Morphology and Mechanical Properties of Polyamide 6 and Polybutylene Terephthalate Blends Compatibilized with Epoxidized Natural Rubber

P Sapsrithong¹, T Sritapunya¹, S Tuampoemsab¹, A Rattanapan¹, MNithitanakul²

¹Division of Polymer Engineering Technology, Department of Mechanical Engineering Technology, College of Industrial Technology, King Mongkut’s University of Technology North Bangkok, Bangkok, 10800, Thailand
²The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, 10330, Thailand

Abstract. Blends of polyamide 6 (PA6) and polybutylene terephthalate (PBT) have been prepared in this work. They were compatibilized using epoxidized natural rubber (ENR-50) by varying amount of ENR-50 i.e., 0, 3 and 5 phr. The effect of blend compositions and compatibilization on the phase morphology and properties of the resulting blends were investigated using a scanning electron microscope, universal testing machine, impact testing machine, and hardness shore durometer. All blends were prepared and shaped by using twin-screw extruder at 260°C and injection molding machine, respectively. The results revealed that the phase morphology of the PA6/PBT blend was incompatible. The separation of PA6 and PBT was observed wherein PBT is dispersed in the form of spherical domains in the PA6 matrix. The mechanical properties exhibit loss in tensile and impact strength. This could be attributed to poor interfacial adhesion between the two polymers. SEM micrographs showed that the addition of ENR-50 improved the compatibility of PA6/PBT blends. With the addition of ENR-50 as a compatibilizer, the uniformity and the maximum reduction of dispersed phase sized were achieved. The water absorption of PA6/PBT blends decreased with an increasing amount of PBT. Additionally, the results indicated that, as the amount of ENR-50 increased, the mechanical properties, including tensile stress at peak, tensile modulus, and izod impact strength were improved.

1. Introduction

High-performance plastics are playing a more important role in the automotive industry because of their many advantages, including high strength, lightweight, minimal corrosion, flexibility, excellent appearance and, recyclability. Many types of plastic are being employed for the application in the automotive industry, such as polystyrene (PS), polypropylene (PP), polyethylene (PE), polyvinyl chloride (PVC), polyamide (PA), acrylonitrile butadiene styrene (ABS), polycarbonate (PC), acrylonitrile styrene acrylate (ASA) and polybutylene terephthalate (PBT), etc. They are frequently used when a low cost, high mechanical strength, good heat and chemical resistant, durable material is desired [1]. Unfortunately, a number of problems limit their extensive applications. So, the utilization of polymer blends is an increasingly important part of the plastic industry. There are many studies...
focus on polymer blend such as PS/PE, PA/PE, PP/PE, PA/PC, etc [2-5]. Additionally, PA6 and PBT are both high-performance engineering polymers with commercial significance. The advantages of PA6 and PBT are mentioned, i.e., high strength, good thermal and chemical resistance and excellent barrier property which versatile industrial applications. However, the limitation of PA6 was also remarked, it has high moisture absorption. In order to create new and useful materials, blends of polyamide (PA) and polybutylene terephthalate (PBT) were successfully determined by many researchers since both polymers are among the most frequently used [6-9]. Unfortunately, blend of two different materials cannot be compatible with each other leading to phase separation and reduce mechanical properties. Therefore, a suitable interaction between the phases must be added to the blends in order to obtain finer morphology and reduce the interfacial tension between the two polymers. The formation of the polyester-polyamide copolymer can be occurred by ester-amide interchange reaction [7]. The compatibility of polyamide and polyester could improve the adhesion between two phases, but the mechanical properties and crystallinity will reduce. Numerous research works have been carried out in order to improve interfacial adhesion and properties of the polymer blend. The addition of suitable compatibilizer is one of the most effective methods to improve compatibility and also properties [10-12]. In 2001, Han and coworker have reported that the compatibility between PA6 and PBT was observed in the presence of ethylene glycidyl methacrylate (EGMA) as a compatibilizer [6]. They found that EGMA could be used as a compatibilizer leading to increasing mechanical properties of the blends. Huang and Chang studied the improvement of morphology and properties of PA/PBT blends with the use of epoxy resin as a compatibilizer, resulting in good mechanical properties were obtained [7]. The addition of acrylic modified polylefin type ionomer to polyester/polyamide6 blends was also reported by Samios and Kalfoglou [13]. They found that a polymer blend with ionomer compatibilizer leads to improve tensile and impact properties.

Solid-state epoxy resin has also been used by several researchers to compatibilize the polymer blends, including PA6/PBT, PC/poly(acrylonitrile-butadiene-styrene), PC/PBT/LCP, PP/PBT [5]. Solid epoxy resin is an attractive compatibilizer because of the formation of in situ block copolymer between the epoxide end-groups with end-groups of PA6, PBT or PC. Epoxidized natural rubber (ENR) is derived from natural rubber by introducing hydrophilic groups (with epoxide units randomly with 25 or 50 mol% epoxidation) along the isoprene backbone. The epoxidation of ENR leads to improve properties and also the miscibility with polar polymers because the oxirane ring increases the hydrophilicity. Recently, epoxidized natural rubber (50 mol% epoxidation: ENR-50) has been considerable interest in the research of polymer blend and composite due to the ability of the epoxide group of ENR that can be used to improve the compatibility of the system [14, 15]. The interaction can take place between the epoxide group of ENR and the polar group of the polymer. The effectiveness of ENR-50 was previously demonstrated in poly(lactic acid)/rice starch composites [14], linear-low-density polyethylene (LLDPE)/soya powder blends [15], poly(lactic acid)/natural rubber blends [16] and PA6/LDPE blends [17]. They reported that the improvement in morphology and mechanical properties was observed. The compatibility between the phase increases because of the incorporation of ENR-50 into the system. The aim of this work is to investigate the compatibilizing effect of epoxidized natural rubber (ENR-50) on the morphology, and mechanical properties of PA6/PBT blends.

2. Experimental

2.1. Materials
Polyamide 6 (PA6 grade 1013 NW8), an injection molding grade polymer, was supplied by UBE Industries, Ltd. Polybutylene terephthalate (PBT: Ultradur® B2550) supplied by BASF (Thai) Limited. Epoxidized natural rubber (50 mol% epoxidation: grade ENR-50) compatibilizer was supplied by San-Thap International Co., Ltd. All materials were used as received.

2.2. Compounding and Specimen Preparation Characterizations
PA6 and PBT were externally mixed using a tumble mixer for 10 minutes, followed by drying them in a hot air oven at 60°C for 24 h before use, to remove any absorbed moisture. Blends of PA6 and PBT were prepared in 100/0, 90/10, 80/20 and 0/100 % by weight. The amount of ENR-50 used as a
compatibilizer was 0, 3 and 5 phr for PA6/PBT: 90/10 and 80/20 % by weight. The materials were blended in a twin-screw extruder at 260°C using a screw speed of 40 rpm. The extruded pellets were dried in an oven at 60°C for at least 24 h. Test specimens were prepared using a Boy 22M injection molding machine at 260°C.

2.3. Characterizations
The fracture micrographs, as well as the dispersed structure of the fractured samples, were studied by using FE-SEM (Hitachi S-4800, Japan) at a voltage of 15.0 kV. The samples were fractured under liquid nitrogen and then coated with platinum on a sputter coater, under vacuum, to make them electrically conductive. The water absorption measurement was conducted per ASTM D570. Samples were dried, weighed after that immersed in distilled water. After 24 h., specimens were removed from the water and wiped with a dry cloth and weighed again. A Universal Testing Machine was used to measure the tensile properties of the obtained materials in accordance with ASTM D638. Izod impact strength was measured using a CEAST Impact tester according to ASTM D256 test procedure method with a 2.7 J pendulum. The hardness was tested by shore hardness durometer (Shore D) in accordance with ASTM D2240.

3. Results and Discussion
Phase morphology of the blends between PA6 and PBT was determined using a field emission scanning electron microscope. Figure 1 presents SEM micrographs taken from the cryogenically fractured surface of 80/20 PA6/PBT blends with different ENR-50 content from 0-5 phr. Morphology of the uncompatibilized blends exhibited two-phase morphology with phase separation between PA6 and PBT and contained numerous voids and rough surfaces. The presence of PBT dispersed phase, consisting of predominantly spherical droplets embedded in a PA6 matrix, was clearly observed from the micrographs. Moreover, big gaps between two phases were clearly observed implying relatively poor interaction. The average diameter of the PBT dispersed phase is about 4.6 µm. However, most of the PBT dispersed phase still kept intact within the PA6 matrix. This could be due to some of the interaction between the polar group of both PA6 and PBT. When the 3 and 5 phr of ENR-50 was used in PA6/PBT blend, the dispersed phase size was reduced. This phenomenon can be explained by the presence of ENR-50, which acted as a compatibilizer leading to enhance the interfacial bonding between the PA6 matrix and PBT. A more stable morphology with a smooth surface and a smaller droplet size can be observed with increasing ENR-50 content in blends. The number average dispersed phase size ranged between 1.2 and 1.8 µm, which were much smaller than in the uncompatibilized blends. This observation is an agreement with work reported by Yew et al. [14] that the presence of the polar group of ENR-50 promoted the compatibility between matrix and filler.

![Figure 1. SEM micrographs of PA6/PBT blends (80/20 %wt) with different amount of ENR-50.](image-url)
Figure 2 illustrated the percentage of water absorption of PA6/PBT blends both with (w/ ENR-50) and without ENR-50 (w/o ENR-50) as a compatibilizer. It is well known that polyamide 6 has a drawback that is moisture sensitive. According to Gadekar et al. the increase in the amount of water in PA6 was mainly due to the amide groups, thus blending PA6 with non-sensitive materials can overcome this problem [3]. Usually, the value of the percentage of water absorption of PBT was lower than that of pure PA6. So, the addition of PBT decreased the amount of water absorbed by PA6/PBT blends (from 1.6% to 1.1%). The percentage of water absorption of PA6/PBT blends increased with the incorporation of ENR-50. This may be attributed to the polarity of ENR-50 that will enhance bonding formation with water molecules.

The effect of blend compositions and ENR-50 content on the tensile properties of PA6/PBT blends is shown in figure 3. For PA6/PBT blends without compatibilizer, a decrease in tensile stress and young’s modulus were observed. This could be due to the poor interfacial adhesion between PA6 and PBT. However, the tensile properties between 90/10 and 80/20 wt% of PA6/PBT blends were slightly different. The addition of ENR-50 (50 mol% epoxidation) into PA6/PBT blends improved both tensile stress and young’s modulus. This may be attributed to the compatibilization effect of ENR-50 that could form interaction with the polar group of PA6 and PBT, which results in better stress transfer between two phases. This behavior can be explained by the observation from SEM micrographs of the blends, which clearly indicated that the finer morphology with the smaller size of the dispersed phase was observed.

Figure 3. Tensile Stress and Young’s Modulus of PA6/PBT/ENR-50 blends.
Figure 4. Impact Strength and Hardness (Shore D) of PA6/PBT/ENR-50 blends.

The notched impact property of blending between PA6 and PBT is illustrated in Figure 4 (a), for PA6/PBT blends without ENR-50, a drastic decrease in notched impact strength with an increasing amount of PBT was reported, which is attributed to phase separation between matrix and dispersed phase. The incorporation of ENR-50 as a compatibilizer was found to improve the impact strength and further increase with an increasing amount of ENR-50. This improvement can also be explained by the reduction of interfacial tension between phases, which allow absorbed energy to transfer from one phase to another and elastomeric behavior of ENR-50 [14, 15]. Additionally, according to figure 4 (b), it could be observed that the hardness of PA6/PBT blends is slightly different as compared with pure PA6 and PBT. The effect of compatibilizer loading on hardness was also investigated. In PA6/PBT blends containing compatibilizer, the values of hardness were lower than that of pure PA6 and PBT for all compositions. The hardness of PA6/LDPE/ENR-50 was slightly decreased as the ENR-50 content increased due to the addition of the elastomeric component.

4. Summary

Blends of two significant engineering plastics were successfully prepared and investigated in this study in order to create new and suitable materials for the automotive industry. The effect of blend composition and compatibilizer content on phase morphology, water absorption and mechanical properties of PA6/PBT blends were reported. The percentage of water absorption of PA6/PBT blends was found to decrease with increasing PBT content. Mechanical properties, including tensile stress and young’s modulus of blends with different amounts of PBT are slightly different and still lower than pure materials due to poor adhesion between the phases. Results of the study also indicated that the epoxidized natural rubber with 50 mol% epoxidation (ENR-50) was capable for using as a compatibilizer for blends of PA6 with PBT. The improvement in phase morphology and mechanical properties of PA6/PBT blends was observed. The number average size of dispersed phase of the compatibilized blends decreased from 4.6 to 1.2 µm. The reduction of dispersed phase size could be attributed to a strong interaction between the polar group of ENR-50, PA6, and PBT, which reduced the interfacial tension between phases. From the results of mechanical properties, it was found that tensile and impact properties increased with the increase in ENR-50 content.

Acknowledgments

Authors gratefully acknowledge the scholarship provided by College of Industrial Technology, King Mongkut’s University of Technology North Bangkok, and Bangkok, Thailand.

References

[1] Patil A, Patel A, Purohit R 2017 An overview of Polymeric Materials for Automotive Applications, Mater. Today: Proceed. 4: 3807-15.
[2] Dobrovsky K, Ronkay F 2016 Investigation of compatibilization effects of SEBS-g-MA on polystyrene/polyethylene blend with a novel separation method in melted state, *Polym. Bull.* **73**: 2719-39.

[3] Gadekar R, Kulkarni A, Jog J P 1998 Blends of Nylon with Polyethylene: Effect of Compatibilization on Mechanical and Dynamic Mechanical Properties, *J. Appl. Polym. Sci.* **69**: 161-8.

[4] Tai C M, Li R K Y, Ng C N 2000 Impact behaviour of polypropylene/polyethylene blends, *Polym. Test.* **19**: 143-54.

[5] Tjong S C, Meng Y Z 2004 Structural-mechanical relationship of epoxy compatibilized polyamide 6/polycarbonate blends, *Mater. Res. Bull.* **39**: 1791-801.

[6] Han M S, Lim B H, Jung H C, Hyun J C, Kim S R, Kim W N 2001 Reactive blends of poly(butylene terephthalate)/polyamide-6 with ethylene glycidyl methacrylate, *Korea-Aust. Rheol. J.* **13**: 169-77.

[7] Huang C C, Chang F C 1997 Reactive compatibilization of polymer blends of poly(butylene terephthalate) (PBT) and polyamide-6,6 (PA66): 1. Rheological and thermal properties, *Polymer* **38**: 2135-41.

[8] Huang C C, Chang F C 1997 Reactive compatibilization of polymer blends of poly(butylene terephthalate) and polyamide 6,6: 2. Morphological and mechanical properties, *Polymer* **38**: 4287-93.

[9] Wang P, Meng K, Cheng H, Hong S, Hao J, Han C C, Haeger H 2009 Reactive compatibilization of polyamide-12/poly(butylene terephthalate) blends with hyperbranched PEI-g-PA12: Morphology and thermal properties, *Polymer* **50**: 2154-60.

[10] Mengual A, Juárez D, Balart R, Ferrándiz S 2017 PE-g-MA, PP-g-MA and SEBS-g-MA compatibilizers used in material blends, *Procedia Manuf.* **13**: 321-6.

[11] Chiu H-T, Hsiao Y-K 2006 Compatibilization of Poly(ethylene terephthalate)/Polypropylene Blends with Maleic Anhydride Grafted Polyethylene-Octene Elastomer, *J. Polym. Res.* **13**: 153-60.

[12] Chiu K-C, Chang F-C 2000 Reactive Compatibilization of Polyamide-6 (PA6)/Polybutylene Terephthalate (PBT) Blends by a Multifunctional Epoxy Resin, *J. Polym. Sci. Part B Polym. Phys.* **38**: 23-33.

[13] Samios C K, Kalfoglou N K 1999 Compatibilization of poly(ethylene terephthalate)/polyamide-6 alloys: Mechanical, thermal and morphological characterization, *Polymer* **40**: 4811-9.

[14] Yew G H, Mohd Yusof A M, Mohd Ishak Z A, Ishiaiku U S 2005 Water absorption and enzymatic degradation of poly(lactic acid)/rice starch composites, *Polym. Degrad Stab.* **90(3)**: 488-500.

[15] Sam S T, Ismail H, Ahmad Z 2010 Effect of Epoxidized Natural Rubber on the Processing Behavior, Tensile Properties, Morphology, and Thermal Properties of Linear-Low-Density Polyethylene/Soya Powder Blends, *J. Vinyl. Addit. Technol.* **16(4)**: 238-45.

[16] Nematollahi M, Jalali-Arani A, Modarress H 2019 High-performance bio-based poly(lactic acid)/natural rubber/epoxidized natural rubber blends: effect of epoxidized natural rubber on microstructure, toughness and static and dynamic mechanical properties, *Polym. Int.* **68**: 439-46.

[17] Tuampoemsab S, Riyajan S, Sritapunya T, Pakeyangkoon P 2014 Effect of Epoxide group in Thermoplastic Elastomer on the Properties of Polyamide6 and Low-density Polyethylene Blends, *Adv. Mater. Res.* **979**: 143-6.