Effect of Hybrid Compatibilizers on mechanical property of ternary blend with Polypropylene, Poly (lactic acid) and Toughening modifier

H.S. Lee¹, ², J.D. Kim²*  
¹Daeduk Research Institute, Honam Petrochemical Corp, Daejeon 305-726, Republic of Korea  
²Department of Chemical & Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Republic of Korea  
* Corresponding author (kjd@kaist.ac.kr)

Keywords: hybrid compatibilizer, GMA, PLA, MAH, Polypropylene

Introduction

In the recent years the increased volume of domestic and industrial waste accumulated in the landfills and sites has generated many environmental problems. Development of biodegradable polymers from renewable resource based feed stocks has received considerable research interests in recent years with a primary aim to reduce the consumption of petroleum polymers in various applications. Poly (lactic acid) (PLA), linear aliphatic biodegradable polyester derived from biomass through bioconversion and polymerization has become a potential candidate for various large-scale industrial applications in the areas of packaging, biomedical, pharmaceutical, etc.[1,2,3]

PLA is a high-strength and high-modulus polymer analogous to polystyrene, its inherent brittleness, low toughness, low heat stability, and low moisture stability due to the low entanglement density and the high value of characteristic ratio that represents the chain stiffness [1, 2, 3, 4, 5] restricting the range of applications.

As a low priced plastic, Polypropylene as semicrystalline polymer shows reasonably good stiffness, high heat stability and high moisture resistance.

Biomax® Strong 120 is an ethylene copolymer, and has been employed as a toughening agent of PLA in polymer blending systems.

These polymer blends, inclusive of PP/PLA/Toughening modifier blend, are of great interest. The ternary blend can lead to materials with improved moisture resistance, thermo mechanical properties, impact resistance, and flexural modulus. However, a PP/PLA/Toughening modifier blend is immiscible due to the high polarity difference among the component polymers. So, the multiphase blends show poor mechanical performance because of the low interfacial adhesion between the polymer phases. To solve the problem of immiscibility, compatibilizers are utilized to reduce the interfacial tension and elevate the interface adhesion between the immiscible phases.

The purpose of this paper is to make clear the effect of hybrid compatibilizers on the mechanical property of ternary blend with PP/PLA/Toughening modifier.

Experimental

Commercial grade PP block copolymer, known as J-370, was received from Honam petrochemical corporation, Korea. PP had a melt flow index of 30g/10min at 230°C. PLA (NatureWorks 3001D) utilized in this study purchased from Cargill-Dow Polymer LLC, and toughening modifier (Biomax® Strong 120) was purchased from DUPONT chemical company. Commercial available grades MAH-g-PP and MAH-g-PE (trade name PH200 and EM200) with MAH graft ratio of 4wt% and 1wt% respectively were received from Honam petrochemical corporation, Korea. Commercial grade GMA-g-PE (trade name AX 8840) with GMA graft ratio of 8wt% was purchased from Arkema Inc.

The PP, PLA, and Strong 120 were dried in a vacuum oven at 60°C for 12 hours before use. Polymer blends with diverse compatibilizer compositions were premixed and extruded in a twin extruder (L/D 40, screw diameter 40mm, screw speed 300rpm, operation temperature 170–200°C), respectively. The blend compositions are given in Table 1.

Therefore, pellet type of ternary blend was injected in an ASTM normalized mould of specimens, with a
temperature profile of 180 to 210°C. The mould temperature was fixed at 30°C. After conditioning for 48 hours at 23°C and 50% relative humidity, the mechanical properties of the specimens were tested as follows. The tensile strength and flexural properties were measured with Instron universal testing instrument, Instron 5566. The tests were performed in accordance to ASTM D 638 and D 790, respectively. Tests were conducted at a constant cross-rate of 50mm/min and crosshead speed of 28 mm/min. According to ASTM D 256, the IZOD impact strength of the notched samples was measured using an impact testing machine (CAT NO. 612, TOYOSEIKI). Heat distortion temperature, HDT, was tested in HDT.VSPT.TEASTER 6-2(TOYOSEIKI) in accordance to ASTM D 648. At least five samples from each formulation were tested. All the tests were carried out at room temperature. In addition to that, the specimens were annealed by the heating oven in a vacuum condition. The annealing temperature was 120°C. The annealing time was varied from 30 minutes to 3 hours, respectively and followed by cooling at 23°C and 50% relative humidity. The heat-resistance property was tested in HDT.VSPT.TEASTER 6-2(TOYOSEIKI) under ASTM D 648. All data were average value for the tested specimens. For microscopic observation, the fracture surfaces were observed using a scanning electron microscope. The rheological measurements performed on an advanced rheumatic system (ARES) in the parallel plate. A sample with a radius of 25mm and thickness of 2mm placed between the plates and tensional shear applied to the sample under 1% strain. The temperature held constant(190°C) during the frequency sweep.[7]

Results and Discussion

Mechanical properties of ternary blend with various compatibilizers

Figure 1 shows the IZOD impact strength and the flexural modulus of the ternary blend following combinations with a compatibilizer and toughening modifier. As shown in Figure 1, Toughness of resin is improved by the combination of PP-g-MAH and PP-g-GMA compatibilizers. On the other hand, Resins applied with a single compatibilizer have unbalanced properties like lower flexural modulus and higher IZOD impact strength compared to the combination of compatibilizers. Resin applied with combination of compatibilizer, especially PP-g-MAH and PP-g-GMA, has balanced properties. Strong 120 gives the effect of increasing impact strength with the addition of 5~10wt%. However, Figure 1 shows unbalanced mechanical properties like high impact and low flexural modulus. The ternary blend, PP/PLA/Toughening modifier, with contents of compatibilizers (3wt% of PP-g-MAH and PP-g-GMA compatibilizer, respectively) showed the excellent mechanical property.

Compatibility of ternary blend with/without hybrid compatibilizers

Figure 2 is SEM images which show compatibility of the ternary blend following the use of several compatibilizers. As shown in Figure 2, the domain size of sample D is smaller than other samples. Figure 3 is shows the stress-strain curve of the ternary blend with various compatibilizer compositions. The tensile strength of the ternary blend with hybrid compatibilizers was higher than others. The elongation at break of the ternary blends, the sample 3 and 4, was insignificantly improved. Figure 4 shows the effect of shear rate on melt viscosity for the ternary blends with various compatibilizer compositions. The changes of the complex viscosity of the blends depend on the degree of compatibility between the components and the complex viscosity of the compatibilizer itself. Viscosity of the sample 3 and 4 was higher than others. This increase of those in viscosity is most likely due to an increase in the mobility of chains at the interface caused by a chemical reaction among the end group of PLA, epoxy group of PE-g-GMA, and MAH group of PP-g-MAH. From these results, it means that hybrid compatibilizers with PP-g-MAH and PE-g-GMA can reduce the interfacial tension among PP, PLA, and Strong 120. Both the MAH units of PP-g-MAH and the epoxy units of PE-g-GMA react with the side chain of PLA when melted in free radical copolymerization to form block or graft copolymers that act as a compatibilizer for the blend. [6] Furthermore, PP units of PP-g-MAH and PE units of PE-g-GMA also elevate the compatibility with PP and TPO matrix, respectively.

Thermal resistance of ternary blend after annealing the specimens

Specimens of resin were annealed to increase the degree of crystallinity because the ternary blend showed the re-crystallization peak at 110°C. Notched IZOD impact strength and flexural modulus followed ASTM methods (ASTM D256 at 23°C and ASTM D790). Figure 5 shows the HDT (Heat Distortion Temperature) change of the ternary blend during annealing testing for 3 hours. As shown in Figure 5, the HDT of specimens after 2 hours
showed the maximum value and the HDT increased to 120°C. In this figure, optimal annealing time to improve thermal stability was 2 hours. It means that the thermal stability of the ternary blend with hybrid compatibilizers was dependent according to the different annealing time.

**Conclusion**

Several compatibilizers are added to verify compatibility with the PP/PLA/Toughening modifier ternary blend. Also, hybrid compatibilizers were applied to verify toughness and compatibility of the ternary blend. Blending with a combination of PP-g-MAH and PP-g-GMA compatibilizers showed improvement of compatibility and balanced mechanical properties due to the potential mechanism as shown in Figure 6. In addition, according to the annealing effect, we found out that the HDT of ternary blends after 2 hours showed the maximum value and the HDT increased to 120°C. Therefore, we plan to do hydrolysis test at specific conditions.

![Fig. 1. IZOD impact strength and flexural modulus following combinations of compatibilizers and ternary blend](image1.png)

![Table 1. Blend compositions](image2.png)

![Fig. 2. SEM Images showing compatibility of PP/PLA blend following several compatibilizers. (A: PH200, B: EM200, C: PH200/EM200=50/50, D: PH200/AX8840=50/50)](image3.png)

![Fig. 3. Stress-Strain curve of PP/PLA Alloy with various compatibilizer compositions](image4.png)

![Fig. 4. The complex viscosity versus frequency curves for the PP/PLA blends at 190°C](image5.png)
Fig. 5. HDT (Heat Distortion Temperature) change of ternary blend after annealing the specimens

Fig. 6. Potential mechanism of hybrid compatibilizer system

References