

Compatibilization of PP/SEBS-MAH blends by grafting Glycidyl Methacrylate onto Polypropylene

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Summary

In this paper, the glycidyl methacrylate(GMA) was grafted to Polypropylene(PP) macromolecular backbone by melt radical grafting. The grafted PP-g-GMA was used to compatibilize PP/SEBS-g-MAH blend in a Haake apparatus. The result of Fourier Transform Infrared(FTIR) spectrum showed that the GMA had been grafted to PP. And the reaction between epoxy groups in the GMA and MAH groups in SEBS-g-MAH had taken place. The result of torque test showed that the torque values of the compatibilized blends were higher than that of the uncompatibilized blends. The observation of Scanning Electron Microscopy (SEM) showed that the dispersed phase domain size of compatibilized blends decreased evidently than uncompatibilized blends. When the content of SEBS-g-MAH was 16 wt% and the PP-g-GMA was 2 wt% in the blend, the rubber particle size had a minimum value. Those indicated that the PP-g-GMA could compatibilize PP/ SEBS-g-MAH blends effectively. Notched Izod impact tests showed the addition of PP-g-GMA in the PP/SEBS-g-MAH blends induced a remarkable improvement of toughness and yielded a tougher PP blends.

Keywords

polypropylene - blend - compatibilization - toughness - morphology

Introduction

PP is a kind of semi-crystalline polymer with good mechanical and thermal properties, but its toughness, in particular its notched toughness, is not sufficient for the application as a kind of engineering plastics. In order to improve its toughness, rubbers such as ethylene-polypropylene copolymer [1-8], ethylene- polypropylene-diene terpolymer[9-14], and styrene-butadiene block copolymer[15-19] had been used as impact modifiers. Although molecular structure of PP and rubber is similar, PP/rubber are considered immiscible[20]. Simple blends of immiscible polymers generally have poor mechanical properties, which results from unfavorable interactions

between the molecular segments of the blend components that exhibit a high interfacial tension and coarse, unstable phase morphologies obtained during melting process. In addition, the poor adhesion between the phase in the solid state often leads to premature failure or debonding under an applied stress.

Thus, many attempts have been made to enhance the interfacial adhesion or blend compatibilization to improve the mechanical properties of the blends. These problems can be mitigated in many cases by the incorporation of a kind of compatibilizer. The compatibilizer is usually an appropriate block or graft copolymer, which preferentially resides at the polymer-polymer interface during melting process. The compatibilizer can be a block or graft copolymer obtained previously with segments similar to the blend components, but this method is limited by the availability of techniques to form such materials. A generally more useful approach is the in situ formation of an interfacially active species during melting process by using appropriate reactive functionalities. The judicious choice of compatibilizer can often result in the improvement of the mechanical properties of the blend. In many cases with synergistic effects, the compatibilizer can effectively stitch itself across the interface and reduce the interfacial tension between the blend components and minimizes dispersed-phase coalescence. Both of these effects promote a stable, fine distribution of the dispersed-phase within the matrix phase and improve the interfacial adhesion between the blend components, which facilitates stress transfer across the interface and reduces the possibility of interfacial failure.[21]

In this paper, the GMA was grafted to PP macromolecular backbone firstly by melt grafting. And this method was studied by many authors[22-26]. In this paper, it was used to compatibilize PP/SEBS-g-MAH Blends. Ester formation by carboxylic acid opening epoxide ring was selected and this reaction has been used in commercial blends [27-28]. However, to our knowledge, there are no papers using this reaction to deal with the PP/SEBS-g-MAH blend system. And the effect of PP-g-GMA on the final morphology, impact strength and rheology of PP/ SEBS-g-MAH blends were investigated. Note that GMA in PP-g-GMA reacts with maleic anhydride group in SEBS-g-MAH, thus a grafted polymer is formed in situ and acts as a compatibilizer between PP and SEBS-g-MAH.

Experimental

Materials

The PP used in this study was a commercial grade(T-H-022) of Qianguo Petrochemical Co, China; the melt flow index(MFI) is 2.60g/10min(230°C,21.6N). The PP was dried in a vacuum oven at 80°C for 24h before being used; the SEBS-g-MAH was also a commercial grade(Kraton G 1901) of Kraton Polymers, USA, it is granulated. The MFI is 4.60g/10min(230°C,21.6N) and the graft degree is 1.0%. The PP-g-GMA was prepared by melting radical graft in twin-screw extruder. The functional monomer, GMA, was purchased from Guangzhou 3rd Chemical Factory, China. Styrene was used for assisting the free radical grafting of GMA. It was purchased from JiLin Petrochemical Co. China .The free radical grafting of GMA was initiated by DCP(dicumyl peroxide), which was purchased from Beijing 2nd Chemical Factory, China.

The preparing of PP-g-GMA

The PP, the monomers GMA, the co-monomers Styrene(St) and peroxide DCP were fed together into twin-screw extruder. The contents of GMA,St and DCP were 3phr, 3phr and 0.3phr, respectively. The L/D proportion of the twin-screw extruder is 32. The grafting temperature and the rotation rate of screw is 200°C and 100 r.p.m, respectively. The reaction products were purified by dissolution in refluxing xylene and precipitation into acetone under continuous stirring at room temperature, in order to remove the unreacted monomers(GMA,St), the homopolymerized GMA and GMA-St copolymer. The precipitation, PP-g-GMA, was filtered, washed again with acetone and dried under a vacuum at 80°C overnight. The purified samples were then compression moulded into thin films and analysed by FTIR in order to determine whether the GMA had been grafted onto PP.

Blending and sample preparation

The PP/SEBS-g-MAH and PP/PP-GMA/SEBS-g-MAH blends, having different rubber contents, were prepared at 200°C for 6 min at rollers speeds of 70 rpm in a Haake apparatus and then hot-pressed in the same hydraulic press 240Kg/cm², at 190°C. The content of PP-g-GMA in the blends is from 2 to 10%(Wt). The compression-moulded sheets were cut into rectangular specimens of 63.5×12.7×3.0mm³ for Izod impact tests, and a notch of 2.5 mm depth with an angle of 45° was made on the specimens.

Izod impact testing

The notched Izod impact strength was measured with an XJU-22(made in jilin university,china) impact testing machine according to ASTM D256. The temperature was 23°C.

Blend morphology

The morphological structure of the blends was characterized by scanning electron microscopy (SEM) (JEOL model JSM5600). Samples were trimmed using glass knife at -110°C. And the samples were etched by Dioxane in order to remove SEBS-g-MAH.

FTIR. spectra

The FTIR.spectra, using the hot pressed films of PP, PP-g-GMA, SEBS-g-MAH and PP/PP-g-GMA/ SEBS-g-MAH blends were recorded on BIO-RAD FTS-7.

Torque rheology

The torque measurements of PP blends were performed on a Thermo Haake mixer. The rotating speed was set at 70rpm and the temperature was set at 200°C.

Results and Discussion

FTIR. spectra

Figure1 (1,2) shows IR spectrum of pure PP and PP-g-GMA. It can be seen from Figure1(2) that the new absorption peak occurred at wave number of 1730 cm⁻¹, which

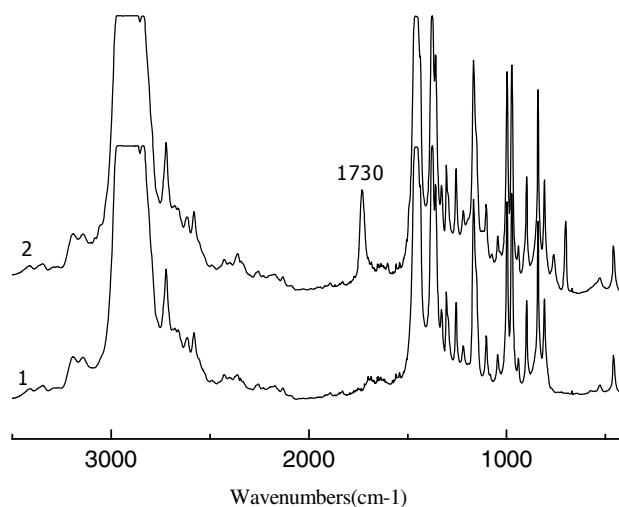


Figure 1 FTIR of PP and PP-g-GMA (1) PP (2) PP-g-GMA

presents stretching of the carbonyl group of GMA. This indicated that the GMA had been grafted onto PP indeed.

Figure2(1) showed IR spectrum of SEBS-g-MAH. There were two peaks of absorption situated around the regions of 1781cm^{-1} and 1862cm^{-1} , which corresponded to the stretching of the carbonyl of MAH in SEBS. There was also a peak of absorption at 1710cm^{-1} , which corresponded to the vibration of carbonyl of carboxylic acid. The intensification of the absorption around 1710cm^{-1} suggested that the conversion of anhydride into carboxylic acid groups partially for the hydrolysis of the MAH in the SEBS-g-MAH. Figure2(2) showed IR spectrum of PP/PP-g-GMA/SEBS-g-MAH blends and the disappearance of peaks 1785 , 1780cm^{-1} and 1710cm^{-1} after melting

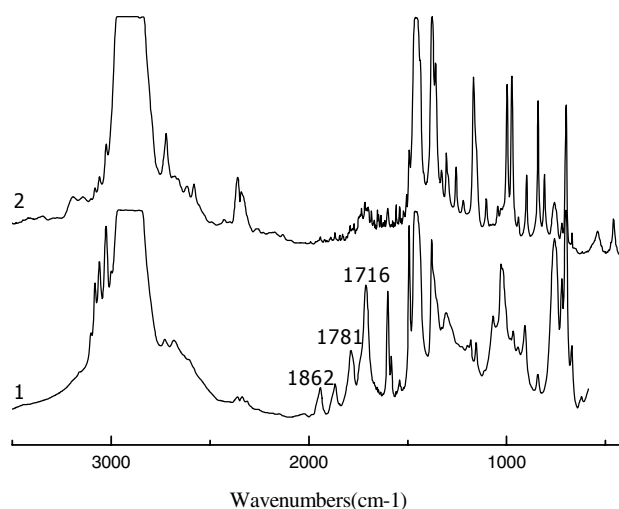


Figure 2 FTIR of the (1) SEBS-g-MAH and (2) PP/PP-g-GMA/SEBS-g-MAH.
PP=84 wt%, SEBS-g-MAH=14 wt%, PP-g-GMA=2 wt%

blend indicated MAH and epoxy ring-opening reactions indeed had occurred, but we were unable to positively identify the chemical structures of the reaction products from the spectra.

Chemical analysis

A small amount (1g) of dried PP/SEBS-g-MAH and PP/PP-g-GMA/ SEBS-g-MAH were dissolved in 100ml of boiling xylene in a conical flask, respectively. And a few drops of water were added to hydrolyze all anhydride functions. Afterwards, 10ml of 0.05N potassium hydroxide solution in methanol was added into the flask. The formed solution was back titiated with 0.03N trichloroacetic solution in xylene using cresol red as indicator. The content of MAH was calculated from Eq.(1):

$$wt(\%) = \frac{V_1 \times N_1 - V_2 \times N_2}{2 \times 1000 \times m} \times 98.06 \times 100\% \quad (1)$$

where, wt(%) is the content of MAH in the above two systems; V_1 (ml) is the volume of potassium hydroxide solution in methanol and N_1 is the concentration(mol/L) of it; V_2 (ml) is the volume of trichloroacetic solution in xylene and N_2 is the concentration (mol/L) of it.; m is the weight of the sample (g). The M_w of MAH is 98.06.

The content of MAH obtained by chemical analysis in the PP/SEBS-g-MAH system was 0.16% and that of PP/PP-g-GMA/ SEBS-g-MAH system was 0.06%. Therefor, we can say that most of the MAH of SEBS-g-MAH had reacted with the GMA in PP-g-GMA. The result was also consistent with that from FTIR.

Torque tests

Plots of torque value in the internal mixer *versus* mixing time at the setting temperature of 200°C for PP blends were given in Figure3. It clearly showed that the torques of PP/PP-g-GMA/SEBS-g-MAH was significantly higher than that of

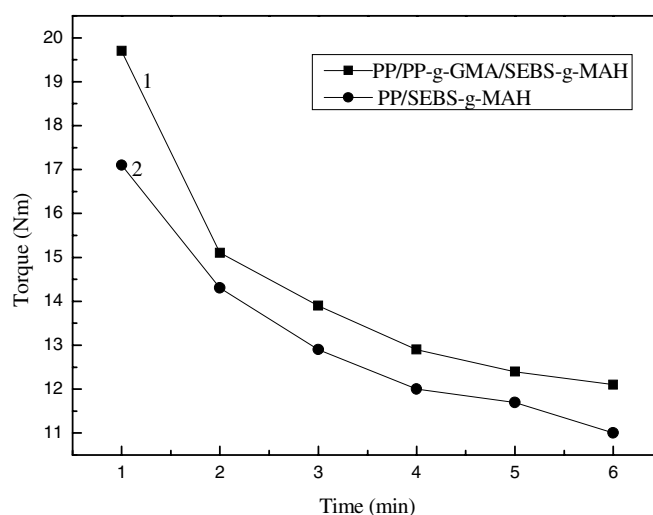


Figure 3 Evolution of torque with time for PP blends in Haake mixer.
PP=84 wt%, SEBS-g-MAH=14 wt%, PP-g-GMA=2 wt%

PP/ SEBS-g-MAH blends. The increase of viscosity (torque increase) could be attributed to the overall increase of the molecular weight from the anticipated epoxy coupling reactions to form PP-g-SEBS copolymers.

Morphology

Figure4(a-d) showed the SEM micrographs of the uncompatibilized and compatibilized 84/16PP/SEBS-g-MAH blends where the SEBS-g-MAH had been removed by solvent etching. Figure4(a) showed the uncompatibilized PP/SEBS-g-MAH blends. Figure4(b-d) showed the morphologies of the blends containing various amounts of PP-g-GMA compatibilizer, from 2 to 10 phrs. For Figure4(a), the shape of the dispersed phase was irregular and its phase domain size was larger. For Figure4(b-d), the domain size decreased with the increase of compatibilizer quantity, which was expected from any efficient compatibilizer. The figure4(b) showed that the domain size decreased apparently when the content of PP-g-GMA was increased to 2 phrs. There was no apparently further decrease in the domain size as the content of PP-g-GMA was increased to 6 phrs. That indicated that the MAH in the SEBS-g-MAH molecules at the interface reacted with the epoxy group in PP-g-GMA by ring opening to form ester linkages. And the PP-g-SEBS molecules were formed on the interface between the PP and SEBS phases. Therefore, the formation of PP-g- SEBS reduced average particle size of dispersed phase due to the suppression of droplet-droplet coalescence through

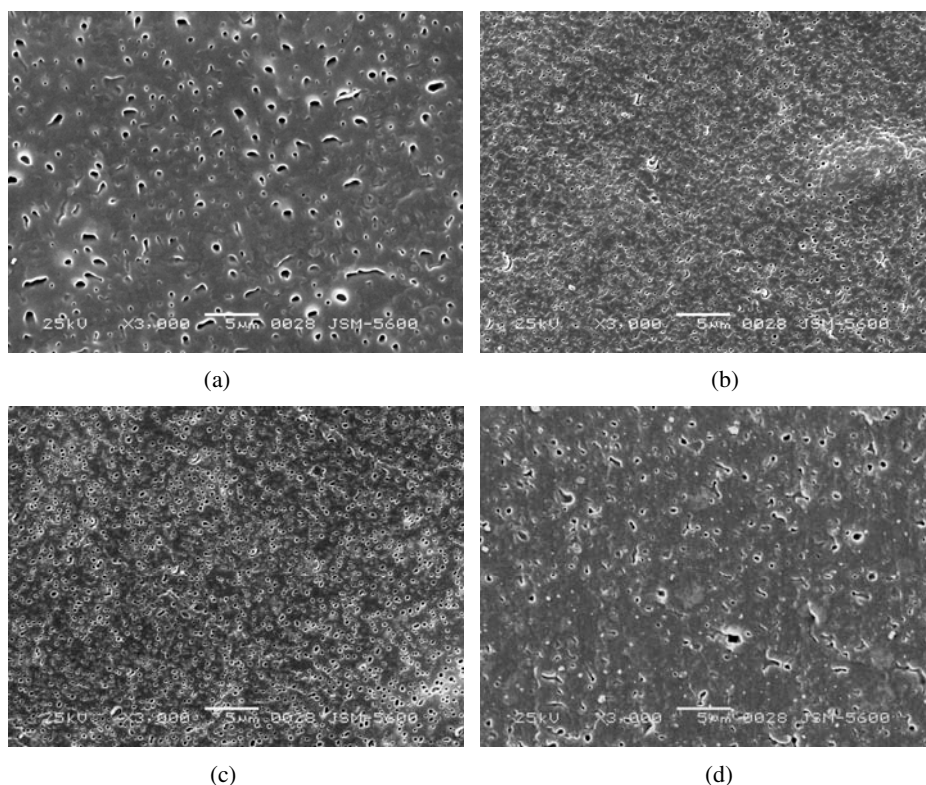


Figure 4 SEM images of the blends with different content of PP-g-GMA (a) 0 (b) 2 (c) 6 (d) 10

steric hindrance by the formation of the copolymer at the interface, which has been reported by Shaughnessy [29] and Fredrickson[30], respectively. Note that when PP-g-GMA was 10%, the dispersed domain became larger and irregular again. This may be degradation of PP in the course of GMA grafting onto PP and it caused the decrease of the molecular weight for the whole matrix. And that decrease made the decrease of compatibilization for PP/SEBS-g-MAH blends.

Impact properties

Figure5 showed Notched impacted strength of PP/PP-g-GMA/SEBS-g-MAH blends with different content of PP-g-GMA. When the PP-g-GMA was 2Wt%, the impact strength achieved the maximum value. And the content of PP-g-GMA was from 2 Wt% to 6Wt%, the impact strength decreased slightly. When the PP-g-GMA was 10Wt%, the impact strength decreased obviously. It was consistent with the phase morphology.

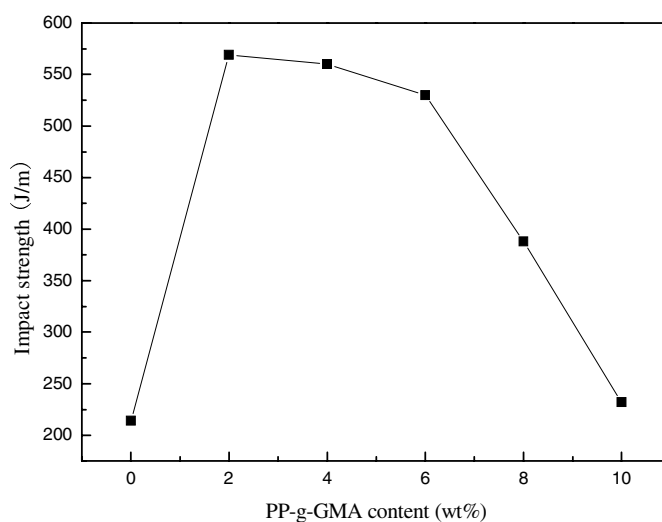


Figure 5 Notched impacted strength of PP/PP-g-GMA/SEBS-g-MAH blend with different content of PP-g-GMA. PP=84 wt%, SEBS-g-MAH=16 wt%

The notched impact strength, obtained by Izod testing, as a function of rubber content for PP/SEBS-g-MAH and PP/PP-g-GMA/SEBS-g-MAH blends, was shown in Figure6. Up to 16Wt% rubber content, the toughness of PP/SEBS-g-MAH improved only a little and the blends still broken in a brittle manner, whereas the toughness of PP/PP-g-GMA/SEBS-g-MAH blend has been improved evidently. As the rubber content was 16Wt%, the PP/PP-g-GMA/SEBS-g-MAH blend becomes tougher and the notched impact strength was about 19 times than that of pure PP.

Figure7 presented the fracture surfaces of PP/SEBS-g-MAH and PP/PP-g-GMA/SEBS-g-MAH blends, which have the same compositions. The SEM micrographs were taken directly behind the notch. The lower impact strength of the PP/SEBS-g-MAH blends was clearly reflected by its fracture surface (Figure7a). The fracture surface showed a smooth zone, and had many naked particles. It displayed

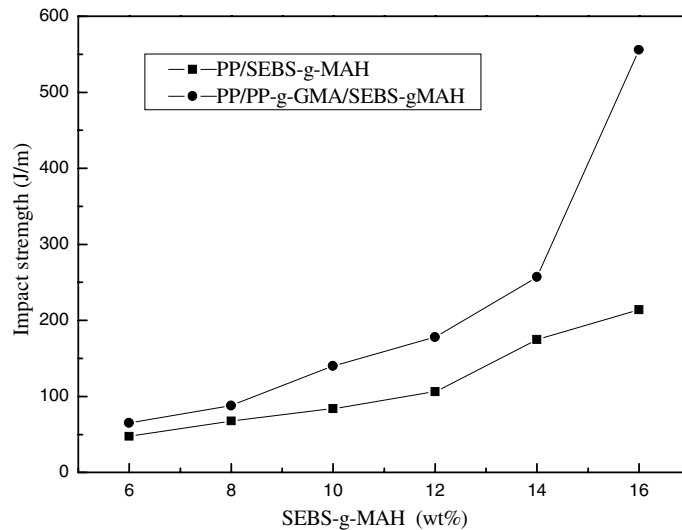


Figure 6 Notched impact strength of PP blends with different SEBS-g-MAH content

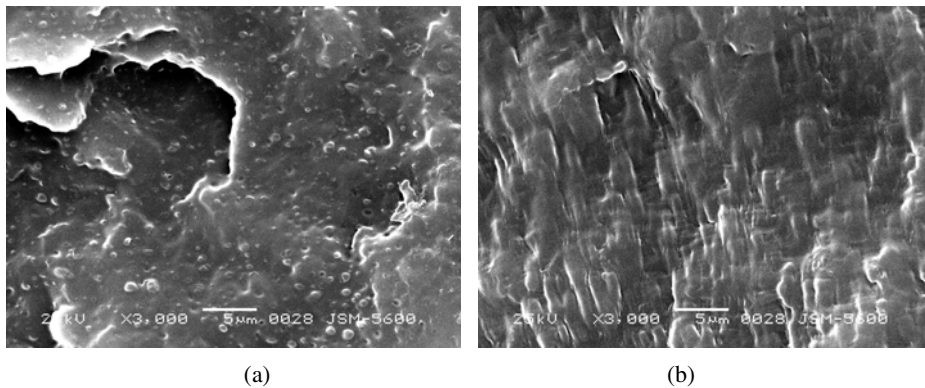


Figure 7 Morphology of the fracture surface for PP blends (a)PP/SEBS-g-MAH(b)PP/PP-g-GMA/SEBS-g-MAH

a brittle fracture mode at 23°C. Figure 7b displayed the fracture in a ductile manner on which ruffled surface could be seen. The ruffles lay parallel to the notch and gave rise to tufts of highly drawn material. The ruffles have been explained as being due to considerable drawing ahead of the crack tip before unstable fracture sets in, the extensive deformation of the cavitation ahead of the crack tip gave rise to that structure [31].

Conclusions

In this study, the GMA was grafted onto PP macromolecular backbone firstly by melt grafting. And then it was used to compatibilize PP/SEBS-g-MAH Blends. FTIR results showed that the GMA had been grafted onto PP and the MAH and epoxy ring-opening reactions indeed had occurred. Torque test showed that the actual torque value

for the compatibilized blends was higher than that of the uncompatibilized blends. SEM images showed that the domain size decreased evidently with increasing the PP-g-GMA content. It was because of the formation of PP-g-SEBS decreased the interfacial tension. The particle size had a minimum value when PP-g-GMA was 2Wt%. This was consistent with its phase morphology. Those indicated that the PP-g-GMA could compatibilize PP/SEBS-g-MAH blends effectively and improve the degree of dispersion and morphology stability. Notched Izod impact tests showed that the formation of PP-g-SEBS copolymer induced a further improvement of impact property and a tougher PP blend was obtained.

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