up speed is possible. The higher the elongation at break of as-spun fiber is, the higher the take-up velocity and mass throughput rate. One of the methods to improve extensibility of polymers is the blending of additive polymers with fiber-forming polymers such as PET.¹²

In this work, small amount of additive polymer was mixed with the fiber-forming PET in the molten state before it was spun. The immiscible additive polymer with matrix PET was synthesized since two polymers have to form two phases separately. The effect of spinning conditions and molecular weight of additive polymers on elongation at break was examined.

EXPERIMENTAL

Additive polymer

The additive polymer used in this work was copolymer of MMA (methyl methacrylate) and styrene. A copolymer was composed of MMA 75% by weight and styrene 25% by weight. A mixture of desalinated water, initiator, and monomer in a 6-L polymerization vessel equipped with a stirrer of turbine type was prepared. The batch was polymerized at 80°C for 120 min and then cooled to 25°C. The obtained polymer powder was filtered, washed, and dried.

Rheological characteristics

Melt viscosity as a function of shear rate was measured using piston-type capillary rheometer with a diameter of 0.5 mm and length to diameter ratio of 3. Temperature was monitored at two positions in the barrel and die section, and the temperature was controlled within $\pm 0.5^\circ\text{C}$. Diameter of barrel was 20 mm and entrance angle into capillary was 80° .

Melt spinning

Fiber-forming polymeric material used in this work was a textile grade PET of which the intrinsic viscosity

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TABLE I
Blend Conditions of PET with Additive Polymer

Variables	Conditions
Amount of additive polymer (wt %)	1, 2, 3, 5
Mixing temperature (°C)	295
Screw (rpm)	300

was 0.63 dL/g. Polymer blend was prepared using a twin-screw extruder with various blend ratios. The melt spinning apparatus with polymer line having static mixer of ten elements was prepared to improve the distribution of additive polymer. Mixed polymer chips were spun with spinneret plate having 36 bores with diameter of 0.20 mm and length to diameter ratio of 2. The blending and spinning conditions are summarized in Tables I and II.

Tensile property and birefringence

The tensile property was measured with an Instron tensile tester (UTM Instron 4201) using a specimen of length 50 mm and cross head speed 100 mm/min. The 36 filaments were used in the measurement, and for each spinning conditions, 10 trials were made to ensure accuracy. The retardation of the optical path of as-spun fibers was measured using a Nikon Optical-Pol polarizing microscope and was measured by compensator method. The wavelength was fixed to 546 nm. The birefringence was calculated using the following equation.¹³

$$\Delta n = \frac{\Gamma}{d} \quad (1)$$

where, Δn is the birefringence, Γ the retardation of the optical path, and d the thickness of sample (fiber diameter).

Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) micrographs were taken with Hitachi S-3000N microscope operating at 40 kV, using gold-covered samples.

TABLE II
Conditions of Melt Spinning

Variables	Conditions
Mass throughput rate (g/min)	12, 20, 28, 36
Spinning temperature (°C)	285, 290, 295
Take-up velocity (m/min)	1350, 1500, 1650, 1800
Quench air velocity (m/sec)	0.45
Quench air temperature (°C)	23

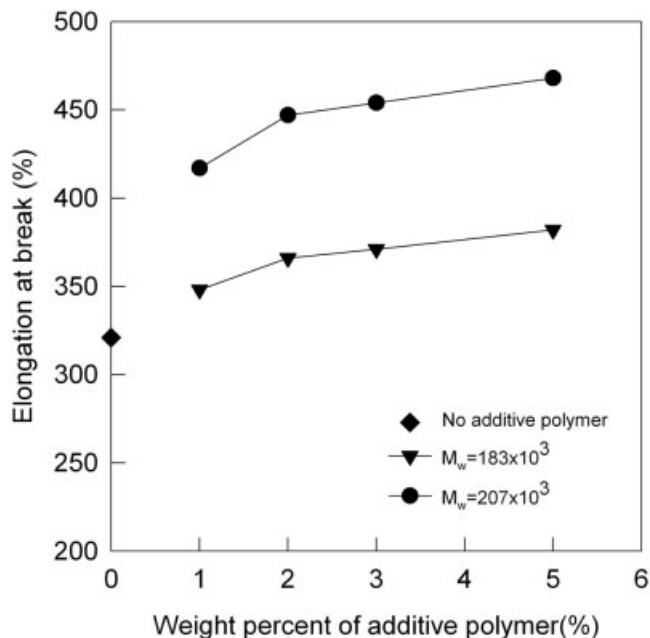


Figure 1 Elongation at break of as-spun filament versus weight percent of additive polymer: mass throughput rate, 28 g/min; take-up speed, 1500 m/min; spinning temperature, 290°C.

RESULTS AND DISCUSSION

Effect of additive polymer

The additive copolymer was mixed with PET using a twin-screw extruder. In the case of blend with additive polymer over 5% by weight, the spinning performance was not good and the tenacity of as-spun fiber was very weak in comparison with homo PET fiber with no additive polymer. Figure 1 shows the effect of amount of additive polymer on elongation at break of as-spun fibers. The elongation at break increases with the amount of additive polymer, irrespective of molecular weight of additive polymer. Figure 2 shows the birefringence change as a function of take-up speed. Birefringence at low take-up speed could not be detected because of lower molecular chain orientation. The additive polymer during spinning plays a role of preventing orientation of the molten matrix PET polymer. Presence of additive polymer prevents the PET molecular chains from enhancing the molecular chain orientation during spinning, and this leads to the increase in elongation of as-spun fibers. In the melt spinning process, the molten polymer stretches hundreds times longer than its original length and, by means of stretching, the molecular chains crystallize and orient along the longitudinal direction. The additive polymer also stretches longer than its original length. However, stretching of additive polymer is smaller than that of matrix polymer because the additive polymer is immiscible with matrix PET and it is distributed in the form of separate phase in the matrix

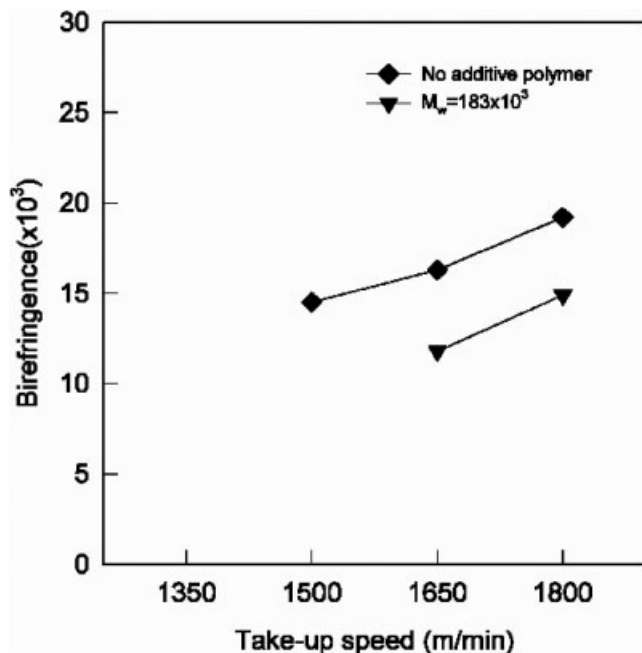


Figure 2 Birefringence of as-spun filament versus take-up speed: additive polymer, 2 wt %; mass throughput rate, 28 g/min; spinning temperature, 290°C.

polymer. Figure 3 shows SEM Photographs of as-spun fiber after resolving with 15% NaOH solution at 100°C for 30 min. By means of SEM, accurate detecting of the additive polymer was not possible; however, the effect of presence of additive polymer was revealed. In Figure 3, additive polymer existing area, which is resistant to alkaline solution, is shown as the type of strand in comparison with homo PET fibers. The thickness of strand, in the fiber mixed with higher molecular weight copolymer, is thinner. The thickness of strand is about 0.6 μm for M_w of 183,000 and 0.26 μm for M_w of 207,000. Figure 4 shows the assumed schematic diagram of additive polymer in molten state and in filament state after spinning. The additive polymer presents in the form of ellipsoid in the molten state and deforms to chopped fiber after spinning. Stretched additive polymer within the matrix polymer inhibits the molecular orientation and crystallization of matrix PET.

Effect of spinning conditions on the process

Effect of mass throughput rate and take-up speed

The mass throughput rate affects the profile development and final dimensions because the spin-draw ratio varies with mass throughput rate. When the take-up speed is fixed, lower mass throughput rate results in higher drawdown ratio and deformation rate.¹⁰

$$Q = \rho v A = \rho v \frac{A_0}{\lambda} \quad (2)$$

$$\lambda = \frac{A_0}{A}$$

where, Q is the mass throughput rate, ρ the density, v the take-up velocity, A the cross-sectional area of as-spun filament, A_0 the cross-sectional area of spinneret, and λ the spin-draw ratio.

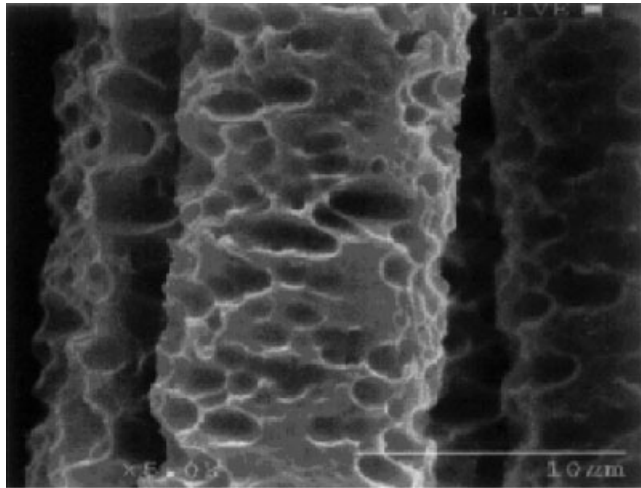
Figure 5 shows the effect of mass throughput rate on elongation at break of as-spun fibers. The elongation at break increases with mass throughput rate. The increase of mass throughput rate results in the decrease of spin-draw ratio and this leads to an increase of elongation at break of as-spun fibers. Like mass throughput rate, the take-up speed is also an important factor in determining the diameter of as-spun fiber. When the mass throughput rate is fixed, the drawdown ratio is determined solely by the take-up speed. The elongation at break of as-spun fibers generally decreases with take-up speed because of the increase in the fiber orientation and crystallization.¹⁴ Likewise, same trend was shown in Figure 6. However, under the presence of additive polymer, elongation at break slightly decreases in comparison with the case of no additive polymer.

Effect of spinning temperature

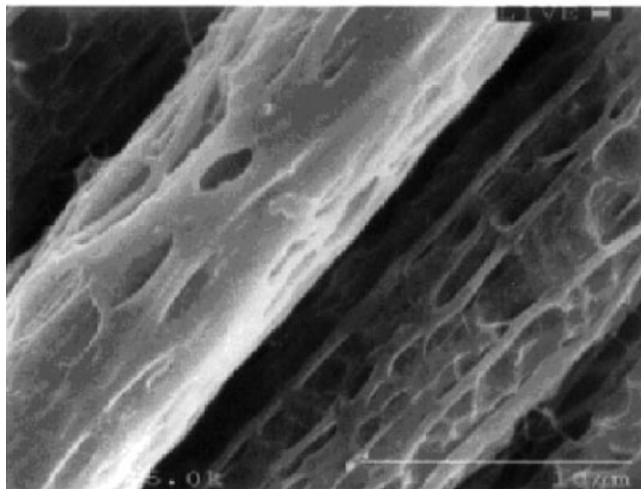
Contrary to other spinning conditions, such as mass throughput rate and take-up speed, the spinning temperature has little effect on the final dimension in the fiber spinning process because of no change in drawdown ratio. As the spinning temperature becomes low, the solidification point moves upward, i.e., the deformation region becomes short. The elongation at break slightly increases with spinning temperature.¹⁴ This is because the higher spinning temperature induces the lower melt viscosity and this leads to decrease in spinline stress. Thus, the elongation at break of higher spinning temperature is a little greater than that of lower spinning temperature. However, PET blended with small amount of additive polymer shows different characteristics. The elongation at break slightly decreases with the spinning temperature (Fig. 7). This may be due to the greater deformation of additive polymer in the lower spinning temperature. Lower spinning temperature induces a slight increase in tensile stress and this causes the larger deformation of additive polymer. More elongated additive polymer in lower spinning temperature results in decrease in orientation of matrix PET molecules. However, the effect of spinning temperature is relatively small.

Effect of molecular weight of additive polymer

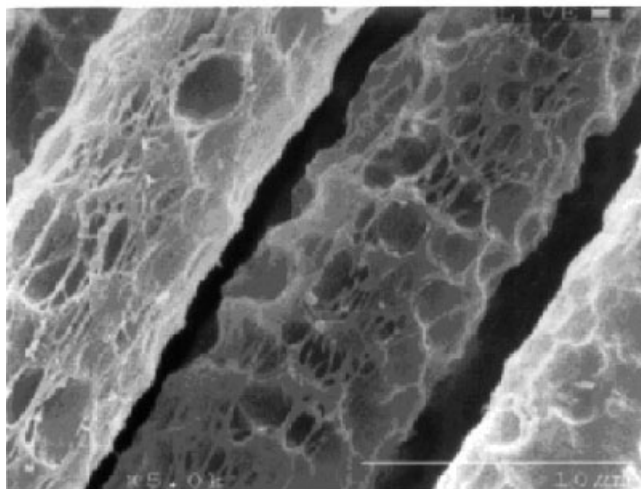
Figure 8 shows the effect of molecular weight of additive polymer. Elongation increases with molecular



(a)



(b)



(c)

Figure 3 SEM Photographs of as-spun fiber after treating 15% NaOH solution (100°C, 30 min) with no additive polymer (a), additive polymer of $M_w = 183,000$ (b), and additive polymer of $M_w = 207,000$ (c).

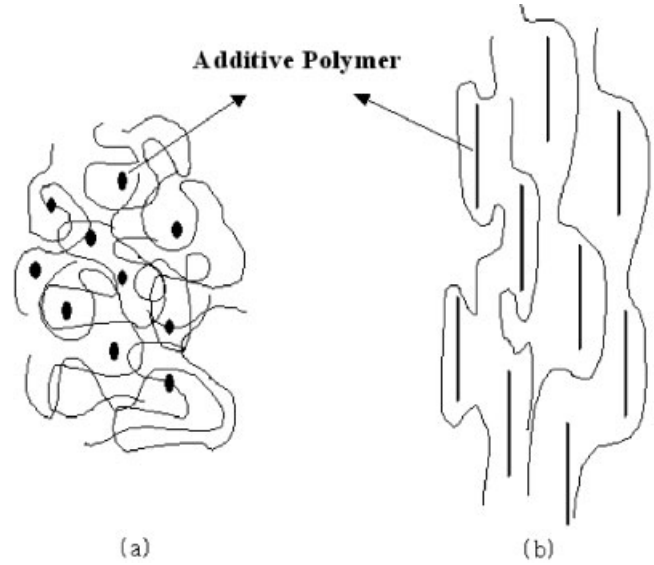


Figure 4 Assumed schematic of additive polymer in the molten state (a) and after spinning (b).

weight of additive polymer and its effect is remarkable from M_w of 207,000. This could be explained by melt viscosity behaviors of PET and copolymer. Spinline stress increases with melt viscosity in the melt spinning.^{15,16} Higher melt viscosity induces larger spinline stress. The extension of high-molecular weight additive polymer would be greater since spinline stress of high-molecular weight additive polymer is relatively larger under the same spinning conditions. As shown

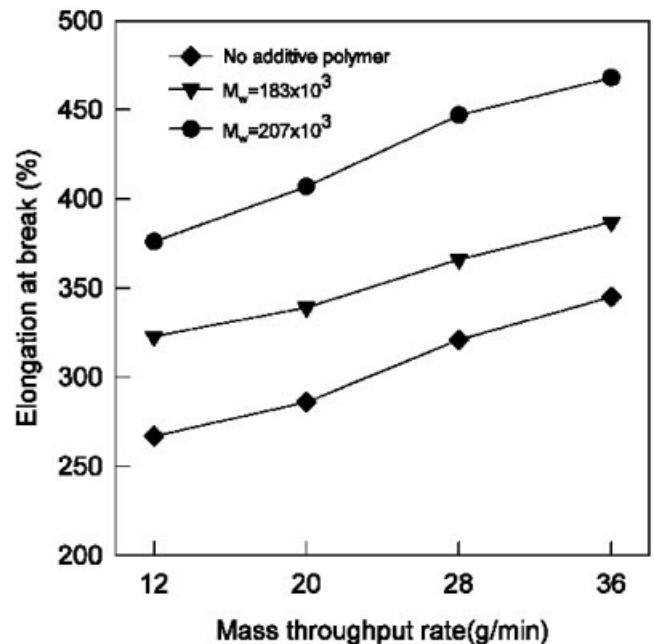


Figure 5 Elongation at break of as-spun filament versus mass throughput rate: additive polymer, 2 wt %; take-up speed, 1500 m/min; spinning temperature, 290°C.

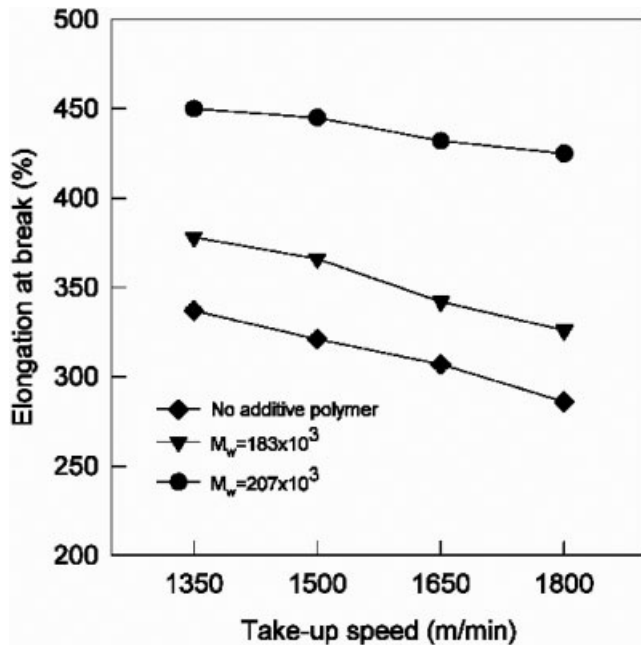


Figure 6 Elongation at break of as-spun filament versus take-up speed: additive polymer, 2 wt %; mass throughput rate, 28 g/min; spinning temperature, 290°C

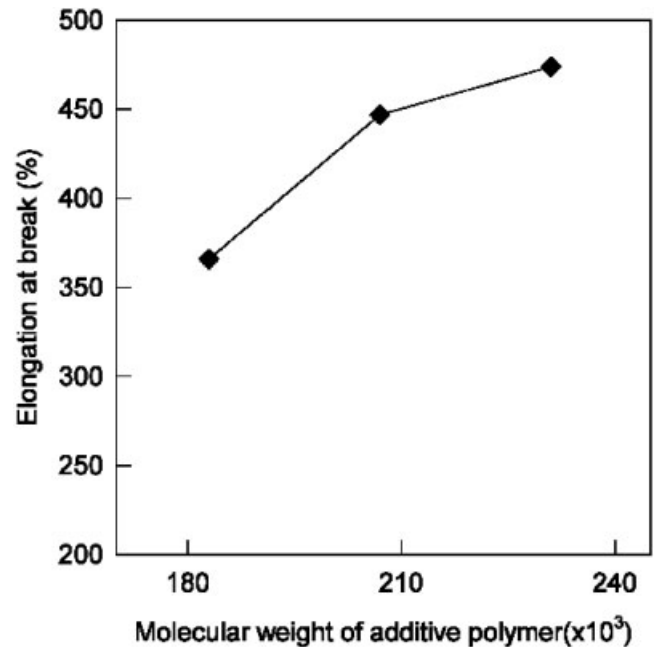


Figure 8 Elongation at break of as-spun filament versus molecular weight of additive polymer: additive polymer, 2 wt %; mass throughput rate, 28 g/min; take-up speed, 1800 m/min; spinning temperature, 290°C.

in Figure 3, thinner strand was shown in fibers mixed with M_w of 207,000 in comparison with M_w of 183,000. The more elongated high-molecular weight additive polymer suppresses the orientation of matrix PET than does the low molecular one. The melt viscosity behav-

iors at high shear rate could explain the remarkable increase of elongation at break around molecular weight of 207,000 (Fig. 9) since melt spinning is processed in the high shear rate range more than 1000 s^{-1} . Melt viscosity of M_w of 231,000 increases stiffly at low shear rate, but that of M_w of 207,000 increases remarkably at high shear rate. Melt viscosity of M_w of 183,000 approximates to that of PET at high shear rate.

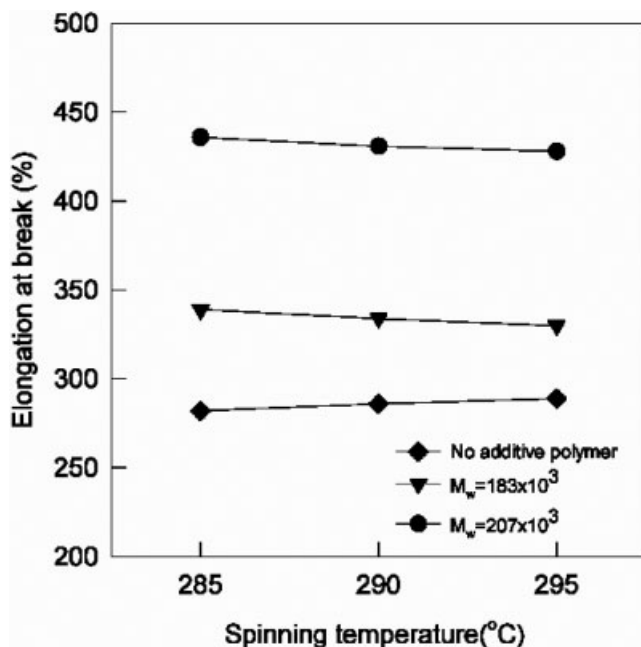


Figure 7 Elongation at break of as-spun filament versus spinning temperature: additive polymer, 2 wt %; mass throughput rate, 28 g/min; take-up speed, 1800 m/min.

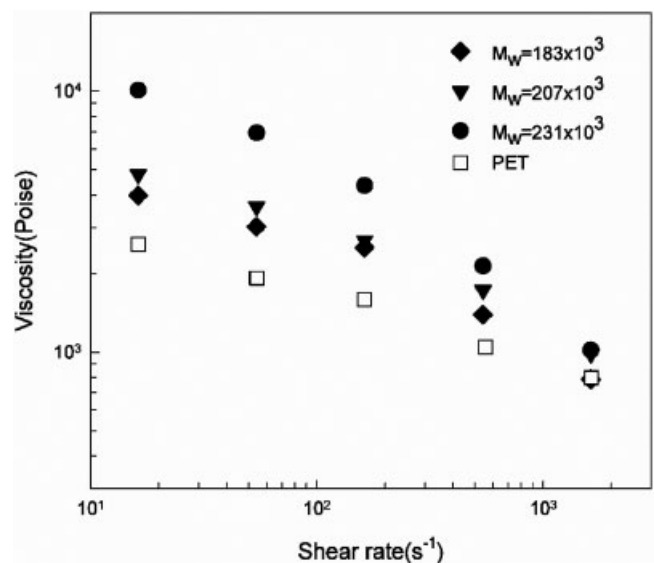


Figure 9 Melt viscosity of additive polymers as a function of shear rate.

TABLE III
Zero Shear Viscosity and Power Law Index of Different Molecular Weight Additive Polymers

Molecular weight ($\times 10^3$)	Zero shear viscosity (Poise)	Power law index
183	4000	0.7
207	4800	0.6
231	10100	0.5

viscosity of M_w of 207,000 exceeds considerably that of PET at high shear rate and then only the effect of additive polymer on elongation is remarkable. Table III shows the zero shear viscosity and power law index for different molecular weight additive polymers. Power law index representing the magnitude of shear thinning was obtained from log-log plot of melt viscosity versus shear rate.^{17,18} Power law index of high-molecular weight additive polymer is smaller than that of low molecular weight additive polymer.

CONCLUSIONS

To analyze the effect of additive polymer in the melt spinning process of PET, additive polymer was mixed with PET using a compounding extruder. The change of elongation at break was investigated with the spinning conditions and characteristic of additive polymer. The additive polymer plays an important role of preventing the orientation of PET molecules during spinning, and this results in the increase of elongation at break of as-spun fibers. The elongation at break increases with the amount of additive polymers and the molecular weight of additive polymer. As the mass throughput rate increases and the take-up speed

decreases, the elongation at break of as-spun filament increases. The spinning temperature has a little effect on the elongation at break, when compared with other spinning variables. The attained elongation at break, by adding additive polymer of molecular weight of 237,000, amounts to 475%, which is one and a half times increase in comparison with no additive polymer.

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