Reactive blends of polyamide-6 and poly(butylene terephthalate) with ethylene glycidyl methacrylate

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Introduction

When the copolymers may be added separately or formed in situ by blending suitably functionalized polymer, it is supposed that the chemical reaction between blend components may cause interfacial tension to decrease or adhesion force of interface to increase. A variety of reactive copolymers have been identified as effective blend compatibilizers in earlier literatures[1].

Polyamide-6(PA6) and Poly(butylene terephthalate)(PBT) are both semicrystalline polymers with commercial siginificance. Blends from them should be an ideal choice to create new and useful polymeric products possesing certain specific properties from base polymers[2,3].

In this study, ethylene glycidyl methacrylate (EGMA) copolymer with GMA content 6% has been used to compatibilized the blends of PA6 and PBT. The epoxy groups in EGMA can react with hydroxyl gruop of PBT and amine group of PA6, and make it possible to form PBT-co-EGMA-co-PA6 copolymer which can act as an *in situ* compatibilizer for the PA6-PBT blends.

Experimental

1. Blends Preparation

Blends of PA6 and PBT were prepared in 70/30, 50/50, and 30/70 PA6/PBT weight concentration using a co-rotating twins screw extruder, with a 7:1 length to diameter screw, and 42mm diameter. Concentration of EGMA copolymer, ranging from 0 to 5 phr with respect to the whole weight fraction of PA6-PBT blends were used.

2. Scanning Electron Microscopy (SEM)

The morphology of the cross-section of the extrudate prepared by cryogenic fracturing was examined by JEOL scanning electron microscopy (Model JSM-5200) at 20kV accelerating voltage.

3. Rheology

Dynamic measurements were carried out on advanced rheometric expansion system (ARES) in oscillatory shear at 5% strain in the parallel-plate arrangement with 25mm plate. The frequency sweeps from 0.01 to 100rad/sec were carried out at 240℃.

4. Fourier Transform Infrared Spectroscopy (FT-IR)

To characterize the functional end group of blends in this study, Fourier transform infrared spectroscopic (FTIR) analyses were carried out using a Bomem DA8 FTIR spectrometer.

Result and Discussion

1. Torque change after reations

The torque change curves with time for the pure components and blends under experimental condition(240℃, 50rpm) are shown in Fig. 1. From Fig.

1(a) and (b), the steady torque value of the PA6 with EGMA 10phr blend is larger than that of the pure PA6. This is probably due to the reaction between the PA6 and EGMA and formation of the PA6-co-EGMA copolymer. Whereas the steady torque value of the PBT with EGMA 10phr blend is slightly increased when it compared to the value of the pure PBT in Fig. 1(e) and (f). In Fig. 1 (c) and (d), the torque valud of the 50/50/10 PA6-PBT-EGMA blend is significantly higher than that of 50/50 PA6-PBT blend. These results give indirect evidence that the reaction between PA6 and PBT with EGMA.

2. Fourier Transform Infrared Spectroscopy (FTIR)

The IR peak at 907cm^{-1} is a characteristic response of the epoxy group that has been used to monitor qualitatively the reaction between EGMA and PA6, PBT functional end groups. Fig. 2 compares the IR spectra of the PA6/EGMA= 100/5 mixtures by dry mixing(Fig. 2(c)) and melt blending(Fig. 2(b)). No reaction is expected from this dry-blended mixture. The weak epoxy charateristic peak(907cm^{-1}) somewhat decreased after melt blending(Fig. 2(b)). This result indicates that the reaction between EGMA and PA6 terminal amine -NH_2 group may occur.

3. SEM morphologies

Fig. 3 show micrographs of the cryogenically fractured cross-section surfaces for the 70/30 PA6/PBT blends. Phase contrast and the sizes of the dispersed spherical particles of 70/30 PA6/PBT blend decrease with the addition of the compatibilizer quantity. In Fig. 3(a), the average radius of the PBT droplet for the 70/30 PA6-rich phase is about 2-3 μm. When the 1, 3, and 5phr EGMA added to the 70/30 PA6-PBT blend, the droplet size decreases in PA6-rich phase. But differences of droplet size between Fig. 7(b)-(d) are negligible. This phenomenon may be due to segregation and formation of unreacted EGMA copolymer as a third phase in the 70/30 PA6-PBT blend and also implies that even small amount of EGMA (1phr) can play an effective compatiblizing role in 70/30 PA6-PBT blend system.

4. Rheological properties

Fig. 4 show the complex viscosity of the 70/30 PA6-PBT blend. Shear thinning behavior, which is the typical behavior of non-Newtonian fluid, is observed in 70/30 PA6/PBT blend except for the pure PA6 and PBT. It can be also seen that complex viscosity of the blends increases with increase of EGMA content at the low frequencies and decreases at the high frequencies in Fig. 4. Molecular weight increases through in situ reaction are mainly responsible for such viscosity increases after compatibilization[4]. Thus, increase complex viscosity at the low frequencies for the PA6-PBT blends with EGMA can be interpreted that the EGMA is effective as a compatibilizer which produced the PA6-co-EGMA-co-PBT copolymer at the interface between PA6, PBT phases. In addition, decrease of complex viscosity with the increase of EGMA content at the high frequencies for the PA6-PBT blends might be explained by that the dispersed domains in the PA6-PBT blends containing the higher amount of PA6-g-PBT copolymer, which is presented in interface of PA6-PBT blends compatibilized with EGMA, are more easily deformed by an oscillation flow[5].

Conclusions

Reactive blends of the PA6 and PBT compatibilized with EGMA copolymer were prepared by twin screw extruder. The torque measurements give indirect evidence that the reaction between PA6 and PBT with EGMA has an opportunity to produce the in situ formed copolymer, which can be an effective compatibilizer to reduce interfacial tension of PA6-PBT blends. From the results of IR-spectrum, reduction of epoxy peak(907cm^{-1}) in PA6-EGMA melt blend can be detected, which means the reaction of epoxy with amine functional group of PA6.

The complex viscosity of the PA6-PBT blend of various composition is observed to be increased with increase of EGMA. This behavior shows similar tendency with mophological data. From the results of SEM microscopy, droplet size of all blends tend to decrease with EGMA addition. These results can be interpreted that the reaction of EGMA with functional end groups of PA6 and PBT produced the in situ copolymer which cause the increase of viscosity and reduce the interfacial tension of PA6-PBT blends.

Acknowledgement

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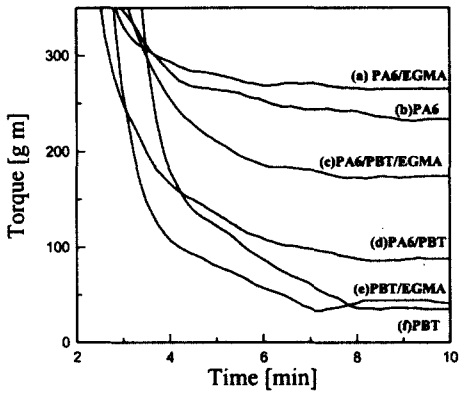

Figure 1. Torque change with mixing time at a temperature 240℃.

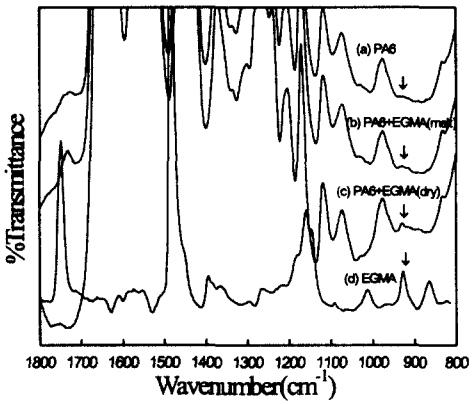

Figure 2. Infrared spectra of the mixtures.

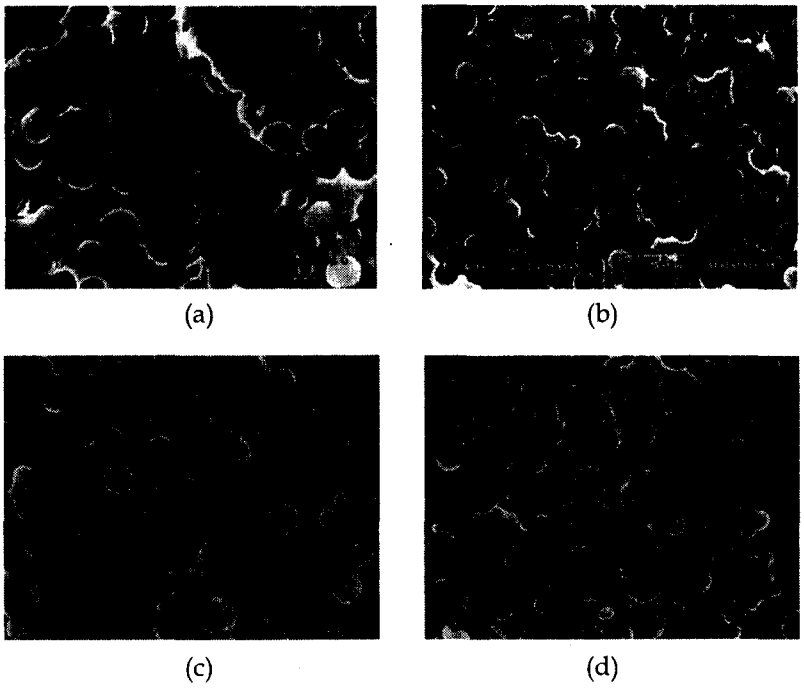

Figure 3. SEM micrographs for the PA6/PBT/EGMA blends: (a) 70/30, (b) 70/30/1, (c) 70/30/3, (d) 70/30/5

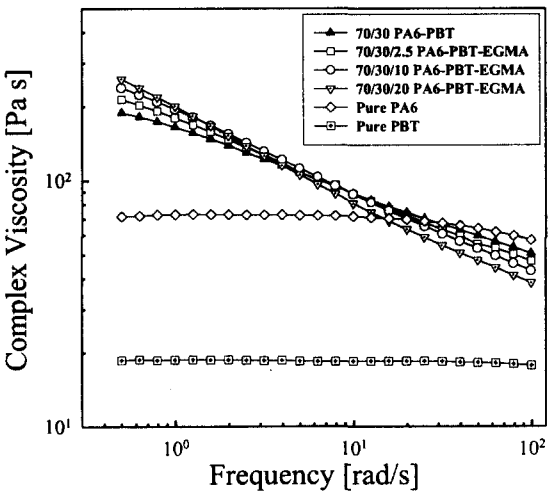

Figure 4. Complex viscosity with frequency for the PA6 and 70/30 PA6-PBT containing various EGMA content