

Material Properties

Mechanical properties of thermoplastic polyester elastomer controlled by blending with poly(butylene terephthalate)

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ABSTRACT

Thermoplastic polyester elastomer (TPEE) blends with poly(butylene terephthalate) (PBT) were prepared by melt compounding for the phase morphology and mechanical property studies. Although PBT is immiscible with the continuous soft poly(tetramethylene glycol) (PTMEG) phase of TPEE, it is miscible with the discrete hard PBT one of TPEE. Therefore, PBT and TPEE are compatible and their blends reveal very low level of interfacial tension and very small size of discrete domains, as well as good interfacial adhesion between two phases, which provide high possibility to prepare TPEE alloys with controllable properties. Mechanical test results reveal that both the modulus and yield and tensile strengths increase with increasing weight ratios of PBT. The increased system rigidity and decreased system plasticity are further confirmed by the cyclic tensile tests. The main objective of this work is to provide useful information on the structure and property control of TPEE by simple mixing with aromatic polyesters.

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1. Introduction

As a new member in the thermoplastic elastomer (TPE) family, thermoplastic polyester elastomer (TPEE) has recently attracted much attention for the application in automotive, fluid power and electronic, as well as sporting goods [1]. Its hard segments are commonly crystalline polyesters such as poly(butylene terephthalate) or poly(ethylene terephthalate), and the soft segments are amorphous polyethers such as poly(tetramethylene ether glycol terephthalate) or poly(alkylene glycol) [2]. Similar with other members in the TPE family, the hard crystalline domains of TPEE determine elastomeric properties and thermal resistance, while the soft amorphous ones exhibit good low-temperature flexibility [3]. Accordingly, TPEE shows combination of high-temperature mechanical properties and good low-temperature flexibility [4,5]. Besides, it has better resistance to tear and impact, and higher resistance to oil and hydraulic fluids relative to the traditional TPEs [6,7].

Hybridization with micro-sized or nano-sized particles, such as clays, talc, mica, silica, fly ash, and carbon nanotubes [8–12], is a

commonly used way to improve overall properties of TPEE. The reported results reveal that the composite technology is very effective for the reinforcement and stability improvement of TPEE. It is also an effective strategy to endow TPEE with new properties, for instance, electrical conductivity. Another convenient way of control of the structure and final properties of TPEE is to blend it with the polymers with various intrinsic properties, including crystalline and amorphous polyesters, and polyolefin [5–7,12–17]. Some new TPEE based blend materials and/or alloys with excellent flex fatigue and broadened service temperature range has been developed successfully using the blending technology. For instance, Hussain et al. [12] found a significant improvement in both the mechanical and thermal properties of TPEE using thermoplastic poly(butylene terephthalate) (PBT) as the blended component. With addition of a small amount of clay, there was further property improvement.

But the reported work on the TPEE blend systems is still very limited because TPEE is a newly-developed material. Some key issues around phase structure and structure-property relationships in the TPEE based blends, for instance, how the presence of second polymer component affect phase separation structure of TPEE, and how the multiphase structure of TPEE blends affect their final properties, etc., are not very clear. Therefore, in this work, a widely used aromatic polyester, PBT, which has the same chain structure

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with the hard segments of TPEE, was chosen as the second component to be blended with TPEE to prepare the TPEE/thermoplastic polyester blends for the phase structure–property relation detected. The immiscible morphology and interfacial structure of the blend systems were studied, aiming at figuring out the relations between phase separation structure of TPEE and additional component phase. Then, the viscoelastic and mechanical properties of the blend system were explored in detail by the step cycle tensile tests. The main objective of this work is to provide useful information on the structure and property control of TPEE by the simple blending approach using the polyesters with similar chain structure with the polyester segments of TPEE.

2. Experimental

2.1. Material preparation

Thermoplastic polyester elastomer (KP3340) was purchased from KOLON Co. Ltd., Korea. Its number-average molecular weight (M_n) is 36,000 g mol⁻¹, with poly(butylene terephthalate) (PBT, 50.69 wt%) as the hard segments, and poly(tetramethylene glycol) (PTMEG, 49.31 wt%) as the soft segments (molar ratio = 25/75, measured by the approach of nuclear magnetic resonance (NMR) [18]). The nanosized domains of hard PBT phase of TPEE, with the average size of about 100 nm, are dispersed in its continuous soft PTMEG phase (Fig. 1), which was studied in the previous work [10]. Its density is about 1.17 g cm⁻³. Poly(butylene terephthalate) (1097A, M_n = 23,200 g mol⁻¹) with the density of 1.31 g cm⁻³ was purchased from Nantong Xinchun Synthetic Material Co. Ltd., P. R. China. Its end –COOH values lower than 0.03 mmol g⁻¹.

The TPEE/PBT blends were prepared by melt mixing using a Haake PolyLab Rheometer (Thermo Electron Co., USA) at 240 °C and 50 rpm for 6 min. For better comparison, the neat TPEE and PBT were also processed to keep the same thermal histories. All materials were dried under vacuum for 24 h before using. The sheet samples with the thickness of about 1 mm for morphological and rheological tests were prepared by compression molding at 240 °C and 15 MPa. The rectangular specimens (30 mm × 5 mm × 1 mm) and the dog-bone shaped ones (32 mm × 4 mm × 2 mm) were prepared by a Haake mini-jet (Thermo Scientific Co., USA) for the mechanical tests. The injection molding was performed at the cylinder temperature of 240 °C, with the injection pressure 600 bar

and holding pressure 500 bar. Hereafter the blends are referred as to TPEEm/PBTn, where m and n ($m + n = 10$) denote the weight ratio of TPEE and PBT, respectively.

2.2. Morphological characterizations

The phase morphologies of the blend samples were studied using a Philips XL-30ESEM (Netherlands) and a Zeiss SUPRA55 (Germany) scanning electron microscope (SEM) with 20 kV accelerating voltage. The sheet samples were frozen in liquid nitrogen and fractured. The fractured surfaces were then coated with gold using an SPI sputter coater for enhanced conductivity. The number average radii (R_n) of the domains were determined respectively according to the following relations:

$$R_n = \frac{\sum_i n_i R_i}{\sum_i n_i} \quad (1)$$

where n_i is the number of the dispersed domains with radii R_i counted from the SEM images. The total number of domains analyzed was about 100. The highest deviations of the calculated average radii were ±0.08 μm. The phase separation morphology of TPEE were detected at the room temperature using an Icon atom force microscope (AFM, Bruker Co. Ltd., USA) in the quantitative nanomechanical mapping mode (QNM). The silicon probes were used (tip radius < 8 nm, force constant 40 N/m, resonance frequency 300 kHz) to acquire images. Image processing and mechanical properties analysis were performed with the NanoScope Analysis software.

2.3. Deformed drop retraction experiments

A modified deformed drop retraction method developed by Bousmina and coworkers [19] was used here to estimate the interfacial tension between TPEE and PBT. This method consists of studying the kinetics of relaxation of a deformed droplet, in this case a short PBT fiber between two TPEE thin films. The relaxation kinetics is based on a theoretical equation describing the shape evolution of an ellipsoidal liquid drop suspended in an infinite fluid domain. Upon cessation of the flow,

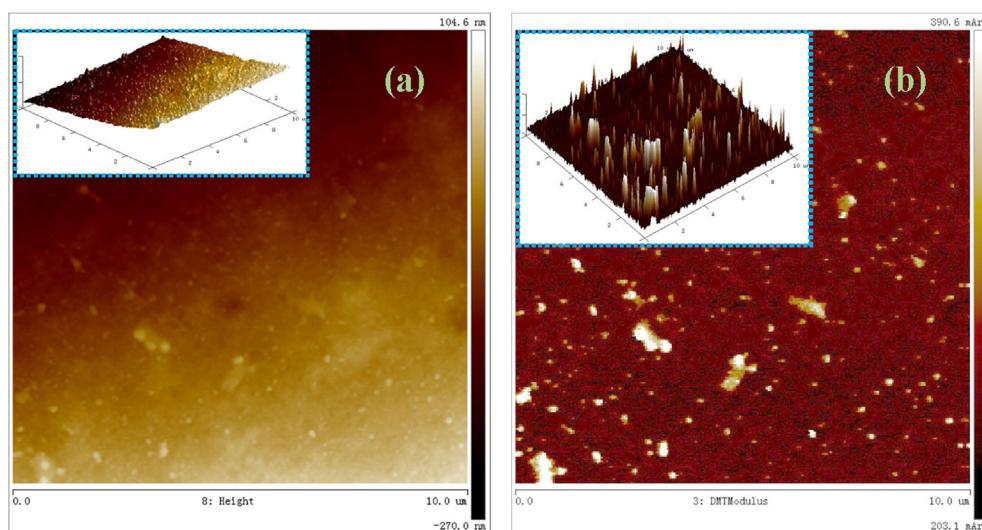


Fig. 1. AFM (a) height and (b) modulus images (10 μm × 10 μm) of neat TPEE. The inset graphs are 3D images of the scanned area.

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