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Rheological properties and processability of Chemically Modified Poly (ethylene terephthalate - co - ethylene isophthalate)

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1. INTRODUCTION

It has been of great interest in recycle system with the rapid growth of the attention to environment in the plastic industry these days [1][2]. As well known poly (ethylene terephthalate) (PET) is one of the most advanced polymers from the view point of the recycle, because large amounts of PET bottles are recovered, more than 60% in Japan in 2005. Further, extensive efforts have been carried out in both academia and industries to widen the application of recycled PET because of the poor processability due to the lack of melt elasticity with low viscosity as well as the brittle nature in the solid state.

In this study, a polymeric material having epoxy functionality is used as a chain extender to improve the processability at extrusion of polyester. It would be preferred to employ a polymeric reagent because of easy handling in both solid state (pellet form) and molten state (high viscosity). Although numerous studies [2][3-8] have been carried out for blends of PET and polymeric modifiers, such as ethylene-vinyl acetate copolymer, ethylene-propylene copolymer, ethylene-glycidyl methacrylate, and ethylene-ethyl acrylate-glycidyl methacrylate, most of them are focused on the improvement of toughness and the relation with the morphology. Since the interest of this study is to control the rheological properties and processability, the amount of the modifier is quite less as compared to the impact modifier.

2. EXPERIMENTAL

2-1 Materials

Poly(ethylene terephthalate-co-ethylene isophthalate) P(ET-EI) was employed in this study instead of PET. P(ET-EI) can be evaluated at lower temperature which avoid thermal degradation because of less crystallinity, rheological properties and extrusion processability.

The modifier employed in this study was styrene-acrylate-based copolymer with glycidyl functionality. The epoxy equivalent is 1.8 [meq/g].

2-2 Processing

Mixing of P(ET-EI) and 10 wt% of the modifier was performed firstly by a co-rotating twin-screw extruder with L/D=22 at 100 rpm. The temperature profile of the extruder was as follows; C1 190 °C, C2 220°C, C3 230°C, and Die 230 °C. The extruded strand was cut into the pellet form. Then, P(ET-EI) and 10 - 40 wt% of the obtained pellet, i.e., 1 - 4 wt% of the modifier, were put into a single-screw extruder with a full-flight screw (L/D=20, CR=2.1) having the following temperature profile; C1 200 °C, C2 210°C, C3 210°C, and Die 210 °C. The screw rotation was 30 rpm, and the Garvey-type die was employed.

2-3 Measurements

The oscillatory shear moduli, such as shear storage modulus G' and loss modulus G'' , were measured by a cone-and-plate type rheometer (UBM, MR500) at 210°C. The molecular weight and its distribution of the extrudates were investigated by a gel permeation chromatograph, G.P.C., (Tosoh, HLC-8020) with TSK-GELTR GMHXL as a polystyrene standard. In G.P.C. measurements, the sample was firstly dissolved into

hexafluoroisopropanol at the concentration of 10 mg/ml and then the solution was diluted by chloroform at the concentration of 1 mg/ml. The measurements were carried out by injection of the diluted solution at 40 °C at a flow rate of 1.0 ml/min.

3. RESULT and DISCUSSION

Figure 1 shows the extrudates from the die. It demonstrates that the modified materials show extrudate swell, which is pronounced with increasing the amount of the modifier. Further, heat sagging, i.e., downward-deformation of a molten polymer by gravitational force, is quite improved by the modifier, implying that the modified material will be applied to various processings, such as extrusion, blow-molding, thermoforming, and foaming.

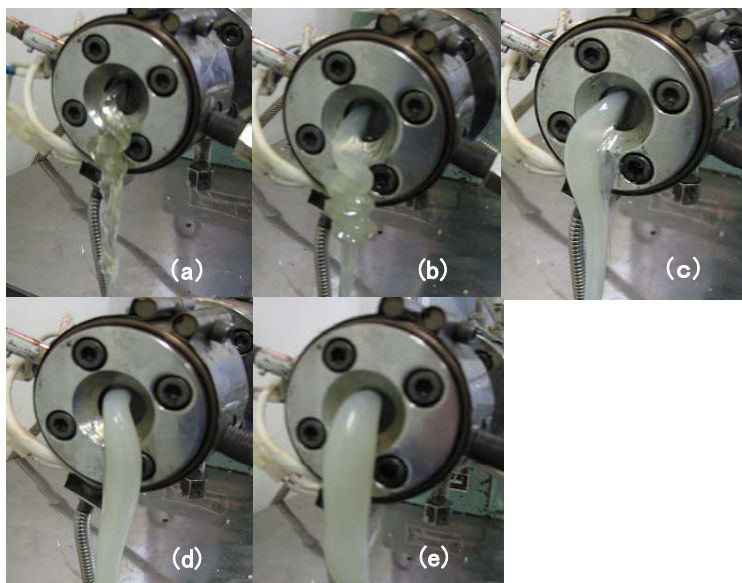


Figure 1 Appearance of extrudates from Garvey-die controlled at 210 °C for (a) P(ET-EI), (b) 1 wt%, (c) 2 wt%, (d) 3 wt%, and (e) 4 wt%.

The rheological properties of the extrudates are measured by a cone-and-plate rheometer. Figure 2 exemplifies the oscillatory shear moduli of P(ET-EI) and the modified P(ET-EI) with 2 and 4 wt% of the modifier. Both G' and G'' increase with the amount of the modifier, suggesting that average relaxation time increases. Further, the slope of G' for the modified P(ET-EI) becomes small especially in the low frequency region. The result indicates the existence of prolonged long-time relaxation mechanism. Consequently, the storage modulus is more sensitive than the loss modulus by the modifier as demonstrated in Figure 3.

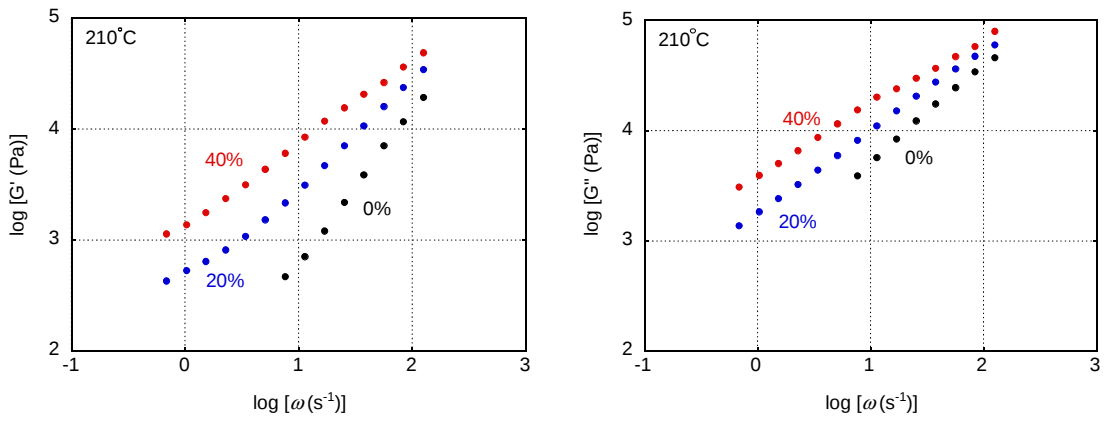


Figure 2 Frequency dependence of oscillatory shear moduli for extrudates of P(ET-EI) and the modified P(ET-EI) at 210 °C.

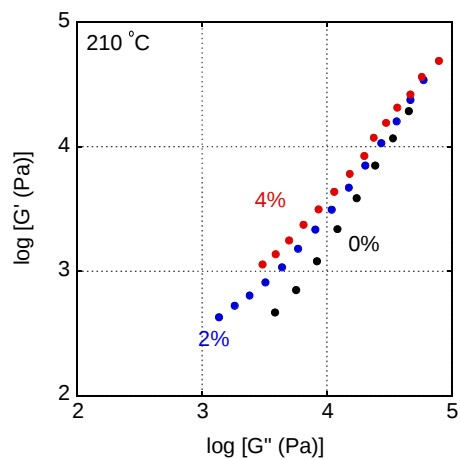


Figure 3 Modified Cole-Cole plot for extrudates of P(ET-EI) and the modified P(ET-EI) at 210 °C.

In order to check the mechanism of the enhancement of melt elasticity, G.P.C. measurements are carried out employing extruded samples. As shown in Figure 4, blending the modifier has little effect on the molecular weight and distribution. Further, it is confirmed, but not presented here, the G.P.C. curves of the modified P(ET-EI) are almost same as that of the pure P(ET-EI). The experimental results of the molecular weight measurements indicate that the enhancement of melt elasticity by the modifier is mainly ascribed to generation of long-chain branches [9].

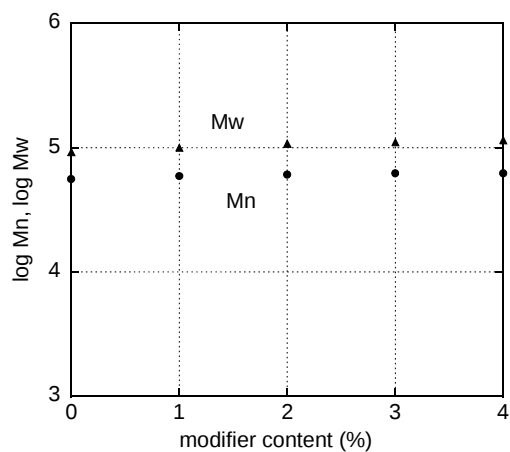


Figure 4 Effect of modifier content on number-average molecular weight Mn and weight-average molecular weight Mw for extrudates.

4. CONCLUSION

The improvement of processability at extrusion of polyester has been carried out by means of reactive extrusion with styrene-acrylate-based copolymer. Adding the reactive modifier enhances melt elasticity to a great extent, which is attribute to formation of branched structure.

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