

GRAFTING OF PEROXIDE-INITIATED MALEIC ANHYDRIDE ON SPHERICAL PE/PP IN-REACTOR BLEND GRANULES*

Yan-zhong Zhang, Zhi-qiang Fan**, Bai-geng Wu, Jun-ting Xu and Qi Wang

*The Institute of Polymer Science, Department of Polymer Science & Engineering,
Zhejiang University, Hangzhou 310027, China*

Abstract Spherical polyethylene/polypropylene (PE/PP) in-reactor blend granules with various ethylene/propylene molar ratios and high porosity were synthesized using a high yield $\text{TiCl}_4/\text{MgCl}_2$ supported catalyst. A solution of benzoyl peroxide (BPO)/maleic anhydride (MAH)/xylene (interfacial reagent) or BPO/MAH/St (comonomer) was absorbed onto the PE/PP in-reactor blend granules, and solid phase graft polymerization of MAH on PE/PP was conducted. The amount of grafted MAH on PE/PP was measured through chemical titration. The results showed that solid phase graft polymerization of MAH in PE/PP in-reactor blend granules produced graft copolymer with high amount of grafted MAH, and the amount of grafted MAH was raised slightly when St was introduced as comonomer. The graft in-reactor blend was fractionated into five fractions through temperature-gradient extraction fractionation (TGEF), and the fractions were analyzed by FTIR. The results revealed that MAH is mainly grafted on the PE segments, whereas MAH was predominantly grafted on the PP segments when St was present in the graft polymerization system. In addition, the final product is still in the form of regular spherical granules, which is beneficial for industrial processing.

Keywords Spherical PE/PP in-reactor blend granules, Maleic anhydride, Graft polymerization

INTRODUCTION

Polyolefins (PE, PP, *etc.*) are now widely employed because of their versatile properties and low cost. However, several applications are limited due to their low surface energy, difficulty of dyeing, poor hydroscopicity, and poor compatibility with polar polymers. Peroxide-initiated functionalization of polyolefins has gained considerable attention as a convenient route to produce new polymer materials with an improved performance/costs balance^[1]. Maleic anhydride (MAH) modified polyolefins are the most important class of functionalized polyolefins and have gained wide industrial application, which is attributed to their unique combination of low cost, high activity and good processability^[2]. They are used as chemical coupling agents^[3], impact modifiers^[4, 5], anticorrosive coatings for metal pipes and containers^[6], metal-plastic laminates for structural use^[7], and multilayer sheets of paper for chemical and food packaging^[8], *etc.*

Despite the large number of studies on MAH grafting and the commercial success of MAH grafted polyolefins, the effect of polyolefin composition and structure on the peroxide-initiated MAH grafting and the position of grafting on polyolefin is still ambiguous. In addition, grafting of MAH on PE/PP in-reactor blend has not been reported in the literature.

Spherical polyethylene/polypropylene (PE/PP) in-reactor blend granules with different ethylene/propylene ratios have been synthesized using a high yield $\text{TiCl}_4/\text{MgCl}_2$ supported catalyst in our previous work^[9]. The nascent PE/PP in-reactor blends prepared in this way are spherical granules with high porosity. This in-reactor blend shows excellent mechanical properties, with impact strength as high as 56.5 kJ/m^2 and flexural modulus

* This work was supported by the Special Fund for Major State Basic Research Projects (Grant no. G1999064803).

** Corresponding author: Zhi-qiang Fan (范志强), E-mail: fanzq@zju.edu.cn

Received January 19, 2003; Revised March 15 2003; Accepted March 17 2003

higher than 2400 MPa. Modification of this material by MAH grafting may further improve its other properties, especially the compatibility with polar polymers. As reported in the literature^[10], PP-g-MAH shows improved compatibility with other polar polymers, especially engineering plastics like Nylon-6 and polycarbonate. The grafting of St/MAH on PP can form a polyolefin alloy showing improved high temperature performance^[11]. This work aims at investigating the effect of the polyolefin structure on the amount of grafted MAH and the graft position of MAH on polyolefin in the solid phase. A series of polyolefins with different ethylene/propylene ratios was modified by MAH grafting under the same conditions. The amount of grafted MAH was determined by chemical titration and from the infrared spectrum (FTIR). The graft copolymer was fractionated into several fractions through temperature-gradient extraction fractionation (TGEF), and the fractions were analyzed by FTIR.

EXPERIMENTAL

Reagents and Materials

PE/PP in-reactor blend granules were produced by a two-step slurry polymerization process catalyzed by a $\text{TiCl}_4/\text{MgCl}_2 \cdot \text{ID}$ supported high-yield spherical catalyst (DQ-1, kindly donated by the Beijing Research Institute of Chemical Industry, ID is the internal donor). The co-catalyst was $\text{Al}(\text{C}_2\text{H}_5)_3$ (Fluka, used without purification). $\text{Ph}_2\text{Si}(\text{OMe})_2$ was used as the external donor, and petroleum ether was used as the solvent. In the first step of the polymerization process, ethylene was polymerized under 0.6 MPa pressure and 53 °C for 1–2 h in a 1 L autoclave with mechanical stirring. The second step was propylene polymerization under 0.5 MPa for 1–2 h. The experiment details have been described in previous work^[9]. The product is in the form of spherical granules. More than 80 wt% of the granules have diameter in the range of 1.0–1.5 mm, and the porosity of granules is about 25–35 mL/100 g polymer (see Fig.1). MAH, (chemically pure reagent) was sublimed before use. BPO, (chemically pure) was recrystallized in ethanol before use. Styrene (St, chemically pure) was washed with 10% KOH solution and distilled to remove the inhibitor, dried with anhydrous CaCl_2 , and distilled under reduced pressure before use. Xylene, (chemically pure) was used as received without purification.

Synthesis of (PE/PP)-g-MAH

An accurately measured solution of BPO/MAH/xylene was added to a round-bottomed flask containing PE/PP granules (MAH: (PE/PP) = 23:100 wt%; BPO: MAH = 1:100 wt%; MAH/xylene = 0.1 g/mL. The flask was sealed under nitrogen, immersed in an oil bath and stirred at 60 °C for 30 min, with the aim of swelling the BPO/MAH/xylene solution into the PE/PP granules. Then the temperature was raised to 105 °C in no more than 4 min and kept at 105 °C for 2 h. After that the grafted copolymer was washed with ethanol and dried under vacuum at 60 °C. The final product was still in the form of regular spherical granules.

Determination of Graft Percentage and Acid Value

A known amount of the reaction products was extracted in a Soxhlet extractor with butanone for 16 h and then dried at 80 °C to constant weight. The graft percentage (*GP*) was calculated according to the following equation^[10]:

$$GP(\%) = \frac{W_{\text{gp}} - W_{\text{PE/PP}}}{W_{\text{PE/PP}}} \times 100$$

where W_{gp} is the sample mass after extraction, $W_{\text{PE/PP}}$ is the mass of PE/PP in the sample.

In order to determine the acid value of the extracted graft copolymers, about 1 g of the graft copolymer was dissolved in 200 mL hot xylene, then 25 mL KOH/ethanol standard solution (0.1 mol/L) was added and refluxed for 1 h. A HCl/ethanol standard solution (0.1 mol/L) was used to titrate the above solution to the end-point with methyl red (a solution of 1% methyl red in methanol) as the indicator. The acid value (*AV*), defined as the weight of KOH neutralized by 1 g of sample, was determined by the following equation.

$$AV(\text{mgKOH/g}) = \frac{56.1 \times (c_{\text{KOH}}V_{\text{KOH}} - c_{\text{HCl}}V_{\text{HCl}})}{M}$$

where c_{KOH} , V_{KOH} are the concentration (mol/L) and volume (mL) of the KOH/ethanol standard solution added, respectively; c_{HCl} , V_{HCl} are the concentration (mol/L) and volume (mL) of HCl/ethanol standard solution used to titrate the refluxed solution. M is the mass (g) of the sample, and 56.1 is the molecular weight of KOH.

Fractionation of (PE/PP)-g-MAH

A modified Kumagawa extractor was used to carry out the temperature-gradient extraction fractionation of (PE/PP)-g-MAH (pretreated by extraction with butanone). *n*-Octane was used as the solvent to successively extract the graft copolymer at different controlled temperatures, from 20 °C to 120 °C. Five fractions were collected by extracting 5 g samples at 20 °C, 100 °C, 113 °C and 120 °C and > 120 °C, respectively (the insoluble part). Purified fractions were obtained after concentrating the extract solutions, precipitating the polymer, washing and drying the fractions under vacuum.

FTIR Analysis

FTIR spectra of the graft copolymer (extracted with butanone) and the fractions were recorded on a Bruker Vector 22 FTIR spectrometer. Films of the samples were prepared by hot pressing. The following empirical equation has been used to estimate the ethylene content based on the intensity of IR spectrum^[9]:

$$C_2(\text{mol}\%) = 37.2990 + 57.817 \times \lg \frac{A_{720}}{A_{1165}} + 27.287 \times (\lg \frac{A_{720}}{A_{1165}})^2$$

SEM Observation

Scanning electron microscopic (SEM) observation of the cryobroken surface of the granules was undertaken on a JSM-T20 SEM instrument. The samples were prepared by breaking up the granules embedded in epoxy resin in liquid nitrogen and coating a thin layer of gold on the broken surface before observation.

RESULTS AND DISCUSSION

Morphology and Composition of the PE/PP In-Reactor Blend

It is necessary to reveal the morphology and composition of the PE/PP in-reactor blend granules before discussing the effect of PE/PP composition on $GP\%$ and AV . As shown in Fig. 1(a), the PE/PP in-reactor blend granules are basically spherical, and their size distribution is quite narrow, with more than 80 wt% of the particles having a diameter of 1.0 mm–1.5 mm. The internal morphology of the granules was disclosed by scanning electron photomicrography of the cryobroken surface of the particles. Just as shown in Fig. 1(b), there are many big and small pores in the PE/PP in-reactor blend granules, and the substrate structure is quite loose. This kind of highly porous internal morphology should be the direct reason for the easy absorption of large amount of BPO/MAH/xylene solution in the granules.

As described in the experimental part, more than 2 mL of the MAH/xylene solution was in contact with 1 g of the PE/PP granules before the graft reaction. After stirring the mixture at 60 °C for 30 min, it was observed that the granules were strongly swelled by the solution, and almost no flowing liquid phase could be seen in the reactor. This is because xylene is a good solvent for PE and PP at high temperature. However, high porosity of the PE/PP granules is also a key factor that makes the rapid swelling possible. Such highly swelled state of the reactants will be beneficial to the graft reaction, because the solution may uniformly distribute in the particle through the small pores. On the other hand, the swelled granules can be uniformly dispersed in the reactor and seldom adhere to each other and to the reactor walls, which is also beneficial to the industrial process.

The composition (ethylene/propylene ratio) of the PE/PP in-reactor blend granule can be adjusted by varying the polymerization time of ethylene and propylene in different reaction stages. The particle size distribution and the porosity of the granules were found to change slightly with varying polymerization conditions. To investigate the compositional distribution of the PE/PP in-reactor blend granule, a typical PE/PP

in-reactor blend (ethylene/propylene weight ratio = 69/31) was fractionated into five fractions through TGEF, and the results are listed in Table 1.

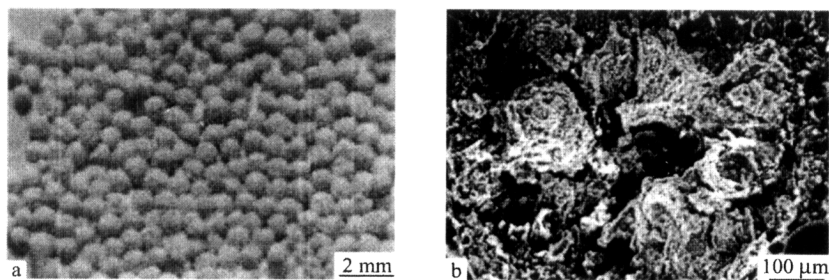


Fig. 1 The surface and internal morphology of PE/PP in-reactor blend granule (C_2/C_3 ratio 69/31)
a) Photograph of the granules; b) SEM photograph of the cross section of a granule

Table 1. Fractionation results of PE/PP copolymer (ethylene/propylene wt ratio = 69/31)

Fractionation temperature (°C)	20	100	113	120	Insoluble fraction
wt%	2.7	4.6	1.2	67.8	23.4
C_3 (mol%) ^a	84.2	73.4	61.5	0.82	77.1

^a Measured by FTIR

As shown in Fig. 2, the FTIR spectrum of the 20°C fraction is characteristic of atactic polypropylene containing small amount of ethylene units. The spectra of the 100°C fraction and 113°C fraction are similar to that of the 20°C fraction, but there is a gradual increase of crystalline PP segments, as indicated by the increase of intensity of the 970 cm^{-1} band. The 120°C fraction contains PE and very small amount of PP, while the spectrum of the insoluble fraction shows the presence of isotactic PP and small amount of PE. The C_3 mol% of the fractions was also calculated based on the IR spectra.

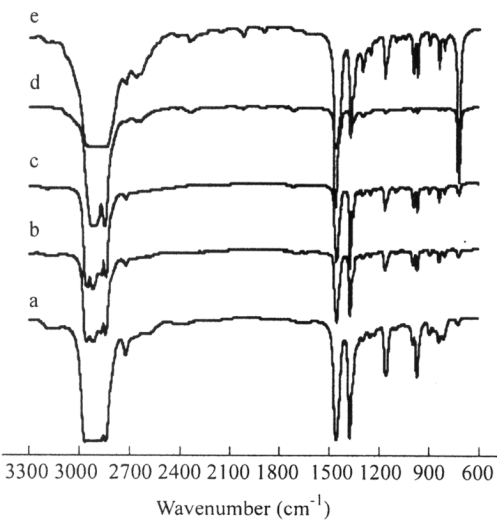


Fig. 2 FTIR spectra of the five fractions of a PE/PP in-reactor blend (C_2/C_3 ratio 69/31)
a) 20°C, b) 100°C, c) 113°C, d) 120°C, e) insoluble fraction

Figure 3 is the ^{13}C -NMR spectra of the major fractions, the 120°C fraction and the insoluble fraction, which comprise more than 90% the in-reactor blend. It is further confirmed that the 120°C fraction comprises more than 99% of PE, while the insoluble fraction contains 80% of PP and 20% of PE. Considering that PE homopolymer is fully soluble in *n*-octane at 120°C, therefore, the PE signal present in the insoluble fraction should come from

the PE segments in the block copolymer of propylene and ethylene. Low solubility of the PP block should prevented dissolution of the block copolymer at 120 °C. Therefore, the PE/PP in-reactor blends are mainly composed of PE, PP and PE-*b*-PP.

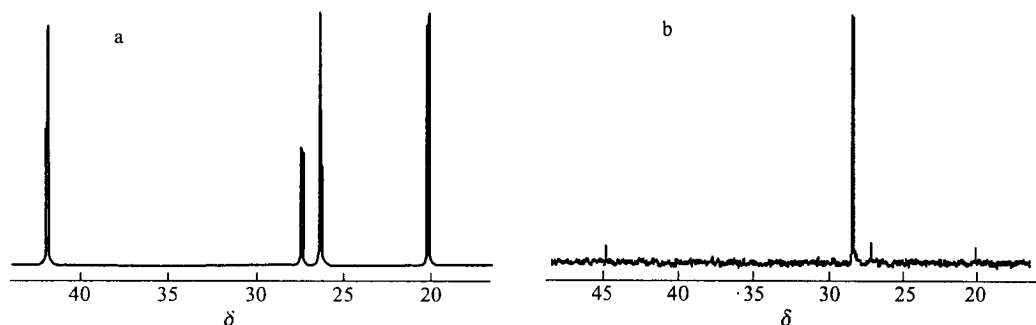


Fig. 3 ^{13}C -NMR spectra of insoluble fraction (a) and 120 °C fraction (b)

Effect of PE/PP Composition on GP% and AV

In Table 2 the results of grafting MAH on PE/PP in-reactor blend granules of different composition under the same reaction conditions are compared. It is clearly seen that GP% and AV successively decrease with increasing propylene content in the PE/PP in-reactor blend, indicating that polyethylene and polypropylene have different activity toward the MAH grafting reaction. Polyethylene is more active for the MAH grafting. A similar phenomenon has also been observed in the literature^[12]. It is reported that when MAH was reacted with polyolefin blends or copolymers of different ethylene/propylene ratios, the graft content decreases with increasing propylene content, both in melt and solution reactions.

Table 2. Effects of PE/PP composition on GP% and AV

Sample	C ₂ /C ₃ (wt)	GP (%)	AV (mg KOH/g)
PE	100/0	5.45	59.2
PE/PP	69/31	2.48	25.5
PE/PP	46/54	1.51	16.4
PE/PP	32/68	1.09	11.7

Reaction conditions: MAH/(PE/PP) = 23 wt%; BPO/MAH = 1 wt%; MAH/xylene = 0.1 g/mL; Pre-swelling time: 30 min; Reaction temperature: 105 °C; Reaction time: 2 h

Effect of Styrene on GP% and AV

In Table 3 the effects of adding different amounts of styrene (St) as comonomer on GP% and AV are compared. It shows that St has complicated effects on the GP% and AV. With the increase of St content in the graft system, the GP% increases markedly, but the AV value increases only slightly. This means that this increase in GP% should be mainly attributed to St. In fact, the amount of MAH in the graft copolymer calculated from the AV value of the graft copolymer is also listed in Table 3. It is shown that the content of MAH in the graft copolymer is only about 2.48%–3.58%. The results indicate that St can increase the amount of MAH graft, and the increase of GP% is mainly derived from St.

Table 3. Effect of MAH/St ratio on GP% and AV

Samples	MAH/St (mol)	GP%	AV (mg KOH/g)	MAH/(PE/PP) (g/100 g)
A	1/0	2.48	25.5	2.48
B	1/1	12.1	26.2	2.52
C	1/2	15.5	35.3	3.39
D	1/3	19.7	37.9	3.58

Reaction conditions: MAH/(PE/PP) = 23 wt%; BPO/MAH = 1 wt%; Pre-swelling time: 30 min; Reaction temperature: 105 °C; Reaction time: 2 h; PE/PP weight ratio = 69/31

In addition, it should be pointed out that the system of grafting BPO/MAH/St on PE/PP in-reactor blend

granules contains no interfacial reagent (xylene). In this case the swelling of BPO/MAH/St in PE/PP in-reactor blend granules may be not sufficient, especially when the St content is low (*i.e.* experiment B in Table 3). The final grafted in-reactor blend granules, (PE/PP)-g-MAH or (PE/PP)-g-MAH/St, just as shown in Fig. 4, are still in the form of regular spherical granules, which is beneficial for the industrial processing.

FTIR Analysis of the Graft Copolymer and the Fractions

Figure 5 shows the FTIR spectra of a typical PE/PP in-reactor blend granule (ethylene/propylene = 69/31) and the corresponding MAH grafted in-reactor blend (extracted with butanone). In comparison to the PE/PP in-reactor blend, the grafted in-reactor blend has several new absorption bands in the range of 1700–1900 cm^{-1} , which can be attributed to the reaction products between PE/PP and MAH. The results further confirm the occurrence of graft reaction of MAH on the PE/PP in-reactor blend granule.

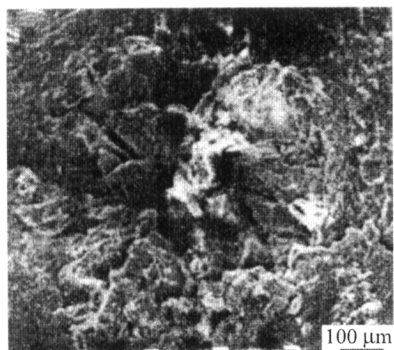


Fig. 4 The internal morphology of a (PE/PP)-g-MAH granule

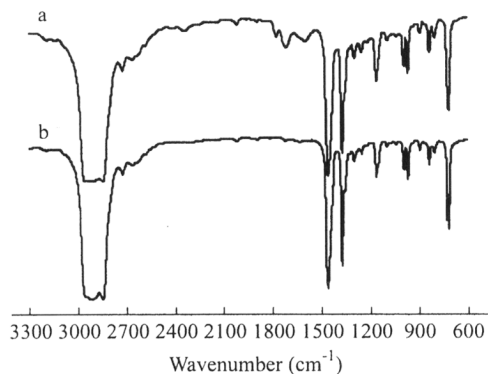


Fig. 5 FTIR spectra of PE/PP in-reactor blend and the corresponding graft copolymer
a) (PE/PP)-g-MAH; b) PE/PP (C_2/C_3 weight ratio 69/31)

The results in Table 2 show that graft in-reactor blend with different *GP%* and *AV* may be prepared using PE/PP in-reactor blend granules of different ethylene/propylene composition. In order to know the actual position of the grafted MAH, the graft copolymer sample of ethylene/propylene = 69/31 (weight ratio) was fractionated into five fractions by TGEF. The results are listed in Table 4.

Figure 6 is the FTIR spectra of the 120°C fraction and insoluble fraction. It clearly shows that the 120°C fraction has several strong bands in the range of 1700–1900 cm^{-1} , but the insoluble fraction shows no such bands. From the band intensities of FTIR spectra of the 120 °C fraction and insoluble fraction of the (PE/PP)-g-MAH copolymer (Fig. 6), the propylene content of the fractions was calculated. The 120°C fraction contains about 99% of PE, and the insoluble fraction contains about 76% of PP. It can be concluded that MAH is predominantly grafted on PE chain. This is because that radicals produced on peroxide (BPO) decomposition can abstract H from polyolefins, leading to the formation of radicals on the polyolefin chain. The alkyl radicals thus formed may undergo MAH addition, coupling, or degradation. Because of the low activity of MAH, alkyl radicals on the PP chain tend to undergo degradation via scission before reacting with MAH. On the other hand, alkyl radicals on the PE chain tend to combine with each other, but the probability of their reaction with MAH is larger than radical combination as a result of low mobility of the PE chains in the near solid state. This may explain the fact that the MAH graft content on the PP chain is lower than that on the PE chain. Because the chemical properties of PE segments in the PE homopolymer fraction and those in the PE-g-PP block copolymer fraction are almost the same, both kinds of PE segments should be able to take part in the reaction with MAH. However, Fig. 6 shows that there are almost no bands in 1700–1900 cm^{-1} in the IR spectrum of the insoluble fraction. This implies that MAH is mainly grafted on PE homopolymer. More accurate experiments are needed to

quantitate the MAH content in different fractions of the in-reactor blend.

Table 4. Fractionation results of (PE/PP)-g-MAH copolymer (PE/PP = 69/31 in wt/wt)

Samples	Original sample	20°C fraction	100°C fraction	113°C fraction	120°C fraction	Insoluble fraction
wt (g)	4.8231	0.1157	0.2460	0.0675	3.2991	1.0755
wt (%)	100	2.4	5.1	1.4	68.4	22.3
C ₃ (mol%)	23	-	-	-	0.64	75.7

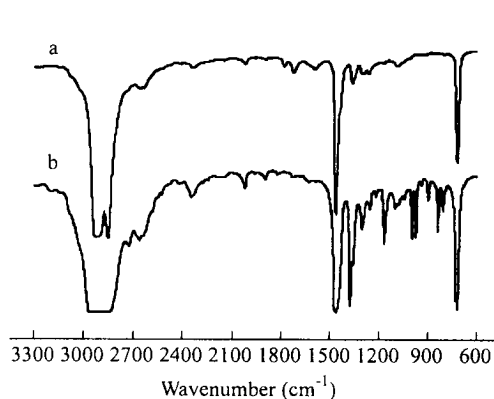


Fig. 6 FTIR spectra of fractions of the graft product (PE/PP)-g-MAH
a) 120°C fraction; b) Insoluble fraction

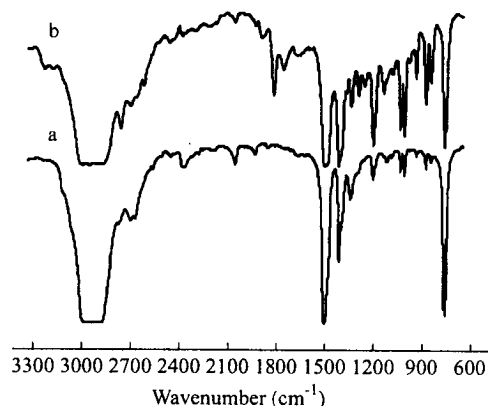


Fig. 7 FTIR spectra of fractions of the graft product (PE/PP)-g-MAH/St
a) 120°C fraction; b) Insoluble fraction

The results in Table 3 show that variation in the content of St as comonomer has certain effect on the *GP*% and *AV* of the graft copolymer under the same reaction conditions. A sample of MAH/St grafted in-reactor blend was also fractionated into five fractions by TGEF. The results are listed in Table 5. It can be seen that the weight percentage of the insoluble fraction is evidently higher than the corresponding fraction extracted from the (PE/PP)-g-MAH sample (see Table 4), though both graft copolymers have been prepared using the same PE/PP in-reactor blend.

Table 5 Fractionation results of (PE/PP)-g-MAH/St copolymer (PE/PP = 69/31 in wt/wt)

Samples	Original sample	20°C fraction	100°C fraction	113°C fraction	120°C fraction	Insoluble fraction
wt (g)	4.9352	0.1530	0.2171	0.0987	2.9364	1.5249
wt (%)	100	3.1	4.4	2.0	59.5	30.9
C ₃ (mol%)	23	-	-	-	1.4	80.7

Figure 7 depicts the FTIR spectra of the 120°C fraction and the insoluble fraction. It clearly shows that the insoluble fraction has strong bands at 1700–1900 cm⁻¹ and 1600 cm⁻¹, but the 120°C fraction has only very weak bands at these wavenumbers. The FTIR spectra also show that the insoluble fraction is mainly composed of PP (C₃ mol% = 80.7), while the 120°C fraction contains more PE than PP. This means that MAH and St are mainly grafted on the PP chain rather than on the PE chain. This may explain the higher weight percentage of the insoluble fraction in (PE/PP)-g-MAH/St than in (PE/PP)-g-MAH. Such different phenomena from the MAH/(PE/PP) grafting system may be explained by the higher reactivity of St than MAH. In the presence of St, radicals on the PP chains that are facily formed by abstracting H from the tertiary carbon on PP will first react with St before degradation, then the alternative copolymerization of MAH with St will happen. As a result, MAH/St were predominantly grafted on the PP segments (see Fig. 7b). On the other hand, it is difficult for the radicals produced from BPO decomposition to abstract H from the secondary carbon of PE, so the probability for

MAH/St grafting on PE chain becomes low.

CONCLUSIONS

Spherical polyethylene/polypropylene (PE/PP) in-reactor blend granules with different ethylene/propylene ratios and high porosity were synthesized using a high yield $\text{TiCl}_4/\text{MgCl}_2$ supported catalyst. MAH can be grafted on the PE/PP in-reactor blend granules in solid phase. The amount of grafted MAH on PE/PP was measured through chemical titration. The grafted in-reactor blend was fractionated into five fractions through TGEF, and the fractions were analyzed by FTIR. The results reveal that MAH is predominantly grafted on the PE chain.

When St was added as comonomer in the MAH grafting PE/PP in-reactor blend system, the $GP\%$ and AV of the final grafted in-reactor blend were increased, but the increase in AV was slight. The increase in $GP\%$ is mainly caused by the incorporation of St, but not MAH. In addition, MAH/St is predominantly grafted on the PP chain.

REFERENCES

- 1 Lu, B. and Chung, T.C., *Macromolecules*, 1999, 32: 2525
- 2 Moad, G., *Prog. Polym. Sci.*, 1999, 24: 81
- 3 Jancar, J., *J. Material. Sci.*, 1989, 24: 4268
- 4 Lin, J.S., Sheu, E.Y. and Tois, Y.H.R., *J. Appl. Polym. Sci.*, 1995, 55: 655
- 5 Sathe, N.S., Devi, S. and Rao, S.G.S., *J Appl. Polym. Sci.*, 1996, 61: 97
- 6 Johnson, A.F., Simmis, G.D., *Composites*, 1986, 17: 321
- 7 Fukushima, N., Kondo, M., Nagai, H., Shiota, T., Sonobe, T., Toya, H. and Kitagawa, Y., *Eur. Pat. EP0078174*, 1983-05-04
- 8 Ashley, R.J., *Adhesion*, 1988, 12: 239
- 9 Zhang, Y.Z., "Synthesis, Structure and Properties of Polyethylene/polypropylene In-Reactor Alloys", Doctoral Dissertation, Zhejiang University, 2003
- 10 Jia, D.M., Luo, Y.F., Li, Y.M., Liu, H., Fu, W.W. and Cheung, W.L., *J. Appl. Polym. Sci.*, 2000, 78: 2482
- 11 Sherman, L.M., *Plast. Technol.*, 1997, 43(2): 25
- 12 Machado, A.V., Covas, J.A. and van Duin, M., *Polymer*, 2001, 42: 3649