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One Step Method for Fabrication of PPO/PA-66/Elastomer Blends

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Summary

Rubber toughened poly(2,6-dimethyl-1,4-phenylene oxide)/polyamide-66 (PPO/PA-66) blends are important engineering plastics in automobile industries. They are generally fabricated by two step procedure. First, a maleation of PPO is carried out to fabricate a maleic anhydride grated PPO (PPO-*g*-MA) as a reactive compatibilizer. Then, PPO/PA-66/elastomer blends are fabricated with the PPO-*g*-MA. In this study, we proposed a novel one step method in which maleation and reactive blending occur simultaneously in a twin screw extruder. Physical properties of the blends by both methods show similar values. Therefore, we can successfully produce PPO/PA-66/elastomer blends with a reduced production cost without deteriorating the physical properties.

Introduction

Rubber toughened poly(2,6-dimethyl-1,4-phenylene oxide)/polyamide-66 (PPO/PA-66) blends are important engineering plastics in automobile industries since they provide the well balanced physical properties for automobile body panels [1, 2]. It was commercialized by General Electric Co. under the trade name Noryl GTX. It is commonly formed by the reactive extrusion of a semicrystalline polyamide which forms matrix in which PPO is dispersed. In addition to this, a rubber toughening is also vital to provide sufficient impact strength. This is normally accomplished by incorporating a styrenic-elastomeric block copolymer into PPO phases [3].
However, PPO is an amorphous polymer and PA-66 is a semicrystalline polymer, which are thermodynamically immiscible, and a proper compatibilizing technique is essential. There are many ways for the compatibilization of PPO/PA blends, including an aryloxytriazine-functionalized PPO [4], a styrene-acrylic random copolymer [5], a carboxylated polystyrene [6], a multifunctional epoxy coupler [7], a styrene-*co*-glycidyl methacrylate [8], a styrene-maleic anhydride random copolymer [9] and various maleic anhydride (MA)-containing copolymers [10-15]. Among them, a largest number of

studies employs MA-containing copolymers as a compatibilizer for the PPO/PA blends since they provide excellent compatibilizing performance as well as economical advantages (e.g. Maleation of PPO and elastomer can be accomplished in a reactive extrusion instead of a synthesis). In general way, a fabrication of a rubber toughened PPO/PA-66 blend takes the following two step procedures. (1) Maleation of PPO to fabricate a compatibilizer, and (2) blending PPO, PA-66, elastomer and the maleated PPO (PPO-*g*-MA). If it is possible to fabricate a rubber toughened PPO/PA-66 blend by one step procedure without deteriorating the physical properties compared to the blends fabricated by the two step method, it can save a production cost.

In this study, one step method for fabrication of the PPO/PA-66/elastomer ternary blends is proposed and compared to the traditional two step method.

Experimental

Materials

Maleic anhydride (MA), and dicumylperoxide (DCPO) were purchased from Aldrich Chemicals. Polyamide-66 (PA-66), trade name Zytel 101, was purchased from Dupont Chemical Co. Poly(2,6 dimethyl-1,4 phenylene oxide) (PPO) was purchased from Asahi chemicals (high flow grade, trade name P402). SEBS, trade name Kraton G1651, from Shell Chemical Co. contains 29 wt. % styrene, and number average molecular weight of 29,000 in the PS blocks and 116,000 in the EB block. The reactive compatibilizer, PPO-*g*-MA, for two step method was prepared as follows: MA of 5 phr and DCPO of 0.5 phr were mixed with PPO. The mixture was then extruded and pelletized at 290°C in a SM Platek twin screw extruder. The grafted MA in PPO-g-MA is about 1.5 wt% as confirmed by a titration.

Blend preparation

Prior to mixing operation, sample mixtures were dried over night at 80°C in an air circulating oven to minimize the hydrolytic degradation of materials during processing. Blending was carried out in a SM Platek intermeshing corotating twin screw extruder with a screw diameter of 45 mm and a length-to-diameter ratio of 37. Barrel temperature was 280°C, screw speed was 250 rpm, and feeding rate was 50 Kg/h. In all blends, the amount of DCPO is 1/10 of MA. We fabricated the blends by two method, namely, one step method and two step method.

In one step method, a mixture of PPO, SEBS, MA and DCPO of predetermined ratio was feed into a hopper followed by melting and maleation of PPO and SEBS. PA-66 was then supplied to MA grafted PPO/SEBS mixture through a side feeding port. The side feeding port is located near the middle of the extruder axis. Therefore, the maleation of PPO/SEBS and the reactive blending of PPO/SEBS/PA-66 are accomplished simultaneously in one step method. The compositions of the PPO/PA6/SEBS blends maintained at 44/50/6 while the MA and DCPO contents varied in one step method.

On the other hand, the maleation and the reactive blending were performed separately in two step method. As described above, PPO-*g*-MA was fabricated independently, and then the sample mixtures of predetermined ratios with PPO-*g*-MA were blended again. Thus, two runs of extrusion are needed in two step method. The composition of (PPO+PPO-g-MA)/PA-66/SEBS maintained at 44/50/6 while the ratio of PPO-g-MA over PPO varied.

Characterization

Standard tensile tests (ASTM-D638) were carried out at a crosshead speed of 10 mm/min. Standard flexural tests (ASTM-D790) were carried out at a crosshead speed of 2.8 mm/min and with a span length of 100 mm. Notched Izod impact tests were carried out at ambient conditions according to the ASTM-D256 standard method with specimens of 3.2 mm in thickness. Melt flow index (MFI) of the blends was measured at 285°C and 5 Kg load according to the ASTM-D1238 standard. Morphology of the blends was observed by transmission electron microscopy (TEM). Thin sections were prepared from molded sample using a Reichert-Jung Super Nova, and then stained with 0.5 wt % ruthenium tetraoxide (RuO4). The thin sections were laid on top copper grids and examined using a JEOL 200CX TEM operating at an accelerating voltage of 90 kV.

Results and Discussions

Fig. 1, 2, 3 and 4 show the mechanical properties of the PPO/PA-66/SEBS blend fabricated by one step method. The grafting of MA onto the PPO has a major effect on the toughness. The Izod impact strength of uncompatibilized blend is 5 Kgf cm/cm; it increases drastically to 47 Kgf cm/cm when the amount of MA reaches only 0.25 phr. Usually, larger amount of MA leads to higher graft ratio, strengthens the interface and consequently improves the toughness of the blends. However, higher graft ratio of MA does not always guaranty the higher toughness. Higher graft ratio of MA in PPO-*g*-MA tends to form pinning type conformation of the compatibilizer along the interface with relatively smaller PPO segment penetrating into PPO dispersed phase. Such pinning conformation leads to poor interfacial adhesion [8]. This phenomenon may explain the fact that further increase of MA leads to slight decrease of the tensile elongation at break and the slope of the Izod impact strength vs. MA content curve decreases.

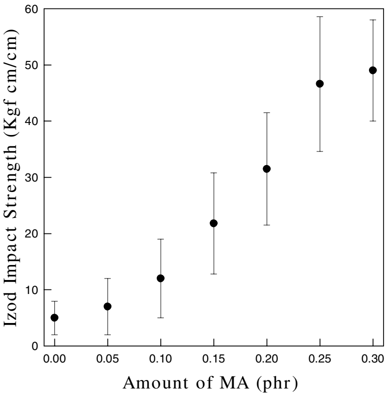

Fig. 1. Izod impact strength of the PPO/PA-66/SEBS blends versus amount of MA used for a maleation by one step method.

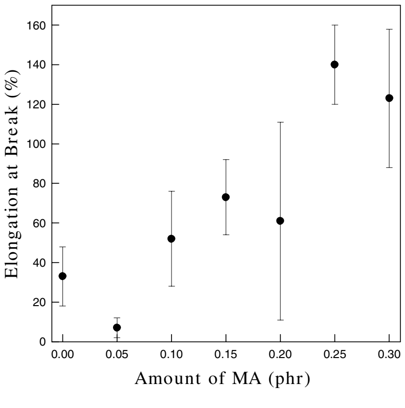

Fig. 2. Elongation at break of the PPO/PA-66/SEBS blends versus amount of MA used for a maleation by one step method.

It is observed that the grafting of MA has a moderate effect on the strength of the blends. Increase of the strength of the blends by compatibilization is within an experimental uncertainty. The PA-66 is relatively tough material, showing yielding behavior in a stress-strain curve. Its stress level at the plastic flow (cold drawing) region is almost constant regardless of a strain [16]. The uncompatibilized PPO/PA-66/SEBS blend already shows a ductile fracture behavior in the tensile test due to the high toughness of PA-66 though the elongation at break of the uncompatibilized blends is much lower than that of pure PA-66. As the graft ratio of MA in PPO-*g*-MA increases, the elongation at break of the blend increases but the stress-strain curves below the elongation at break of the uncompatibilized blend overlap regardless of the degree of compatibilization, rather than the increase of yield stress, tensile stress, and the modulus.

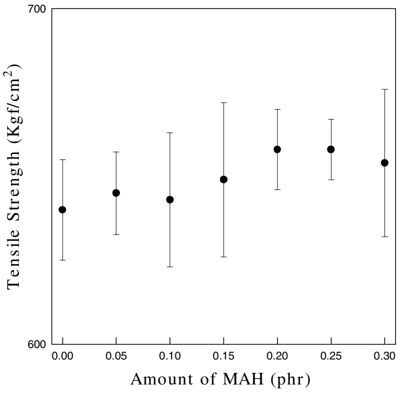

Fig. 3. Tensile strength of the PPO/PA-66/SEBS blends versus amount of MA by one step method.

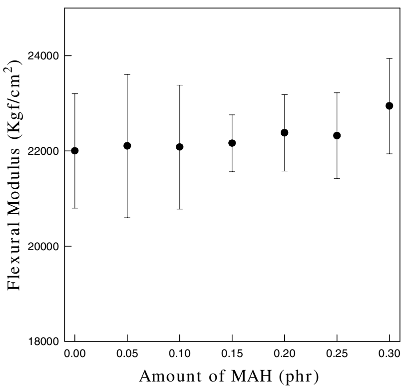

Fig. 4. Flexural modulus of the PPO/PA-66/SEBS blends versus amount of MA by one step method.

Fig. 5 shows selective TEM micrographs of PPO/PA-66/SEBS blends fabricated by one step method. Morphology of the PPO/PA-66/SEBS blend can be identified with RuO_4 staining. By controlling the staining time, PA-66 appears as black regions, PPO as gray, and SEBS as white and dark grey. It is observed that PA-66 forms the continuous phase and PPO forms the dispersed phase due to the lower viscosity of PA-66, in spite of the fact that the amounts of PPO and PA-66 in the blend are similar. It is also noticeable that elastomers exclusively reside in the dispersed PPO phase, which suggests that the elastomer is more compatible with the PPO phase. This is because the PS block in SEBS is miscible with the PPO phase and also implies that the maleation of SEBS does not occur in large extent. As observed by Chiou *et al.*, MA grafted SEBS in 2 wt. % resides in the PA phase and/or exist along the interface due to the reaction between MA and amine end group of PA, which lowers the impact properties of the blends compared to the blend in which elastomers reside in the PPO phase. It is clamed that the final elastomer destination is a crucial factor for a rubber-toughening in the PPO/PA-66 system [3].

The size of the PPO dispersed phase decreases with the amount of MA and DCPO. The size-reduction of the dispersed phase is reflected in the impact property as shown in Fig. 1. The Izod impact strength increases with the amount of MA. Thus, it is assessed that *in situ*-formed PA-66-*g*-PPO has excellent compatibilizing effect in the PPO/PA-66/SEBS blend.

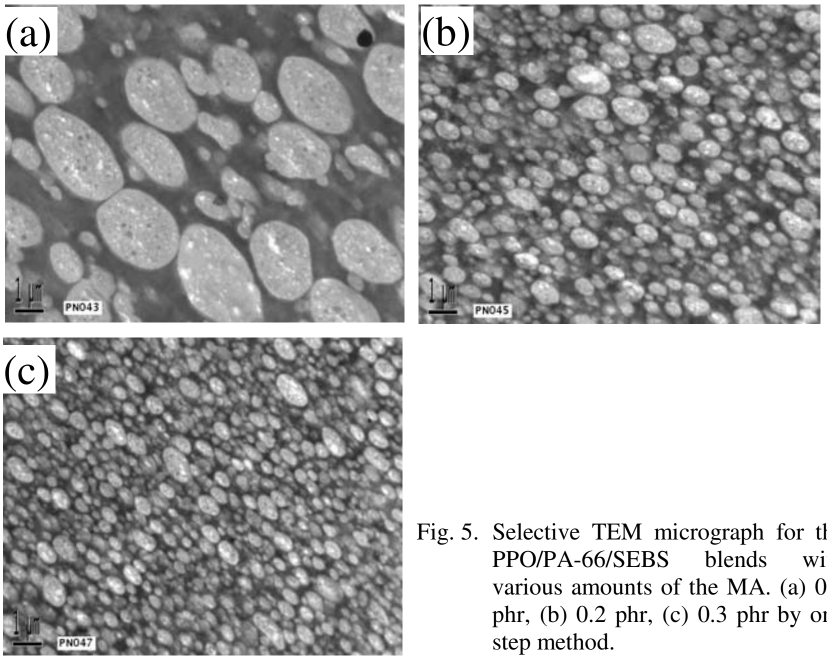

Fig. 5. Selective TEM micrograph for the PPO/PA-66/SEBS blends with various amounts of the MA. (a) 0.1 phr, (b) 0.2 phr, (c) 0.3 phr by one step method.

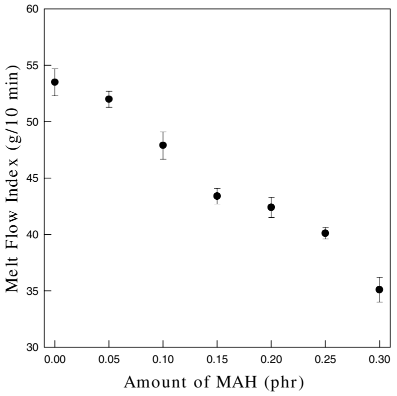

Fig. 6. Melf flow index of the PPO/PA-66/SEBS blends versus amount of MA .

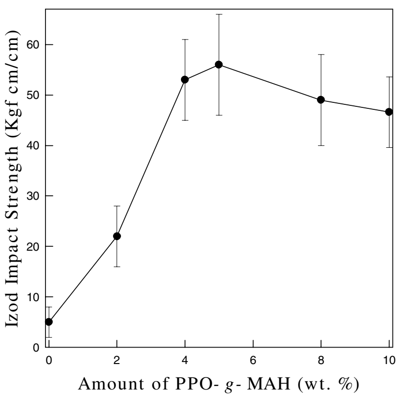

Fig. 7. Izod impact strength of the PPO/PA-66/SEBS blends fabricated by the two step method versus amount of PPO-*g*-MA.

Fig. 6 shows the melt flow index (MFI) of the blends versus the amount of MA. The MFI (inversely proportional to the shear viscosity) decreases with the degree of the compatibilization, which is consistent with many other studies [3, 17]. In spite of thermal degradation accelerated by a radical initiator, DCPO, the viscosities of the blends increase with the degree of the compatibilization. This is mainly due to the reaction between MA of the PPO-g-MA and amine end group of the PA-66, forming PA-66-*g*-PPO copolymers. The reaction increases the molecular weight and the degree of branching, which increase the viscosity of blends. [17]

Fig. 7 shows the Izod impact strength of the PPO/PA-66/SEBS/PPO-g-MA blends fabricated by the traditional two step method. The Izod impact strength of the blend increases with the amount of PPO-*g*-MA up to 5 wt. % and then slightly decreases with the further addition of the reactive compatibilizer. This decrease of the toughness is most probably due to the pinning conformation as discussed above. Maximum Izod impact strength of the PPO/PA-66/SEBS/PPO-g-MA blends fabricated by the two step method is 55 Kgf cm/cm which is comparable with that by one step method. It is proved that it is possible to fabricate compatiblized PPO/PA-66/SEBS blends without deteriorating the physical properties by one step method. For the blends providing maximum toughness, the amounts of MA added are 0.25 phr in both one step method and two step method (PPO-g-MA of 5 wt.% is added for blending and MA of 5 phr is used for the maleation of PPO). Mean residence time of the twin screw extruder used is about 2 min to side feeding port and 4 min to exit. Though the graft reaction time for one step method is shorter than that for two step method, both methods provide blends having similar toughness. This is probably due to the following fact. In one step method, the graft reaction occurs in entire PPO while the graft reaction occurs in the PPO of only 11 wt.% over entire PPO phase (PPO-g-MA of 5 wt. % over PPO phase of 44 wt. %) in two step method.

One step method is enough to fabricate the compatibilized PPO/PA-66/SEBS blends having the similar physical properties with those fabricated by two step method. Another advantage of one step method is that it can reduce the thermal decomposition of PPO since PPO-*g*-MA in two step method stays in a extruder for a longer time (extruded twice). PPO is very weak material upon high temperature. It easily produces bubbles and black burns at high temperature, which consequently deteriorates the physical properties.

Conclusions

We could successfully fabricate the reactive compatibilized PPO/PA-66/SEBS blends by novel one step method. The physical properties of the blends fabricated by one step method is similar with those fabricated by two step method. This is possible because in one step method, the graft reaction occurs in entire PPO while the graft reaction occurs in a portion of entire PPO in two step method.

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