

Effect of GMA Polymer Compatibilizers on Highly Filled Composites of Low Density Polyethylene/Magnesium Hydroxide

Ke-rui Guo, Su-yun Xiang, Jiang-bo Sun and Chang-gong Meng*

Department of Chemistry, Dalian University of Technology, Dalian 116024, China

Abstract Functional polymers such as polyethylene grafted glycidyl methacrylate (PE-g-GMA) and ethylene-methyl acrylate-glycidyl methacrylate terpolymer (E/MA/GMA) were used as compatibilizers in the preparation of highly filled composites of polyethylene/magnesium hydroxide (PE/MH). Comparative studies were performed on the effect of magnesium hydroxide and stearic acid on the interface within polymer and magnesium hydroxide composites. The effect of polymeric compatibilizers on the properties of the composites was studied using tensile and impact tests, torque rheological analysis, differential scanning calorimetry and environmental scanning electron microscopy (ESEM). The microstructure of highly filled PE/MH composites changed after the addition of functional polymers. The mechanical properties of the composite material increased after compatibilization. The compatibilization processes of PE-g-GMA and E/MA/GMA were different. The grafted polymer was more compatible with polyethylene, which led to a polar polymer phase. In contrast, the tercopolymer tended to adhere to the surface of MH particles.

Keywords: GMA; Grafted polymer; *co*-polymer; Polyethylene; Magnesium hydroxide.

INTRODUCTION

Filled polymer composites are an important structural material and an area of research interest. Filler is added to a polymer material to decrease the amount of polymeric material required and decrease costs. It is also used to modify mechanical properties. An example of this is the production of highly filled polyethylene (PE)/magnesium hydroxide (MH) composites^[1, 2]. The mechanical properties of polymer composites can be affected by several factors including properties of the polymer matrix, filler particle size and shape, distribution of the filler in the polymer, and interfacial adhesion between filler and matrix. Typical coating agents for hydroxyl groups containing fillers are fatty acids such as stearic acid and their salts. These coating agents can react with hydroxyl groups and improve filler dispersion. This enhances lubrication and lowers the melt viscosity of the materials^[3].

To improve the adhesion between filler particles and the polymer in polyolefin based composites, polymeric compatibilizers are added^[4–12]. The hydrophobic polyolefins become hydrophilic after copolymerization or grafting polar monomers. Reactive groups interact with functional groups on the inorganic filler, and long hydrocarbon tails are anchored to the polymer matrix through physical entanglements and van der Waals interactions^[13, 14]. A durable connection between the filler and the matrix is thereby established. Short chains, such as stearic acid, are too short for this purpose. However, they are capable of reducing interfacial tension^[13]. Polymeric compatibilizers of interest include acrylic acid functionalized polypropylene (PP-g-AA)^[15–17], maleic anhydride functionalized polyethylene (PE-g-MAH)^[5], polypropylene (PP-g-MAH)^[13, 18, 19] and ethylene-propylene rubber (EPR-g-MAH)^[20]. Copolymers are also applied as compatibilizers and include poly(ethylene-

* Corresponding author: Chang-gong Meng (孟长功), E-mail: cgmeng@dlut.edu.cn

Received May 9, 2013; Revised July 2, 2013; Accepted July 4, 2013

doi: 10.1007/s10118-014-1401-5

co-vinyl acetate), poly(ethylene-co-ethyl acrylate)^[21] and ethylene-methyl acrylate-glycidyl methacrylate terpolymer(E/MA/GMA)^[3].

The use of grafted polymers or copolymers to improve highly filled composite performance is not well studied. The compatibilization mechanism of grafted polymers and co-polymers in high filled composites is not well understood. We found the nature of the interface played a substantial role in compatibilization. Modification of the inter-phase region by pre-coating the filler surface with a coating agent or encapsulating the fillers with compatibilizers altered the final properties of the composites. We investigated real composite interface morphology and polymer compatibilization mechanisms. Environmental scanning electron microscopy (ESEM) observation was also performed.

EXPERIMENTAL

Materials

Low density polyethylene (LDPE) with the trade name PEFAS-1C7A was provided by Yan Shan Petrochemical Co. (Beijing, China). Its density was 0.923 g/cm³ and the melt flow rate (MFR) was 7 g/10 min (JIS K6760). The particle size of magnesium hydroxide (MH) and coated magnesium hydroxide (MH_C) was about 1–5 μm. MH_C was coated with stearic acid to a stearic acid content of 1.2 wt%. PE-g-GMA was prepared in our laboratory. The grafting degree was about 1% (estimated by infrared spectroscopy). E/MA/GMA with the trade name LOTADER AX8900 from Arkema Co. was used. GMA monomer content was 8% (estimated by infrared spectroscopy).

Blending and Injection Molding

The composites consisted of 40 wt% polyethylene and 60 wt% MH. The amount of compatibilizer (10 wt%) was included in the polyethylene content (40% polyethylene was changed to 30% polyethylene with 10% compatibilizer. The total amount, 40%, remained unchanged). Commercial compatibilizers were dried over night at 60 °C before blending. The blends were prepared in a single screw extruder ($D = 40$ mm, $L/D = 45$). The extrusion temperature was set at 135 °C, 160 °C, 180 °C, 190 °C and 165 °C in sequence. After extrusion and pelleting, the blend was injection molded into tensile and impact test specimens with an injection molding machine. The injection temperature was 220 °C and injection pressure was 7.2 MPa.

Characterization of Blends

Tensile properties were characterized with a SHIMADZU AG-2000 using a test speed of 50 mm/min and type 1A specimens, according to the standard ISO 527-1993(E). Charpy impact was tested using type 1eAb specimens, according to ISO 179-1, at 18 °C and a relative humidity of 40%. Haake rheological analysis was carried out using a Haake Rheomix mixer equipped with roller blades (HAAKE PloyLab System, Thermo). The mixing speed was maintained at 20 r/min. The reaction temperature was set at 175 °C. The morphology of the fractured surfaces of the specimens was investigated with an environment scanning electron microscope (ESEM, FEI Quanta 200). Melting and crystallization behavior were studied with a differential scanning calorimeter (DSC) NETZSCH DSC 204 under a nitrogen atmosphere. The rate of heating was 10 K/min and the temperature range varied from 30 °C to 200 °C.

RESULTS AND DISCUSSION

Mechanical Properties

The tensile strength, elongation at break and Charpy impact strength of notched specimens of PE/MH (40/60) and PE/MH_C (40/60) blends with and without 10 wt% PE-g-GMA or E/MA/GMA were determined (Table 1).

The impact strength of PE/MH_C was 50% greater than that of PE/MH (40/60). The elongation at breaking of PE/MH_C was 36% greater than that of PE/MH (40/60). Stearic acid is used in making composites of PE/MH (40/60) in order to improve their toughness and to modify the inorganic particle surface. The impact strength of PE/MH/PE-g-GMA (30/60/10) was 100% greater than that of PE/MH (40/60) and the elongation at break of PE/MH/ PE-g-GMA (30/60/10) was 57% greater than that of PE/MH (40/60). The compatibilizer PE-g-GMA

had a better effect than stearic acid. The impact strength of PE/MH_C/PE-g-GMA (30/60/10) was similar to that of PE/MH/PE-g-GMA (30/60/10), and the tensile strength and elongation at break slightly less. The mechanical properties of the materials improved after the addition of PE-g-GMA. This improvement was attributed to the interaction between polymer and particles rather than the change in polymer matrix, as the tensile strength of PE/MH_C was higher than that of PE/MH_C/PE-g-GMA. The composite mixture used was PE/MH/(E/MA/GMA) (30/60/10). Composites made of PE/MH_C/(E/MA/GMA) had improved toughness and decreased tensile strength.

Table 1. Composition and mechanical properties of PE/MH/PE-g-GMA and PE/MH/(E/MA/GMA) composites

Code	PE (wt%)	MH (wt%)	MH _C (wt%)	PE-g-GMA (wt%)	E/MA/GMA (wt%)	Impact strength (J/mm ²)	Tensile strength (MPa)	Elongation at break (%)
a	40	60				2.56	10.88	7.94
b	40		60			3.99	12.25	10.81
c	30	60		10		5.24	12.54	12.50
d	30		60	10		5.30	11.27	8.05
e	30	60			10	6.61	13.92	15.10
f	30		60		10	10.30	9.60	26.00

Haake Rheological Analysis

A Haake Rheocorder was used to investigate the interface and thermorheologic properties of composite materials. The ingredients in the samples are listed in Table 1. Torque-time curves of the samples are shown in Fig. 1. Torque was used to characterize the melt viscosity of PE/MH composites, as the ratio of PE to MH was fixed. The melt viscosity of PE/MH_C (40/60) was lower than that of PE/MH (40/60). MH particles modified with stearic acid decreased melt viscosity.

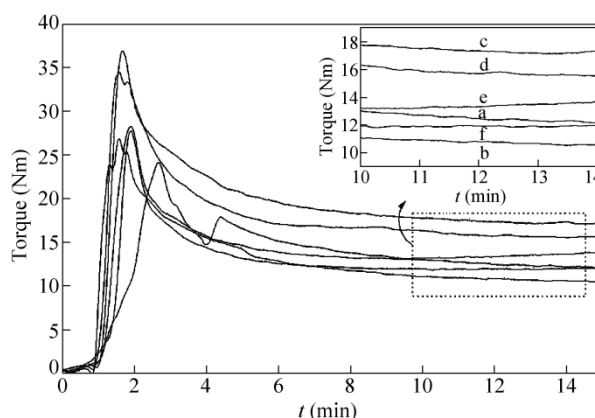


Fig. 1 The effect of compatibilizers on the rheology of PE/MH and PE/MH_C: (a) PE/MH, (b) PE/MH_C, (c) PE/MH/PE-g-GMA, (d) PE/MH_C/PE-g-GMA, (e) PE/MH/(E/MA/GMA) and (f) PE/MH_C/(E/MA/GMA)

The motion of polyethylene macromolecules was improved after the MH particles were modified. Reducing polyethylene and adding PE-g-GMA to form the composite PE/MH (40/60) increased the melt viscosity. The addition of PE-g-GMA to PE/MH_C (40/60) increased the torque. The torque difference between PE/MH/PE-g-GMA (30/60/10) and PE/MH_C/PE-g-GMA (30/60/10) were the same as that between PE/MH (40/60) and PE/MH_C (40/60). It is likely that there was no interaction between PE-g-GMA and stearic acid. The melt viscosity in composite PE/MH/(E/MA/GMA) (30/60/10) increased, but remained lower than that of PE/MH/PE-g-GMA (30/60/10). The E/MA/GMA copolymer had better adhesion between polyethylene and MH when the melt flow rate of E/MA/GMA was higher than that of polyethylene. The difference in torque between PE/MH/(E/MA/GMA) (30/60/10) and PE/MH_C/(E/MA/GMA) (30/60/10) was the same as that between PE/MH (40/60) and PE/MH_C (40/60). This suggests there were no interactions between E/MA/GMA and stearic acid.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) measurements were carried out to evaluate the influence of MH particles on melt and the crystallized behavior of polyethylene. These finding helped explain how the addition of GMA grafting polymer (10 wt%) or GMA copolymer (10 wt%) changed the composite properties.

Figure 2 shows the DSC heating thermograms of PE/MH and PE/MH/PE-g-GMA composites. The stearic acid had no effect on the melting behavior of polyethylene in PE/MH (40/60). A polyethylene melting multipeak was seen after the addition of PE-g-GMA. This indicates that the composite was divided into a polyethylene phase and a PE-g-GMA phase. When the melting temperature (T_m) of PE-g-GMA was higher than that of polyethylene alone, the multi-melting peak was blunted. The peak tended to occur at higher temperatures, which indicates the polyethylene phase was affected by the PE-g-GMA phase. The PE/MH (40/60) and PE/MH/(E/MA/GMA) DSC heating thermograms are compared in Fig. 3. The addition of E/MA/GMA had no effect on the T_m of PE/MH (40/60). The melting peak of PE/MH/(E/MA/GMA) and PE/MH_C/(E/MA/GMA) was similar to that of PE/MH (40/60).

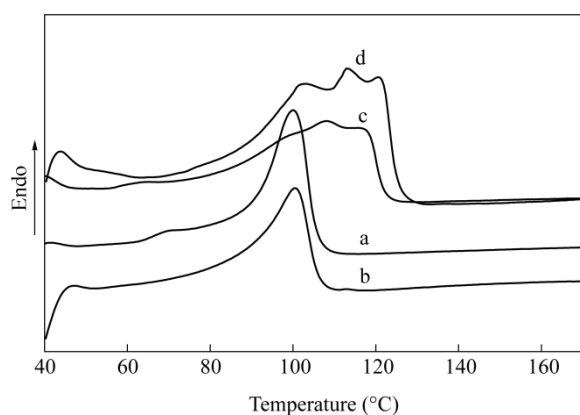


Fig. 2 DSC heating thermograms of PE/MH and PE/MH/PE-g-GMA composites: (a) PE/MH, (b) PE/MH_C, (c) PE/MH/PE-g-GMA and (d) PE/MH_C/PE-g-GMA

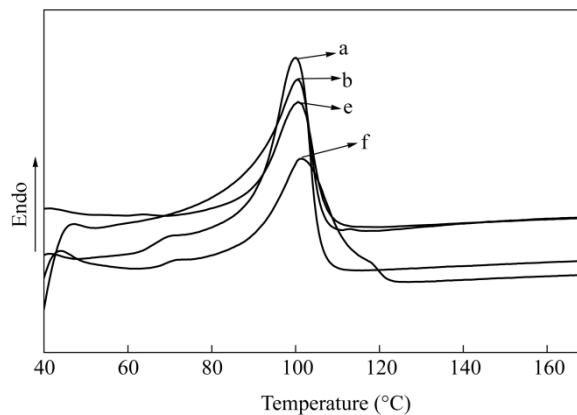


Fig. 3 DSC heating thermograms of PE/MH and PE/MH/(E/MA/GMA) composites: (a) PE/MH, (b) PE/MH_C, (e) PE/MH/(E/MA/GMA) and (f) PE/MH_C/(E/MA/GMA)

Morphologic Analysis

Figure 4 shows the fractured surface morphology of the specimens. The surface of unmodified MH particles were smooth and almost separate from the polymer phase (Fig. 4a). Figure 4(b) shows the surface topography of PE/MH_C. The surface of modified MH particles was partially coated and the interface between MH particles and polymer was closer than in PE/MH. The addition of 10 wt% PE-g-GMA made the composite denser than PE/MH_C, especially in the polymer phase (Fig. 4c). The morphology of the polyethylene changed and the polyethylene macromolecules appeared to coalesce after treatment. The coated MH particles separated from the composite made of PE/MH_C/PE-g-GMA, which showed that PE-g-GMA was not compatible with the blends (Fig. 4d).

Figures 4(e) and 4(f) show the surface of PE/MH/(E/MA/GMA) and PE/MH_C/(E/MA/GMA). The MH particles were covered with thick “coats”. As the copolymer E/MA/GMA was the only addition to the PE/MH composite, the “coats” were thought to be composed of E/MA/GMA. This was different from the stearic acid coating we observed (Figs. 4b and 4d). MH particles were thickly coated. The increase in impact strength and elongation at break found in PE/MH/(E/MA/GMA) was thought to result from the altered interface and its effect on the mechanical properties of the composites. The MH particles were uniformly dispersed (Fig. 4f). The polyethylene phase and MH phase were tightly adherent. This suggests that the compact structure was caused by the interaction of stearic acid and E/MA/GMA.

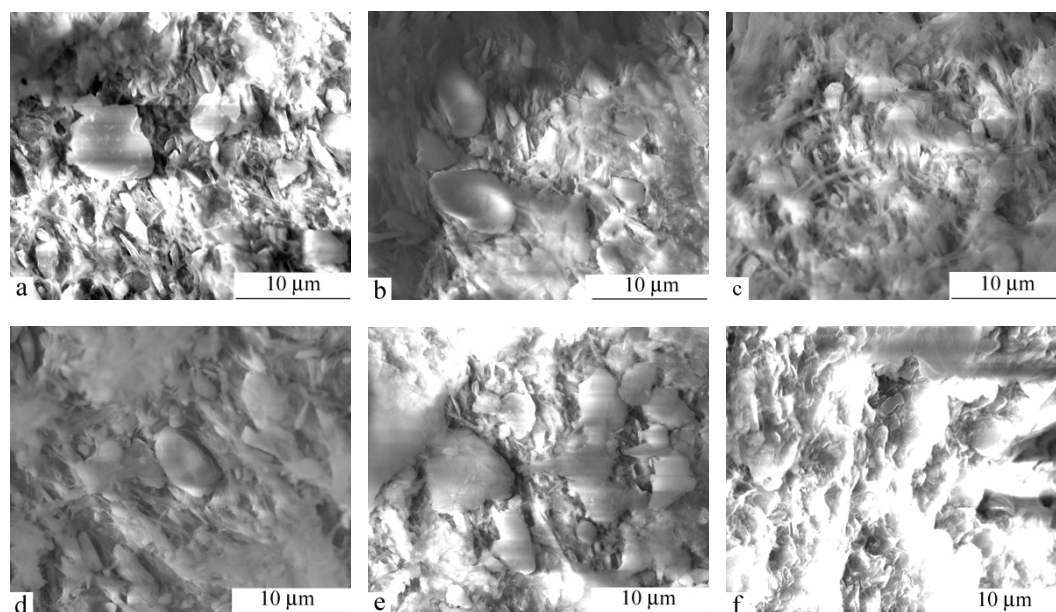


Fig. 4 ESEM photos of PE/MH composites: (a) PE/MH, (b) PE/MH_C, (c) PE/MH/PE-g-GMA, (d) PE/MH_C/PE-g-GMA, (e) PE/MH/(E/MA/GMA) and (f) PE/MH_C/(E/MA/GMA)

CONCLUSIONS

PE-g-GMA was more compatible with polyethylene in composites of PE/PE-g-GMA, which improved adhesion between polymer matrix and MH particles. In contrast, E/MA/GMA tended to adhere to the surface of MH particles, forming a coating on the particles. E/MA/GMA and stearic acid had a synergistic effect on PE/MH composites, allowing the MH particles to disperse uniformly in the polyethylene.

REFERENCES

- 1 Fang, Z.P. and Hu, Q.L., *Angew. Makrom. Chem.*, 1999, 265: 1
- 2 Enikolopyan, N.S., Fridman, M.L., Stalnova, I.O. and Popov, V.L., *Adv. Polym. Sci.*, 1990, 96: 1
- 3 Hippi, U., Mattila, J., Korhonen, M. and Seppälä, J., *Polymer*, 2003, 44: 1193
- 4 Hong, C.H., Lee, Y.B., Bae, J.W., Jho, J.Y., Nam, B.U., Chang, D.H., Yoon, S.H. and Lee, K.J., *J. Appl. Polym. Sci.*, 2005, 97: 2311
- 5 Hausmann, K. and Flaris, V., *Polym. Comp.*, 1997, 5: 113
- 6 Shen, H., Wang, Y.H. and Mai, K.C., *Thermochim. Acta*, 2009, 483: 36
- 7 Othman, N., Ismail, H. and Mariatti, M., *Polym. Degrad. Stab.*, 2006, 91: 761
- 8 Antunes, M., Velasco, J.I. and Haurie, L., *J. Cell. Plast.*, 2011, 47: 17
- 9 Yang, Z., Zhou, C.G., Cai, J., Yan, H., Huang, X., Yang, H. and Cheng, R.S., *Eng. Chem. Res.*, 2010, 49: 6291
- 10 Shen, H., Wang, Y.H. and Mai, K.C., *Thermochim. Acta*, 2007, 457: 27
- 11 Uotila, R., Hippi, U., Paavola, S. and Seppälä, J., *Polymer*, 2005, 46: 7923
- 12 Liu, S.P., Ying, J.R., Zhou, X.P., Xie, X.L. and Mai, Y.W., *Compos. Sci. Technol.*, 2009, 69: 1873
- 13 Janáčč, J. and Kucera, J., *Polym. Eng. Sci.*, 1990, 30: 714
- 14 Rahma, F. and Fellahi, S., *Polym. Comp.*, 2000, 21: 175
- 15 Mai, K.C., Li, Z.J., Qiu, Y.X. and Zeng, H.M., *J. Appl. Polym. Sci.*, 2001, 80: 2617
- 16 Hornsby, P.R. and Watson, C.L., *J. Mater. Sci.*, 1995, 30: 5347
- 17 Chiang, W.Y. and Hu, C.H., *Composites Part A*, 2001, 32: 517

- 18 Janáčĉ, J., J. Mater. Sci., 1989, 24: 4268
- 19 Xie, X.M., Chen, N.H. and Li, S., Acta Polymerica Sinica (in Chinese), 1999, (3): 351
- 20 trålin, S.A. and Hjertberg, T., J. Adhes., 1993, 41: 51
- 21 Morgan, A.B., Cogen, J.M., Opperman, R.S. and Harris, J.D., Fire Mater., 2007, 31: 387