

The effect of epoxy and tetramethyl thiuram disulfide on melt-grafting of maleic anhydride onto polypropylene by reactive extrusion

Jinfen Lou,¹ Zhu Luo,² Yang Li³

¹Guizhou Material Industrial Technology Institute, Guiyang, China, 550014

²Polymer Engineering Department, College of Materials Science and Metallurgy, Guizhou University, China, 550025

³Guizhou Institute of Technology, Guiyang, China, 550003

The experimental operation and data analysis of this text was mainly conducted by Jinfen Lou. Zhu Luo is responsible for the idea, guidance, and amendments. Li Yang assisted in completing the operation of the experiment.

Correspondence to: Z. Luo (luozhu2000@sina.com)

ABSTRACT: In this report, melt grafting of maleic anhydride (MAH) and epoxy resin onto polypropylene (PP) by peroxide-initiated reactive extrusion has been investigated. As evidenced by Fourier transform infrared spectroscopy, both MAH and epoxy resin were successfully grafted onto PP through the reactions of MAH with PP and epoxy resin with MAH. It was found that tetramethyl thiuram disulfide could promote the grafting of MAH and inhibit the degradation of PP, as revealed by chemical titration and melt flow experiments, through prolonging the lifetime of the macroradical; meanwhile, epoxy resin could reduce the sublimation of MAH and the maximum grafting degree of MAH. Furthermore, the introduction of grafted products was found to enhance the mechanical properties of PP/glass fiber composites, and this influence was very significant at high grafting degrees with a high content of epoxy resin, which could be interpreted in terms of improved compatibility and adhesion at the interface. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43422.

KEYWORDS: addition polymerization; extrusion; polyolefins; properties and characterization; structure–property relations

Received 16 August 2015; accepted 6 January 2016

DOI: 10.1002/app.43422

INTRODUCTION

The functionalization of polypropylene (PP) through grafting with unsaturated polar monomers, such as maleic anhydride (MAH), acrylic acid, and their derivatives, by peroxide-initiated reactive extrusion has been a routine method to improve the interfacial adhesion and compatibility between PP and fibers or other polymers. The grafting reaction is generally performed chemically¹ or photochemically² in the solution,³ melt,^{4,5} or solid⁶ state with organic peroxides. Grafting reactions of MAH onto PP have been carried out often using torque rheometers and single-screw⁵ or twin-screw⁷ extruders in melt. Reaction in the melt, by reactive processing, has been preferred because the process has a number of advantages, such as simple operation, less investment in equipment, continuous production, and low cost.

Previous studies have shown that the reaction between PP and MAH in extrusion is often accompanied by undesirable side reactions that will result in degradation of the PP. The grafting of MAH can reach a certain level only at the expense of greatly reduced molecular weight. Furthermore, compared with some other polar monomers, such as itaconic acid (IAc), 2-octen-1-

ylsuccinic anhydride (OY), 3-allyloxy-1,2-propanediol (AP), or 2-hydroxyethyl methacrylate (HEMA),⁸ the grafting efficiency is often very low despite a high concentration of initiator and the unsaturated polar monomer used. This is partly explained by the low free-radical reactivity of MAH with PP due to its orbital symmetry and the low solubility of MAH in the PP melt,⁸ as well as sublimation of MAH.⁹ The product resulting from extrusion is a mixture containing the residual reactants and low-molecular-weight graft products.

Grafting MAH onto PP has been illustrated as the process of the simultaneous occurrence of graft reaction and β -scission (as shown in scheme 1).^{10–16} The key to enhance the grafting ratio or to reduce the degradation of PP is to stabilize the macroradicals formed through hydrogen abstraction and reducing sublimation of MAH at the reaction temperature. Polyfunctional acrylate (PFA) has a higher reactivity with PP macroradicals than MAH and can form stabilized macroradicals, thus reducing the β -scission of macroradicals.⁸ The presence of thiurams or C₆₀ could prolong the lifetime of PP macroradicals and reduce degradation of PP.^{17,18} Styrene¹⁹ or α -methylstyrene²⁰ also could be a comonomer to improve the MAH reactivity by reaction

with MAH to form styrene–MAH copolymer before the two monomers can graft onto the PP backbone, thus controlling the chain scission to some extent. In general, the addition of an electron donor as a comonomer to the grafting reaction system is a good method, however, the graft efficiency was improved but was still unsatisfactory. So, on the basis of this, how to further reduce the degradation of PP, and inhibit the sublimation of MAH, and thus increase the graft rate in the reactive process has implications.

To our knowledge, there is still no published report on the application of epoxy in the maleation of PP. The epoxy can absorb onto the anhydride groups, thus inhibiting the sublimation of MAH. By the reaction of multifunctional epoxy resin with the grafted anhydride groups, a certain degree of PP coupling structure could be made, which may reduce the degradation of PP, and the compatibilizing efficiency of the graft product may be improved through simultaneous grafting of different types of polar monomers onto the molecular chain of PP. In this article, we described how epoxy together with tetramethyl thiuram disulfide (as a macromolecular free-radical stabilizer) influenced the grafting of MAH on PP during the reactive extrusion process, as well as the properties of PP/glass fiber (GF) composites containing the grafted products. The maximum temperature was limited to 210 °C in this work. Considering that a higher initiator concentration should give higher MAH grafting degree but more severe degradation because more radicals generated by the initiator would be prone to result in greater β -scission, 0.25 phr dicumyl peroxide and 2 phr MAH were chosen as initiator and grafting monomer.

EXPERIMENTAL

Materials

An isotactic PP (i-PP), T30s, was obtained from Dushanzi Petrochemical, a branch of China National Petroleum Corporation (Kalamayi, Xinjiang, China), with a melt flow index (MFI) of 3.4 g/10 min (230 °C, 2.16 kg). Maleic anhydride (MAH) was supplied by Tianjin Damao Reagent Co. (Tianjin, China). Dicumyl peroxide (DCP) was produced by Shanghai Ling Feng Chemical Reagent Co. (Shanghai, China). Bisphenol epoxy resin, E51, with epoxy value of 0.51, was supplied by Shanghai Resin Factory Co. (Shanghai, China). The glass fiber (diameter 13 μ m), ER5305A-2400, surface-treated with a silane coupling agent (3-aminopropyltriethoxysilane), was produced by Chongqing International Co. (Chongqing, China). Tetramethyl thiuram disulfide (TMTD) was supplied by Puyang Weilin Chemical Co. (Puyang, Henan, China). Xylene, acetone, ethanol, isopropanol, potassium hydroxide, and hydrochloric acid were of analytical grade and commercially available.

Preparation of PP-g-MAH

The grafting of MAH onto PP (PP-g-MAH) was achieved by twin-screw extrusion. Before the extrusion, the PP granules were dried at 100 °C for 3 h. Then the dried PP, initiator (DCP), MAH, TMTD, and epoxy resin (E51) were blended in a high-speed mixer at 25 °C. The melt-grafting reactions were carried out in a TSE-40A intermeshing corotating twin-screw extruder (produced by Nanjing Ruiya Polymer Processing Equipment Co., Nanjing, China) with a 40:1 length-to-diameter

ratio. The temperature profile of the extruder was 180 °C, 190 °C, 200 °C, 210 °C, 210 °C, and 210 °C, and the rotation speed of the screws was 240 rpm. The rods from the extruder were cut into granules of about 1 cm length after cooling in a water bath and drying at 100 °C for 5 h.

Purification

Approximately 5 g of sample and 300 ml of xylene were placed in a 500 ml round-bottom flask and then boiled for 2 h at 135 °C. The mixed solution was moved to a beaker. Thereafter, a large quantity of acetone was added to precipitate the PP and PP-g-MAH, while the unreacted epoxy, TMTD, and ungrafted MAH still remained in solution. In this way, PP and PP-g-MAH were separated from the unwanted reactants and additives. The precipitate was poured into a Buchner funnel for filtration, washed twice with a suitable amount of acetone, and then dried at 100 °C under vacuum for 10 h.

Characterization

The grafting degree (GD) of PP-g-MAH was determined by the chemical titration method. About 1 g of the purified product was dissolved in 120 ml of refluxing xylene in a flask for 20 min, then 10 ml 0.1 mol/L KOH–ethanol standard solution was added to the cooled xylene solution at 90 °C to neutralize carboxylic acid groups. After that, the xylene–KOH solution was refluxed again for 2 h to ensure a complete reaction of the KOH with the graft groups. The hot solution was titrated with a 0.1 mol/L HCl–isopropanol standard solution. The GD (wt %) was calculated by the following equation:

$$GD = \frac{(10 \times C_{\text{KOH}} - V \times C_{\text{HCl}}) \times M_0}{2 \times W \times 1000} \times 100\% \quad (1)$$

wherein C_{HCl} is the concentration of the HCl–isopropanol standard solution (mol/L) used, C_{KOH} is the concentration of the KOH–ethanol standard solution (mol/L) used, W is the weight of the purified product (g), M_0 is the molecular weight of MA (98.06), and V is the volume of the HCl–isopropanol standard solution (ml) used. The titration was repeated four times for each sample; all samples showed a very good reproducibility in GD.

The melt flow index (MFI) was measured by a SRZ-400 Melt Indexer, (Intelligent Instrument Equipment Co., Changchun, China). The measurement was performed at 230 °C with a load of 2.16 kg, using the melt extrusion products.

After the samples were purified by solubilization in xylene and precipitated with acetone to eliminate the residual unreacted additives, a small amount of the purified precipitation powder was added to KBr and compressed into a transparent pellet for Fourier transform infrared spectroscopy (FTIR) measurements. The FTIR spectra were recorded on a Nexus 670 spectrometer (Thermo Nicolet Co., Wisconsin, USA) at a resolution of 4 cm^{-1} with an accumulation of 32 scans in the spectral range 4000–400 cm^{-1} .

The crystallization and melting behaviors were analyzed on a differential scanning calorimeter system (DSC, Q10, TA Instruments, New Castle, USA) purged with nitrogen. The samples,

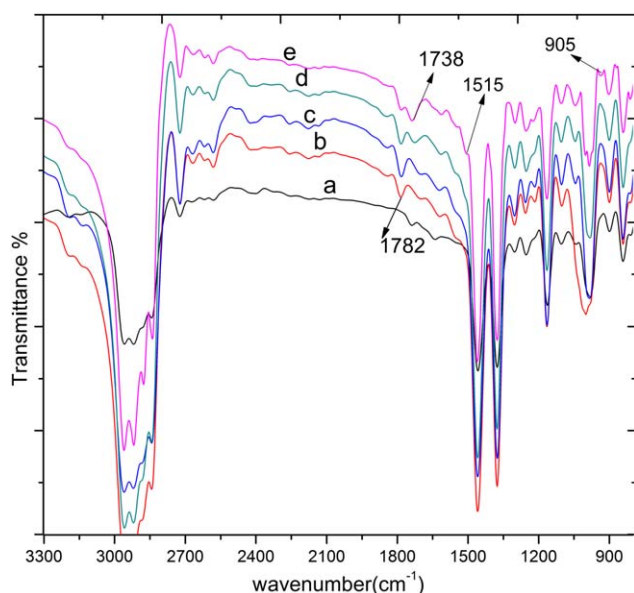


Figure 1. IR spectra of the maleic anhydride grafted products. (a) pure PP; (b) PP+DCP+MAH; (c) PP+DCP+MAH+TMTD; (d) PP+DCP+MAH+EP; (e) PP+DCP+MAH+TMTD+EP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

about 5 mg, were subjected to heating at a rate of 10 °C/min to 260 °C and then kept at that temperature for 5 min to erase any heating history. Then cooling was carried out at a rate of 10 °C/min to 80 °C. The second heating run was conducted under the same conditions as the first run.

The degree of crystallinity was calculated by means of the following equation:

$$X_c = \frac{\Delta H_c}{\Delta H_0 \cdot \Omega_{pp}} \times 100\% \quad (2)$$

where ΔH_c is the melt enthalpy of the sample, ΔH_0 is the melt enthalpy of the hypothetical PP with crystallinity of 100% (209 J/g), and Ω_{pp} is the mass fraction of PP.

The PP/GF blends were prepared by twin-screw extrusion in the presence of the grafted products. Before extruding, the grafted products were dried at 80 °C under vacuum for about 8 h. The composite was injected into standard samples by an injection-molding machine (PL860, Wuxi Haitian Machinery Co., Wuxi, Jiangsu, China), and then the mechanical properties were tested by a universal mechanical testing machine (WdW-10C, Shanghai Hualong Test Instruments, Shanghai, China) and pendulum impact tester (ZBC-4B, the Xinsansi Metering Technology Co., Shenzhen, Guangdong, China). The tensile strength was tested according to ISO 527:1993 with a tensile rate of 50 mm/min; the flexural experiment was done according to ISO 178:2001, with a rate of 2 mm/min; the cantilever impact strength was tested according to ISO 180:2000.

To determine the content of the glass fibers, 10 g of the PP/GF composites was accurately weighed and placed into a crucible and weighed, after which the crucible was placed into a muffle furnace (KSW resistance furnace, Nanjing Baodu Instrument

Co., Nanjing China) at 700 °C for 3 h. The crucible was weighed and put in the furnace for another half an hour and weighed again, until the deviation of the last two weighings was less than 0.1 g. Then the glass fiber content was determined based on the residual weight. The morphologies of fractured surfaces of the PP/GF composites were observed with a SEM (KYKY-2800B, Beijing KYKY Technology Co., Beijing, China) under the condition of 25 KV, and all samples were coated with gold prior to SEM examination.

RESULTS AND DISCUSSION

FTIR Spectra

Figure 1 shows the FTIR spectra of pure PP [Figure 1(a)] and purified grafted products using different formulas [Figure 1(b–e)]. An absorption peak at 1782 cm^{-1} was observed after reaction, corresponding to the unsymmetric stretching of carbonyl groups (C=O) of anhydride groups, which means that MAH was grafted to PP.^{21–25} Besides, the characteristic absorption peaks of the MAH monomer at 1592 cm^{-1} and 1060 cm^{-1} do not appear in the infrared spectrum curve.²⁶ Hence the unreacted MAH monomer was removed from the purified grafted product. In conclusion, the infrared spectrum indicates clearly that the initiator-induced MAH grafting on the backbone of PP chains is achieved.

Comparing curve (c) with curve (b), for the formula containing TMTD or no TMTD, we do not find different absorption peak at 1020 cm^{-1} to 1225 cm^{-1} that belongs to the characteristic group C=S of tetramethyl thiuram disulfide, so TMTD was not grafted to the PP in the grafting reaction. In curves (d) and (e), an absorption peak at 1738 cm^{-1} appears for the formula containing E51, which is ascribable to the symmetric stretching of the carbonyl group of the ester group formed by reaction between the anhydride and epoxy groups.^{21,22} Meanwhile, comparing curve (e) with curve (d) (the formula containing E51 in the presence or absence of TMTD), we notice that the ester absorption was enhanced and that the anhydride characteristic absorption was decreased, suggesting that TMTD promoted the grafting reaction of the MAH with the epoxy group. The weak

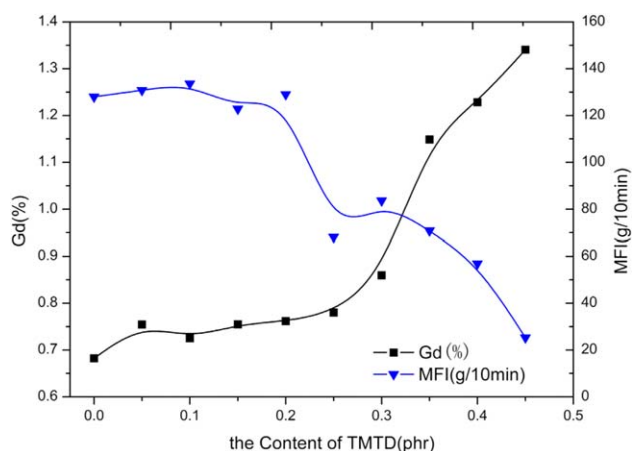
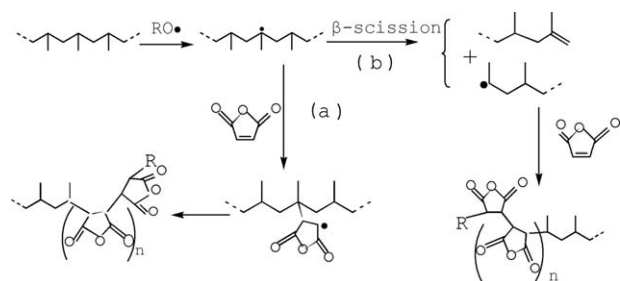
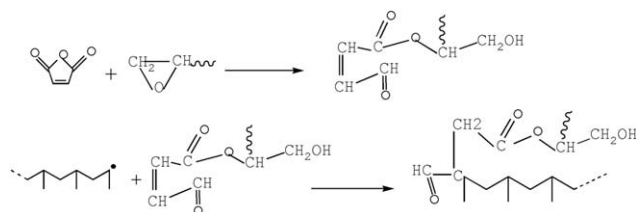


Figure 2. Effect of tetramethyl thiuram disulfide on the grafting and the melt flow index of the graft products. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Scheme 1. Maleic anhydride reacts with polypropylene.



Scheme 2. Maleic anhydride reacts with epoxy group and macroradicals.

absorption peaks at 905 cm^{-1} and 1515 cm^{-1} are attributed to unsymmetric stretching of the epoxy ring and benzene skeleton vibration, respectively. This indicates the ester was produced by the reaction of the epoxy group with anhydride groups, and the epoxy resin was grafted onto the macromolecular chain of PP.

Effect of TMTD on Grafting Degree and Melt Flow Index

As can be seen from Figure 2, when different contents of TMTD were employed in the grafting reaction of PP that contained 0.25 phr DCP and 2 phr of MAH, the grafting ratio of the graft product was increased with the increase of the TMTD content. The influence is significant when the content of TMTD was above 0.20 phr.

Because the grafting of MAH onto PP is a radical reaction, the PP macroradicals undergo scission, which results in a lower molecular weight. The MFI of a polymer can reflect the size of the molecular weight, and a smaller MFI value means the polymer is of higher molecular weight. With the increase of the con-

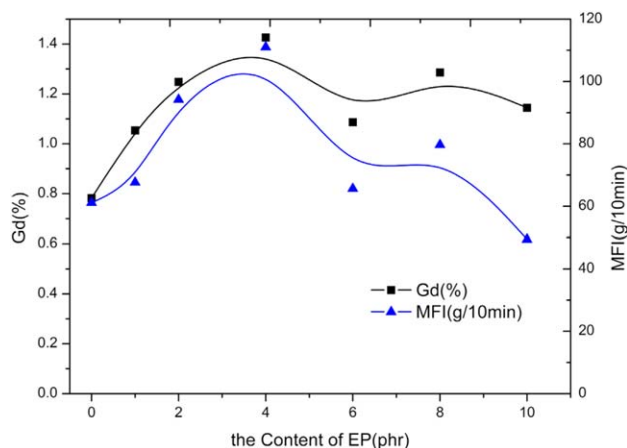


Figure 3. Effect of epoxy resin on the grafting degree and the melt flow index of the graft products. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tent of TMTD, the MFI decreased. When the thiuram content was 0.0–0.20 phr, the melt flow index of the grafted product was little changed; then the melt flow rate decreased rapidly with the increase of TMTD content. When the content of TMTD was 0.45 phr, the melt flow rate of the product was 20 g/10 min, far below the melt flow rate of the product without TMTD, manifesting that the degradation of PP was inhibited. Again, the impact is significant when the content of TMTD was above 0.20 phr.

The decomposition of TMTD generates dithiocarbamoyl radicals in the extrusion process, and the radical was capable of combination with macroradicals reversibly.²² Therefore, the reaction time of the macroradicals with the unsaturated monomer was prolonged, and the graft yield was increased by successive regeneration of the macroradicals in the reversible reaction. Meanwhile,

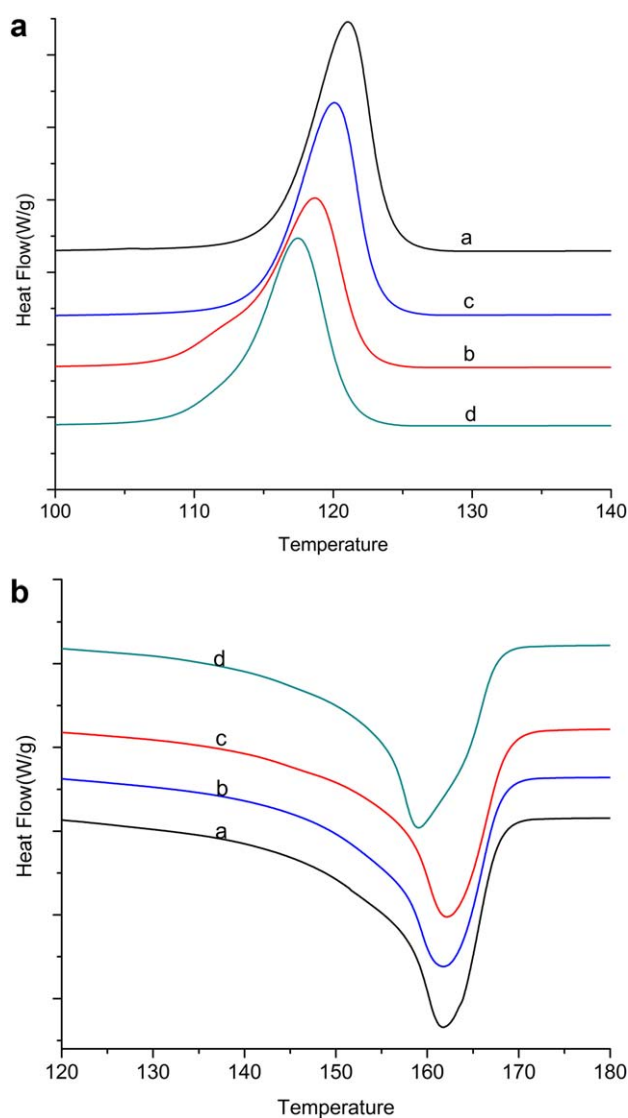


Figure 4. DSC (1) crystallization and (2) melting curves of different maleic anhydride grafted products: (a) PP+DCP+MAH; (b) PP+DCP+MAH+TMTD; (c) PP+DCP+MAH+EP; (d) PP+DCP+MAH+TMTD+EP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Parameters of Crystallization and Melting of the Grafted Products

DCP+MAH+ TMTD+EP	Crystallization peak (°C)	Crystallization start temperature (°C)	Crystallization enthalpy (J/g)	Peak temperature of melting (°C)	Melting enthalpy (J/g)	Crystallinity (%)
0.25 + 2	121.0	123.9	99.5	161.9	100.8	48.23
0.25 + 2 + 0.25	118.6	122.1	95.5	162.2	92.0	44.02
0.25 + 2 + 0 + 4	120.1	123.1	97.7	161.8	96.8	46.32
0.25 + 2 + 0.25 + 4	117.4	121.1	97.3	159.1	89.3	42.73

that combination can help to stabilize the macroradicals and reduce the degradation of PP, thereby improving grafting efficiency. Besides, we notice that the grafting ratio rose rapidly and the melt index declined vigorously both at a content above 0.2 phr. Thus the regulatory role of TMTD was obvious only when its content was greater than the content of initiator.

In our experiment, when the content of TMTD was more than 0.3 phr, the color of the graft product was deepened, which has a negative impact on the application.

Effect of Epoxy on Grafting Degree and Melt Flow Index

Considering the effect of TMTD on the grafting ratio, the melt flow index, and the color contamination of the grafted product above, 0.25 phr TMTD was used in the following experiment, while the content of E51 was varied in the reaction system. The reaction scheme of the epoxy group with MAH monomer is shown in Scheme 2. The above infrared spectrum of the product verifies the formation of ester, and the reactant contains the epoxy resin chain segment grafted on the PP chain. The active dithio-carbamoyloxy radicals produced by decomposition of TMTD cannot attack the PP backbone,²⁷ but the nucleophilic sulfur atom plays a role in promoting the epoxy group ring-opening reaction.²⁸ So, in the presence of TMTD, more epoxy molecules were grafted onto the PP molecular chain through reacting with the grafted anhydride (as shown in Figure 1).

The grafting degree and melt index of the products are shown in Figure 3. The changes in grafting rate and MFI with E51 content have the same trend. When the content of E51 was less than 4 phr, the grafting rate and MFI increased with the increase of the epoxy content. In the presence of epoxy, MAH monomer was absorbed by the epoxy group, due to the strong affinity between epoxy groups and anhydride groups, and we found that the evaporation of MAH during the reactive extru-

sion process was observably reduced, which contributed to increasing the grafting rate and significantly reducing the product's irritating odor in the preparation process. On the other hand, the lone pair of electrons of the oxygen atom has a certain affinity to the carbon atoms of the epoxy group, so with the addition of epoxy resin, oxygen in the air is brought into the blend. According to the test results of Bertin *et al.*,²⁹ traces of oxygen might enhance the degradation of PP, which contributes to increase the MFI of the polymer, and the formation of more β -scission could promote the grafting reaction.³⁰ When the E51 content was more than 4 phr, MFI was obviously decreased and the graft ratio was slightly decreased, while the coupling structure formed among a part of the PP molecular chains via the reaction of epoxy groups of the multifunctional epoxy resin with the grafted anhydride groups had become the main factor affecting the MFI, and a part of the grafted anhydride groups were converted to esters, which caused the decrease in MFI and the grafting rate detected by acid-base titration.

Crystallization Behavior

Pendant groups or a coupling structure leads to a decrease of the structural regularity of PP chains, which can affect the crystallization behavior of PP. Figure 4 presents the DSC curves of the graft products, and crystallization and melting parameters are listed in Table I. The data show that both the crystallization temperature and the degree of crystallinity of the graft products decrease when TMTD is added. As mentioned before, the introduction of TMTD would promote the grafting reaction, so the structural regularity of PP chains was damaged. When adding thiuram and epoxy simultaneously, the degree of crystallinity of the grafted product reached the minimum because the coupling structure was formed by the reaction of epoxy groups of the

Table II. Mechanical Properties of Polypropylene/Glass Fiber Composite Grafted with 5 phr Grafted Products

Sample	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
DCP+MAH+ TMTD+EP	0.25 + 2 + 0 + 0	0.25 + 2 + 0.25 + 0	0.25 + 2 + 0.25 + 1	0.25 + 2 + 0.25 + 2	0.25 + 2 + 0.25 + 4	0.25 + 2 + 0.25 + 6	0.25 + 2 + 0.25 + 8	0.25 + 2 + 0.25 + 10
Graft rate(%)	0.68	0.78	1.05	1.25	1.43	1.09	1.30	1.15
Glass fiber content (%)	27.58	28.24	27.45	27.83	27.60	28.63	28.89	27.28
Tensile strength (MPa)	79.67	82.87	89.60	94.41	95.65	97.83	99.06	94.30
Bending strength (MPa)	82.50	93.37	105.92	111.19	116.33	117.75	118.57	113.59
Impact toughness (kJ/m ²)	9.49	9.98	10.98	11.25	11.89	11.55	11.22	11.02

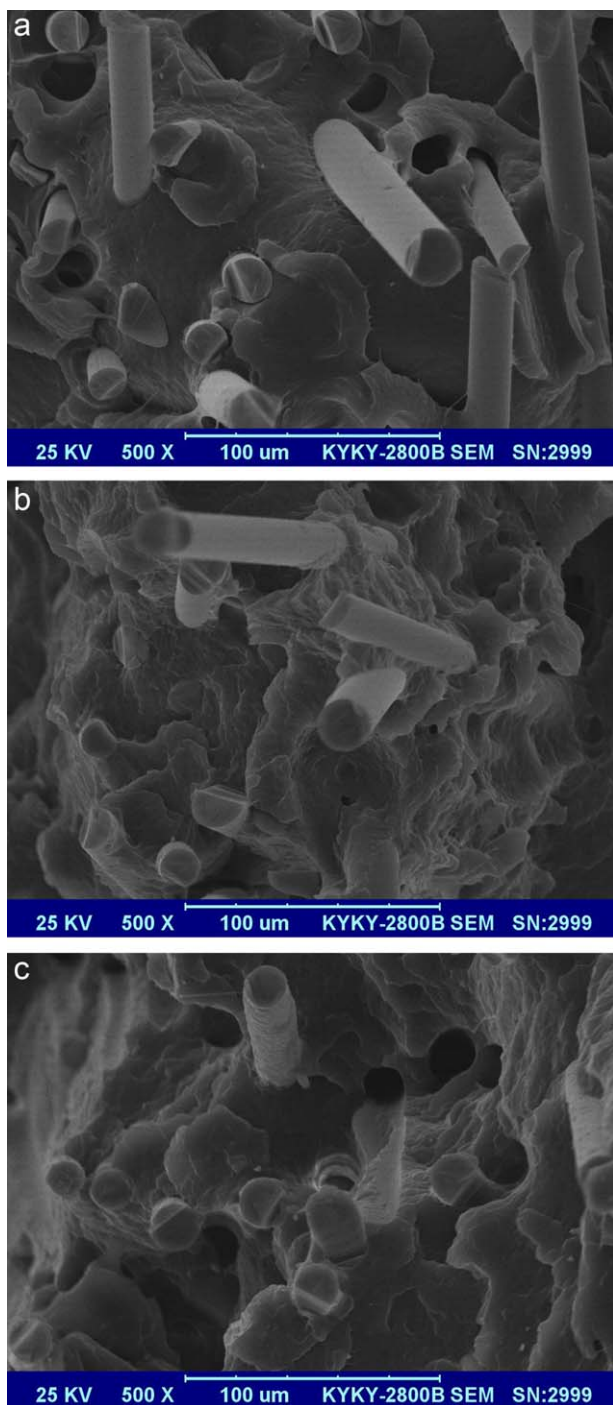


Figure 5. SEM micrographs of the tensile fracture surfaces of the composites with 5 phr different grafted products (DCP+MAH+TMTD+EP): (a) 0.25 + 2 + 0.25 + 1; (b) 0.25 + 2 + 0.25 + 4; (c) 0.25 + 2 + 0.25 + 8. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

multifunctional epoxy resin with anhydride groups of the PP-g-MAH, and thiuram enhanced the reaction.

Application of Grafted PP in PP/GF Composite

PP mixed with 5 phr grafted products produced by reactive extrusion was poured into the extruder, and three bunches of

glass fiber were pulled into the extruder from the feeding port at the same time. In the extruder, the glass fiber was cut into short fibers with length of about 0.5 mm, which were dispersed in the PP matrix. The glass fiber reinforced PP was moved out and injected into standard samples by an injection-molding machine for mechanical property testing. The experimental data obtained are listed in Table II.

The glass content is about 28%. In comparison with the PP/GF composites without any compatibilizers (the tensile strength was 51 MPa, the flexural strength was 78 MPa, impact toughness was 5 kJ/m²), the mechanical performance of PP/GF composites with graft products has been improved on the whole. Comparing sample (2) with (1) in Table II, the mechanical properties of the composites rose only a little by the addition of TMTD because of the increase of grafting degree. Comparing (3)–(8) with (2), when E51 and TMTD were added, the improvement of the mechanical properties was much more significant.

Figure 5 shows the SEM micrographs of the tensile fracture surfaces of the composites with 5 phr of different grafted products. Comparing Figure 5(c) with Figure 5(a) and Figure 5(b), we notice that the glass fiber in the composite is cohered with more matrix material after adding the grafted product that contained 8 phr E51. It is indicated that the composite interface was obviously improved with the increase of the content of epoxy resin in the grafted product used.

The grafting degree reached a maximum value when the epoxy content was 4 phr, while the tensile and bending strength reached their maximum values with the epoxy content of 8 phr. It is suggested that the grafted epoxy resin helped to improve the compatibility of the composites. Although the grafting rate detected by acid–base titration was slightly reduced by the esterification reaction of epoxy with grafted anhydride groups, the tensile strength and flexural properties were still increased with the increasing epoxy content. It is indicated that different types of polar monomers grafted onto the molecular chain of PP have a synergistic effect on the improvement of mechanical properties of the composites. When the epoxy content was more than 8 phr, the mechanical properties of the composite decreased, perhaps because of the softening effect of the unreacted liquid epoxy resin.

CONCLUSIONS

Maleic anhydride grafted polypropylene was prepared with a twin-screw extruder. The addition of TMTD improved the graft degree of MAH and reduced the melt index, the crystallization temperature, and the degree of crystallinity. The degradation of PP decreased when the content of TMTD was more than 0.25 phr.

The addition of a certain content of epoxy resin in the reaction system could reduce sublimation of maleic anhydride and improve the graft reaction of MAH. FTIR shows that the epoxy grafted onto the polypropylene molecular chain through the reaction of maleic anhydride with the epoxy. The addition of TMTD was conducive to the reaction. The maximum MAH graft degree was attained when 4 phr of epoxy was added. According to the results of DSC, the grafted PP in the presence

of TMTD and epoxy exhibited a lower melting point and lower crystallization temperature in comparison with that without epoxy or TMTD.

When the graft products were added to the PP/GF composites, the mechanical properties of the composites were improved significantly, especially for the PP-g-MAH containing epoxy.

ACKNOWLEDGMENTS

This work was financially supported by Scientific and Technological Fund of Guizhou Province, China (Qian Ke He (2009) 3010) and Project of Science and Technology Innovation Team of Guizhou Province, China.

REFERENCES

1. Wang, Z. M.; Hong, H.; Chung, T. C. *Macromolecules* **2005**, *38*, 8966.
2. Qian, J.; Huang, Z.; Dang, S.; Xu, Y. *Polym. Res.* **2011**, *18*, 1557.
3. Ruggeri, G.; Aglietto, M.; Petraghani, A.; Ciardelli, F. *Eur. Polym. J.* **1983**, *19*, 863.
4. Zhu, L. C.; Tang, G. B.; Shi, Q.; Cai, C.; Yin, J. *React. Funct. Polym.* **2006**, *66*, 984.
5. Bratawidjaja, A. S.; Gitopadmoyo, I.; Watanabe, Y.; Hatakeyama, T. *J. Appl. Polym. Sci.* **1989**, *37*, 1141.
6. Rengarajana, R.; Parameswarana, V. R.; Lee, S. *Polymer* **1990**, *31*, 1703.
7. Ni, Q. L.; Fan, J. Q.; Niu, H.; Dong, J. *J. Appl. Polym. Sci.* **2011**, *121*, 2512.
8. Sadik, T.; Massardier, V.; Becquart, F.; Taha, M. *J. Appl. Polym. Sci.* **2013**, *129*, 2177.
9. Bettini, S. H. P.; Agnelli, J. A. M. *J. Appl. Polym. Sci.* **1999**, *74*, 256.
10. Luo, W.; Liu, X. X.; Fu, Y. *J. Polym. Eng. Sci.* **2012**, *52*, 814.
11. Gaylord, N. G.; Miskra, M. K. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 23.
12. Roover, B. D.; Sclavons, M.; Carlier, V. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 829.
13. Roover, B. D.; Devaux, J.; Legras, R. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 1195.
14. Heinen, W.; Resenmoller, C. H.; Wenzel, C. B. *Macromolecules* **1996**, *29*, 1151.
15. Russel, K. E.; Kelusky, E. C. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 2273.
16. Zhu, Y. T.; An, L. J.; Jiang, W. *Macromolecules* **2003**, *36*, 3714.
17. Mohebbi, K.; Ebrahimi, N. G. *Iran. Polym. J.* **2015**, *24*, 309.
18. Wan, D.; Xing, H. P.; Zhang, Z. J.; Wang, Y. J.; Wang, L.; Wang, Y. H. *J. Appl. Polym. Sci.* **2013**, *127*, 1394.
19. Bettini, S. H. P.; Mello, L. C. D.; Munoz, P. A. R. *J. Appl. Polym. Sci.* **2013**, *127*, 1001.
20. Luo, W. H.; Liu, X. X.; Fu, Y. *Polym. Eng. Sci.* **2012**, *52*, 814.
21. Jiang, X. L.; Huang, H.; Zhang, Y. *Polym. Compos.* **2004**, *12*, 29.
22. Jiang, X. L.; Sun, K.; Zhang, Y. X. *eXPRESS Polym. Lett.* **2007**, *1*, 283.
23. Henry, G. R. P.; Drooghaag, X.; Rousseaux, D. D. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 2936.
24. Sclavons, M.; Franquinet, P.; Carlier, V. *Polymer* **2000**, *41*, 1989.
25. Sclavons, M.; Laurent, M.; Devaux, J.; Carlier, V. *Polymer* **2005**, *46*, 8062.
26. Chen, M. C.; Liu, T.; Zhao, L. *Funct. Polym.* **2005**, *18*, 334.
27. Mohebbi, K.; Ebrahimi, N. G. *Iran. Polym. J.* **2015**, *24*, 309.
28. Zhang, G. P.; Cheng, J.; Shi, L.; Lin, X.; Zhang, J. Y. *Thermochim. Acta* **2012**, *538*, 36.
29. Bertin, D.; Leblanc, M.; Marque, S. R. A.; Siri, D. *Polym. Degrad. Stabil.* **2010**, *95*, 782.
30. Roover, B. D.; Sclavons, M.; Carlier, V. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 829.