Improvement of mechanical properties using structure control via processing techniques for thermoplastic polyester elastomer

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Due to a recent increase in the interest in environmental issues, recyclability has been considered as the most important performance for industrial materials. Conventional elastomers like cross-linked rubbers are inevitable in many industrial fields because of their unique mechanical properties, i.e., low modulus, high heat resistance, and rubber elasticity which is the ability to recover to the original shape. However, their recyclability is poor due to the chemical cross-linking among their molecular chains. Thermoplastic elastomers (TPE) are expected as a great candidate to replace from cross-linked rubbers because of their recyclability, processability, and rubber elasticity. In particular, thermoplastic polyester elastomer (TPEE) shows the highest heat resistance and mechanical properties in the commercially available TPEs due to its multiblock structure of poly(butylene terephthalate) (PBT) hard-segments and poly(tetramethylene glycol) (PTMG) soft segments. However, the rubber elasticity of TPEE is not good enough compared with cross-linked rubbers. Therefore, they have not been used in some applications like tires and conveyor belts. Hence, I tried to improve the rubber elasticity of TPEE by processing techniques.

First, the effect of processing temperature on the structure and mechanical properties of TPEE was investigated by thermal analyses and rheology measurements. At slightly above the peak melting point, TPEE showed flow ability even though it had unmolten crystals. Also, TPEE showed characteristic rheological behaviors, i.e., marked non-Newtonian behavior at such temperature with modulus increase. Moreover, the compression-molded sample processed at the temperature showed a well-developed crystalline structure, which was confirmed by differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), small-angle X-ray scattering (SAXS), dynamic mechanical analyses, and transmission electron microscopy. Considering these rheological behaviors, it can be summarized that this drastic structural change was caused by the melt memory effect, which is the strong crystallization effect promoted by the unmolten crystals. According to the remarkable phase separation by the melt memory effect, the tensile properties and rubber elasticity at a constant stress of TPEE were improved. These results suggest that the rubber elasticity of TPEE can be controlled by the modification of phase-separated structure using processing techniques.

Considering the industrial applications of TPEE, the effect of melt memory on the extrusion and drawing process was also examined. At slightly above the melting point, TPEE showed prolonged relaxation time, which was detected by the linear viscoelasticity measurement. Also, the extruded strand showed a higher swell ratio and drawdown force, i.e., the force needed to stretch a molten strand. These results suggested that the unmolten crystals acted as crosslink points of a network structure in TPEE. Also, the strand extruded with the melt memory effect showed an apparent orientation which is confirmed by the polarized optical microscope, 2D-WAXD, 2D-SAXS, and Raman spectroscopy. The orientation was promoted by the prolonged relaxation time and increase in crystallization rate due to the melt memory effect. More interestingly, the oriented structure was anomalous, i.e., the crystalline chains oriented perpendicular to the drawing direction although the amorphous chains oriented to the drawing direction. Because of a fibrous shape of TPEE lamellae, the unique cross-orientation structure was generated. In other words, the crystal lamellae oriented to the flow direction due to hydrodynamic force at the capillary extrusion. These unique oriented strands showed improved mechanical properties because of their orientation and well-developed crystals.

Finally, the technique to modify the melt memory effect of TPEE was examined. In actual processing operations, the processing temperature is not constant. To widen the applicable temperature range of the melt memory effect, therefore, a small amount of PBT was mixed. Pure TPEE showed the melt memory effect 15 ^{o}C above the peak melting point. In contrast, the TPEE/PBT blend showed such effect 30 ^{o}C above the peak melting point. Considering that the melting point of PBT is higher than that of TPEE, this modification was caused by the co-crystallization of TPEE and PBT. The compression-molded films of the TPEE/PBT blend showed well-developed crystalline structure and favorable mechanical properties in a wide temperature range by the PBT crystals. In the extrusion process, the effect was more apparent because of the oriented structure generated by the melt memory effect. This technique is expected to be employed as a practical method using the melt memory effect in industry.

Keywords: Thermoplastic polyester elastomer, Rubber elasticity, Melt memory effect, Orientation, Polymer blend