

Evaluations of PP-g-GMA and PP-g-HEMA as a Compatibilizer for Polypropylene/Clay Nanocomposites

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ABSTRACT

In this study, we investigated the performances of a hydroxyl ethyl methacrylate grafted PP (PP-g-HEMA) and a glycidyl methacrylate grafted PP (PP-g-GMA) as a compatibilizers in PP/clay nanocomposites. The compatibilizers were prepared by melt grafting with a radical initiator. Since the PP-g-MA is successfully and widely used in the PP/clay nanocomposites, we also studied three PP-g-MAs containing different amount of MA and having different molecular weights for a comparison. PP/clay nanocomposites compatibilized by the PP-g-HEMA and the PP-g-GMA show similar level of the clay interlayer distances with those of the PP-g-MAs. We also investigated the effect of molecular weights of the compatibilizers. In general, the compatibilizer of lower molecular weight was observed to exhibit lower performance as a compatibilizer. It is observed that increase of polar group content in the modified PP (PP-g-HEMA, PP-g-GMA and PP-g-MA) always accompanies the molecular weight reduction which deteriorates the mechanical properties. Thus, we prepared the PP-g-HEMA and PP-g-GMA by incorporation of a styrene comonomer. The compatibilizers (PP-g-HEMA-*co*-styrene and PP-g-GMA-*co*-styrene) thus obtained show good performance as a compatibilizer in the PP/clay nanocomposites. We observed that the PP/clay composites containing the PP-g-HEMA-*co*-styrene and the PP-g-GMA-*co*-styrene have very well balanced mechanical properties.

Keywords: PP/clay nanocomposites, PP-g-HEMA-*co*-styrene, PP-g-GMA-*co*-styrene

1 INTRODUCTION

In this study, we investigated a hydroxy ethyl methacrylate grafted PP (PP-g-HEMA) and a glycidyl methacrylate grafted PP (PP-g-GMA) as a compatibilizer in the PP/clay nanocomposites. Additionally, the effects of molecular weights of the PP-g-HEMA and the PP-g-GMA were also investigated. As far as we know, PP-g-HEMA has never been tried as a compatibilizer in the PP/clay

nanocomposite. Though a few studies have reported the performance of PP-g-GMA [1], there has been no study on the effect of the molecular weight of the PP-g-GMA. It has been reported that the incorporation of styrene as a comonomer improves the grafting yield of GMA and MA onto PP [2-4]. Thus, we fabricated PP-g-HEMA and PP-g-GMA by incorporation of styrene comonomer and evaluated their efficiencies as a compatibilizer. Since PP-g-MA has been successfully and widely used as a compatibilizer for the PP/clay nanocomposites, it is used as a reference in this study.

2 EXPERIMENTAL

Materials

Two different PPs were used in this study. Commercial homo PP, used for fabrication of PP-g-HEMA and PP-g-GMA, was from Samsung-Total Chemicals. Metallocene catalyzed poly(ethylene-*co*-octene) was used as an elastomer in PP/clay nanocomposites to increase the impact strength. Organoclay (trade name: Cloisite 20A) based on dimethyl, dehydrogenated tallowquaternary ammonium was purchased from Southern Clay Products, Inc. Hydroxy ethyl methacrylate (HEMA), a glycidyl methacrylate (GMA), styrene and 1,3-bis-(*t*-butyl peroxy-isopropyl) benzene were from the Aldrich Chemicals.

Preparations of the compatibilizers

Preparations of the compatibilizers and the nanocomposites were carried out in a twin screw extruder. The powdery PP was tumble-mixed with a polar monomer (HEMA or GMA), 1,3-bis-(*t*-butylperoxy-isopropyl) benzene as an initiator and antioxidant (Irganox1010) in a sealed plastic bag. The mixture was immediately put into a hopper of the twin screw extruder for compounding. The content of the polar monomer varied from 1.2 to 2.0 phr. The ratio of polar monomer/initiator was set to 10. The compatibilizers incorporated by the styrene comonomer were also prepared. In this paper, a code for the compatibilizer will be used as follows:

The code PP-g-HEMA2.0St2.0 represents a compatibilizer prepared from the mixture of PP of 100 g, HEMA of 2.0 g, styrene of 2.0 g and an initiator 0.2 g. In

the same rule, PP-g-GMA1.2 represents the compatibilizer prepared from the mixture of PP of 100 g, GMA of 1.2 g and an initiator of 0.12 g.

Preparations of the nanocomposites

Since the nanocomposites prepared by masterbatch method provide better micro scale dispersion [5-9], all composites were prepared by a two-step masterbatch method. The first step was blending the compatibilizers and clay at a ratio of 7/3 wt./wt. (compatibilizer/Cloisite20A), creating a masterbatch. In the second dilution step, each of the masterbatch samples was dry mixed with predetermined amounts of PP and elastomer and subsequently metered to the screws. The amounts of the masterbatch, PP, and elastomer were 50, 35, and 15 (by weight), respectively. Therefore, the percentages of clay, compatibilizer, PP, and elastomer in the nanocomposites were 15, 35, 35, and 15, respectively.

Characterizations

Wide angle X-ray data were collected on a Rigaku D/MAX-IIIC X-ray diffractometer (Cu K α radiation, wavelength = 1.5418) with accelerating voltage of 40 kV. Diffraction spectra were obtained over a 2 θ range of 1.28 – 10 $^\circ$.

Tensile properties and Flexural properties were tested using a universal mechanical testing machine (Model Hounsfield H25KS). Notched Izod impact tests were carried out at a room temperature. Melt flow index (MFI) was measured at 230 $^\circ$ C and 2.16 Kg load (ASTM D1238).

3 RESULT & DISCUSSION

It is known that achieving the homogeneous dispersion of the silicate layers (well exfoliated or at least intercalated structure) within the polymer matrix is a key factor to achieve good physical properties of the polymer/clay nanocomposites. Thus, we investigated the level of the polymer intercalation by the XRD. Fig. 1 shows the XRD patterns for the PP/clay nanocomposites. The vertical line in Fig. 1 represents the position of the d001 peak of the organo clay (Cloisite 20A). Based on the XRD data, the d001 spacings (clay interlayer distance) are calculated and the values are shown in each curve. As can be seen, all composites except the PP/PP-g-MA2.6/C20A show the intercalated structures. The PP/PP-g-MA2.6/C20A does not show the clay characteristic peak implying the exfoliated structure. The d001 peaks of the other nanocomposites are observed to shift to lower angles compared to the peak of the organo clay, showing the clay interlayer distances are enlarged from 2.4 nm to around 2.8 nm.

Since the performance of PP-g-MA as a compatibilizer is affected by the level of the MA contents and the molecular weight, we investigated three PP-g-MAs containing different MA contents and molecular weights. It is known that PP-g-MA having higher MA content provides

better dispersion of the silicate layers. Thus, it is understandable that PP/PP-g-MA2.6/C20A, which has the highest MA content among the PP-g-MAs investigated, shows the well exfoliated structure. On the other hand, the other composites compatibilized by PP-g-MAs (PP-g-MA0.5 and PP-g-MA0.8), PP-g-GMA1.2 and PP-g-HEMA1.2 provide the intercalated structures. As Fig. 1 shows, those four compatibilizers significantly increase the clay interlayer distance in the composites. The PP-g-GMA1.2 and PP-g-HEMA1.2 show similar levels of the interlayer distances to those of PP-g-MA0.5 and PP-g-MA0.8.

Selective physical properties of the PP/clay nanocomposites are shown in Table 1. When looking at the properties of the nanocomposites compatibilized by the PP-g-MAs, it is seen that the stiffness (tensile strength and flexural modulus) tends to increase with the MA content. This is because the dispersion of clay interlayers increases as the MA content increases. Due to economic reasons, the grafting of MA onto PP is generally carried out in an extruder with aid of radical initiators. To increase the MA content, the amounts of MA and the initiator should generally be increased. The radical initiator enhances not only the radical formation but also the chain scission of the polymer. Therefore, the molecular weight of PP-g-MA produced by the melt grafting method decreases with the MA content. Additionally, the maleated polymer becomes more brittle as the MA content increases. Though PP/PP-g-MA2.6/C20A exhibits the exfoliated nanostructure due to the highest polarity, the miscibility between PP and PP-g-MA2.6 is expected to be low because the high level of the polar MA group prevents a good mixing of PP-g-MA2.6 with the non polar PP, which may deteriorate the impact property of the nanocomposite [10] Though the stiffness of PP/PP-g-MA2.6/C20A is highest among composites investigated, its toughness (elongation at break and Izod impact strength) is poor because of the two reasons mentioned above. It is noteworthy that MFIs of PP/PP-g-MA2.6/C20A are much lower than those of PP/PP-g-HEMA1.2/C20A and PP/PP-g-GMA1.2/C20A, implying that the melt processibilities of PP/PP-g-MA2.6/C20A are poor compared with those of PP/PP-g-HEMA1.2/C20A and PP/PP-g-GMA1.2/C20A. This is a somewhat unexpected result because the MFI of PP-g-MA2.6 is higher than those of PP-g-HEMA1.2 and PP-g-GMA1.2. It is well known that rheological properties of the nanocomposites are very sensitive to the dispersion of nano-fillers. It has been frequently reported that the complex viscosity of the nanocomposites increases (especially at low frequency), the Newtonian plateau at low frequency weakens, and the yielding phenomenon becomes more pronounced as the level of clay dispersion increases. Therefore, MFI (sensitive property to low shear rate) of the nanocomposites compatibilized by PP-g-MA of the highest MA content is lowest as a consequence of the well-dispersed nanostructure.

In order to be used as a commercial plastic, property balance is important. Thus, PP-g-MA2.6 (with higher MA content) is regarded to be an inappropriate compatibilizer for PP/clay nanocomposite. It should be noted that there is a proper level of MA content in PP-g-MA to have the nanocomposite of well-balanced properties. In this study, the proper level of MA content is around 0.8 wt. % since the property balance of PP/PP-g-MA0.8/C20A is best among three nanocomposites compatibilized by the PP-g-MA. Many studies reported similar levels of MA content to this study [11]. Thus, we will compare the performance of PP-g-HEMA and PP-g-GMA with PP-g-MA0.8 afterward.

The physical properties of PP/PP-g-HEMA1.2/C20A are well balanced, as can be seen in Table 1. PP/PP-g-HEMA1.2/C20A is superior to PP/PP-g-MA0.8/C20A in most properties; especially, MFI. PP/PP-g-GMA1.2/C20A exhibits a similar level of physical properties with those of PP/PP-g-MA0.8/C20A. Thus, it can be concluded that the PP-g-HEMA and PP-g-GMA provide good performances as a compatibilizer in PP/clay nanocomposites.

The effects of the polar group content and molecular weights of PP-g-HEMA and PP-g-GMA were also investigated. Fig. 2 is the XRD patterns for the PP/clay nanocomposites compatibilized by the PP-g-HEMA and PP-g-GMA having various molecular weights and polar group contents. The physical properties of the corresponding nanocomposites are shown in Table 2. It is seen that the interlayer distance of PP/PP-g-HEMA/C20A and PP/PP-g-GMA/C20A is affected by the polar group content. PP/PP-g-HEMA1.5/C20A and PP/PP-g-GMA1.5/C20A exhibit slightly larger interlayer distance than those of PP/PP-g-HEMA1.2/C20A and PP/PP-g-GMA1.2/C20A. This is due to the compatibilizing effect of more polar PP derivative. However, PP/PP-g-HEMA2.0/C20A and PP/PP-g-GMA2.0/C20A show the smallest interlayer distance in spite of the highest polar group content. This is an inconsistent result with that of PP-g-MA.

Intercalation ability of a compatibilizer onto clay interlayers is affected by the interaction with clay and the viscosity of the compatibilizer. Higher polarity tends to increase the intercalation ability due to the better interaction with the organosilicates. Higher molecular weight tends to increase the intercalation ability due to the higher viscosity and stress during melt mixing since the higher stress can easily break the clay tactoids. As mentioned earlier, the molecular weight of the polar monomer grafted PP produced by the melt grafting method decreases with the amount of the grafted polar group. Therefore, two opposite effects exist in PP-g-HEMA and PP-g-GMA containing higher amounts of HEMA and GMA. In these polymers, the effect of molecular weight (thus viscosity) is inferred to be more dominant than the polarity.

The stiffness of PP/PP-g-HEMA1.5/C20A and PP/PP-g-GMA1.5/C20A is slightly higher than that of the PP/PP-g-HEMA1.2/C20A and the PP/PP-g-GMA1.2/C20A due to the better dispersion of the clay interlayers by the higher polarity. However, their toughness is decreased with the amount of the polar group. The processibility is also decreased with the amount of the polar group due to the same reason mentioned earlier. The physical properties of PP/PP-g-HEMA2.0/C20A and PP/PP-g-GMA2.0/C20A are observed to be the lowest. Again, it should be noted that the highest amount of a polar group does not guaranty the highest performance of the nanocomposite.

We observed that increasing the amount of the polar group in the modified PP derivative always accompanies the drastic decrease in molecular weight. It is reported that the incorporation of styrene as a comonomer improves the grafting yield of MA and GMA onto PP [2-4]. It is also expected that the incorporation of styrene comonomer prevents the chain scission in a certain degree, and consequently the polar group grafted PP having the high molecular weight and high grafting yield can be obtained. Therefore, we prepared the PP-g-HEMA and PP-g-MA by the incorporation of the styrene.

In this study, we evaluated the performance of PP-g-HEMA and PP-g-GMA as a compatibilizer in the PP/clay nanocomposites. PP-g-HEMA is first tried as a compatibilizer in the PP/clay nanocomposites. We observed that PP-g-HEMA and PP-g-GMA have similar levels of the compatibilizing efficiency with PP-g-MA. PP-g-HEMA gives slightly better efficiency than PP-g-GMA. In most previous studies on PP/clay nanocomposites, an improvement of the clay dispersion and increased stiffness of the nanocomposite by using the polar monomer grafted PPs have been highlighted and focused on. However, losing the toughness is always accompanied when the polar monomer grafted PPs are employed. We solved this problem by an incorporation of the styrene comonomer in the melt grafting step.

4 CONCLUSION

We evaluated the performance of PP-g-HEMA and PP-g-GMA as a compatibilizer in PP/clay nanocomposites. It was observed that PP-g-HEMA and PP-g-GMA show similar levels of compatibilizing effect with the PP-g-MA. It was also observed that an increase of the polar group content leads to a decrease of the molecular weight in the polar group grafted PP, which deteriorates the physical properties of the PP/clay nanocomposites. It was found out that the preparations of PP-g-HEMA and PP-g-GMA by incorporation of styrene monomer solve this problem. PP-g-HEMA-*co*-styrene and PP-g-GMA-*co*-styrene thus obtained show very good performances as a compatibilizer in the PP/clay nanocomposites.

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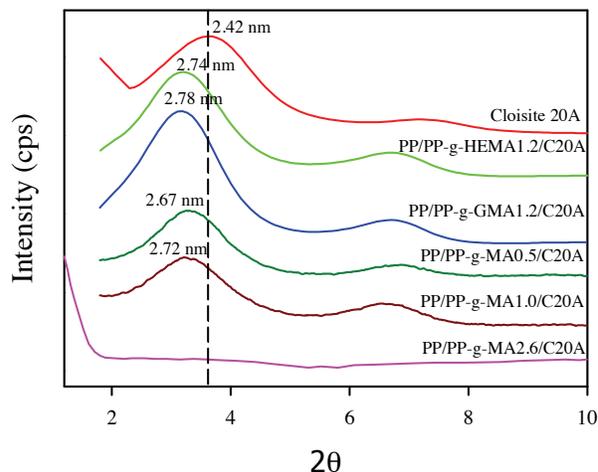


Figure 1: X-ray diffraction patterns of the PP/clay nanocomposites. Vertical line represents the position of the d_{001} peak of the organo clay (Cloisite 20A). Numbers shown in each peak represent the clay interlayer distances of the composites.

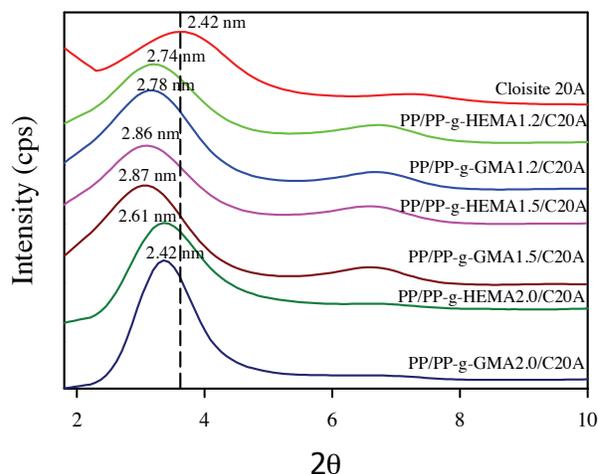


Figure 2: X-ray diffraction patterns of the PP/clay nanocomposites compatibilized by PP-g-HEMA and PP-GMA with different polar group contents. Vertical line represents the position of the d_{001} peak of the organo clay (Cloisite 20A). Numbers shown in each peak represent the clay interlayer distances of the composites.

| Samples properties | PP/PP-g- HEMA/MA/GMA/C20A | | | | | | | | | | | | | |
|---|---------------------------|-------------|--------------|-------------|--------------|-------------|------------|------------|------------|------------|-------|-------|-------|-------|
| | HEMA1.2/C20A | GMA1.2/C20A | HEMA1.5/C20A | GMA1.5/C20A | HEMA2.0/C20A | GMA2.0/C20A | MA0.5/C20A | MA0.8/C20A | MA2.6/C20A | MA0.5/C20A | | | | |
| MFT ^a (g/10min) of the nanocomposite | 8.5 | 4.9 | 0.7 | 2.6 | 4.5 | 15 | 18 | 257 | 110 | 10 | 230 | 210 | 14500 | 20.5 |
| MFI (g/10min) of the compatibilizer | 15 | 18 | 170 | 50 | 60 | 248 | 257 | 260 | 40 | 260 | 230 | 210 | 17500 | 20.5 |
| Tensile Strength (Kgf/cm ²) | 380 | 110 | 10 | 40 | 210 | 380 | 110 | 40 | 40 | 110 | 40 | 210 | 17500 | 20.5 |
| Elongation at break (%) | 15200 | 16600 | 25300 | 17500 | 14500 | 15200 | 16600 | 25300 | 17500 | 15200 | 16600 | 25300 | 17500 | 14500 |
| Flexural modulus (Kgf/cm ²) | 21.3 | 20.7 | 3.5 | 5.9 | 20.5 | 21.3 | 20.7 | 3.5 | 5.9 | 20.5 | 21.3 | 20.7 | 3.5 | 5.9 |
| Tzod impact Strength (Kgf/cm) | 21.3 | 20.7 | 3.5 | 5.9 | 20.5 | 21.3 | 20.7 | 3.5 | 5.9 | 20.5 | 21.3 | 20.7 | 3.5 | 5.9 |

Table 1: Physical properties of PP/clay nanocomposites.

| Samples Properties* | PP/PP-g- HEMA/MA/GMA/C20A | | | | | | | | | | | | | |
|---------------------------|---------------------------|-------------|--------------|-------------|--------------|-------------|------------|------------|------------|------------|-------|-------|-------|-------|
| | HEMA1.2/C20A | GMA1.2/C20A | HEMA1.5/C20A | GMA1.5/C20A | HEMA2.0/C20A | GMA2.0/C20A | MA0.5/C20A | MA0.8/C20A | MA2.6/C20A | MA0.5/C20A | | | | |
| MFI of the nanocomposite | 8.5 | 4.9 | 5.1 | 2.6 | 4.5 | 15 | 18 | 257 | 110 | 10 | 230 | 210 | 14500 | 20.5 |
| MFI of the compatibilizer | 15 | 18 | 49 | 42 | 82 | 248 | 257 | 263 | 97 | 216 | 232 | 210 | 17500 | 20.5 |
| Tensile Strength | 380 | 110 | 184 | 101 | 115 | 380 | 110 | 184 | 101 | 115 | 380 | 110 | 184 | 101 |
| Elongation at break | 15200 | 16600 | 18700 | 19400 | 15600 | 15200 | 16600 | 19400 | 15600 | 15200 | 16600 | 19400 | 15600 | 15200 |
| Flexural modulus | 21.3 | 20.7 | 8.2 | 11.2 | 6.4 | 21.3 | 20.7 | 8.2 | 11.2 | 6.4 | 21.3 | 20.7 | 8.2 | 11.2 |
| Tzod impact Strength | 21.3 | 20.7 | 8.2 | 11.2 | 6.4 | 21.3 | 20.7 | 8.2 | 11.2 | 6.4 | 21.3 | 20.7 | 8.2 | 11.2 |

Table 2: Physical properties of PP/PP-g-HEMA/MA/GMA/C20A and PP/PP-g-GMA/C20A nanocomposites. *The units are same as Table 2.