Melt Grafting of Maleic Anhydride onto Polypropylene with 1-Decene as a Second Monomer

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ABSTRACT: The influence of 1-decene as the second monomer on the melt-grafting behavior of maleic anhydride (MAH) onto polypropylene (PP) was studied with differential scanning calorimetry and Fourier transform infrared spectroscopy. We found that the value of the grafting degree increased from 0.68% for pure MAH-g-PP to 1.43% for the system with a 1-decene/MAH molar ratio of 0.3, whereas the maximum value with styrene (St) as the second monomer was 0.98% under an St/MAH molar ratio of 1.0. Compared with the contribution of St/MAH-g-PP to the peeling strength between the PP and polyamide (PA) layer for a PP/PA laminated film, the introduction of 1-decene/MAH-g-PP increased the peeling strength from 180 g/15 mm to 250 g/15 mm. 1-Decene inhibited the chain scission behavior of PP. 1-Decene reacted with MAH to form a 1-decene/MAH copolymer or the Alder-ene reaction product before the two monomers grafted onto PP. The grafting of the reactive product onto PP greatly improved the grafting degree of MAH. What is more, because of the similar chemical structures of 1-decene and PP, the affinity of 1-decene with PP was higher than that of St. Compared with St, the introduction of less 1-decene led to a higher grafting degree and higher peeling strength. Therefore, we concluded that 1-decene was more effective for improving the grafting degree of MAH onto PP. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 102–110, 2011

Key words: functionalization of polymers; graft copolymers; poly(propylene) (PP); reactive processing

INTRODUCTION

Polypropylene (PP)/polyamide (PA) multilayer films have been used in numerous applications in the food and pharmaceutical industries. PP, which is nonpolar by nature, is an excellent moisture barrier, but its oxygen-blocking properties are poor. As a polar material, PA shows good gas-barrier abilities, but it is not as good as PP in protecting against moisture. Sandwich films made of PP and PA can protect against both moisture and gas. However, because of the poor compatibility between PP and PA, the adhesion between them is a critical issue. It is necessary to develop a functionalized PP to improve the affinity between the PP layer and the PA layer. In recent years, the grafting of polar monomers, such as maleic anhydride (MAH), onto PP has attracted great attention.[1–4] MAH-modified PP has been used for the compatibilization of PP/PA blends and laminated films.[5–7] However, the improvement is not satisfactory because of the lower grafting degree of MAH, and delamination is mostly responsible for the poor physical properties of the layered struc-

tures. Therefore, it is necessary to improve the grafting properties of MAH onto PP.

MAH-g-PP can be prepared under solution[8] or melt[9] and in the solid state.[10] The graft polymerization of MAH onto PP under the melt state, such as in a twin-screw extruder and in the presence of a radical initiator, is the simplest and most widely used method, especially with peroxide initiators.

However, on one hand, because of the immiscibility between PP and MAH, it can be very difficult for the MAH monomers to diffuse into the PP molecular chains in the limited residence time within the twin-screw extruder. On the other hand, the reactivity of MAH toward free radicals is very low because of its structural symmetry and deficiency of electron density around the double bond.[2] A consequence is that the grafting reaction is accompanied by undesirable side reactions such as chain scission, and the grafting degree and the grafting efficiency are relatively low.[11]

Recently, some methods have been reported for improving the grafting behavior.[1] By improving the mixing efficiency and thereby controlling the local monomer concentration or by adding appropriate coagents, one can improve the grafting degree and minimize the extent of side reactions. Gaylord and Mishra[11] reported that some nitrogen-, phosphorus-, and sulfur-containing compounds could depress

both the homopolymerization of MAH and the degradation of the substrate polymer during the melt grafting of MAH onto polymers. Wang and Wang[12] and Wu et al.[13] observed that divinyl benzene induced a pronounced increase in the grafting degree of MAH-g-poly(ethylene–octene)/PP blends. Li and coworkers[14,15] and Zhang et al.[16] reported that the addition of styrene (St) in the melt grafting of MAH reduced the PP chain scission and increased the grafting degree of MAH. At a styrene/maleic anhydride (SMA) blend ratio of 1.0, the maximum value of grafting degree was obtained. In this system, the formed SMA copolymer was grafted onto PP; this resulted in a higher grafting degree.

However, the affinity between St and PP was lower because of the structural difference. What is more, under the reaction conditions of MAH melt grafting in a twin-screw extruder, St was easily evaporated because its boiling point was low, 145.2°C. This resulted in lower contents of St involved in the grafting reaction and a lower grafting efficiency.

α-Olefins are olefins or alkenes with the chemical formula C_xH_{2x}; they are distinguished by having a double bond at the primary or α position. This location of a double bond enhances the reactivity of the compound and makes it useful for a number of applications. It has been reported that α-olefins can react with MAH through the Alder-ene reaction or copolymerize with MAH to form an α-olefin/MAH copolymer.[17–19]

In this study, 1-decene (one kind of α-olefin) with a boiling point of 172°C was used, and its effect as a comonomer on the melt-grafting behavior of MAH onto PP was investigated. The grafting degree was characterized by chemical titration, differential scanning calorimetry (DSC), and Fourier transform infrared (FTIR) spectroscopy. The application of MAH-modified PP in a PP/PA laminated film was examined, and finally, the possible grafting mechanism of MAH onto PP under the existence of 1-decene was determined.

EXPERIMENTAL

Materials

The sample of PP was commercially obtained from Maoming Petrochemical Co. (Maoming, China). It had a density of 0.91 g/cm³ and a melt flow rate of 3.0 g/10 min (ASTM D 1238). The casting polypropylene film (CPP) and casting polyamide film (CPA) were afforded by Foshan Plastics Group Co. (Foshan, China). Dicumyl peroxide (DCP) and benzoyl peroxide were obtained from Shanghai Dongyi Chemical Agent Co. (China); these were dried at room temperature under 0.02 MPa. The MAH monomer and St monomer used were commercially available (analytical grade). 1-Decene was obtained from Leqing Zhongyi Petrochemical Co. (Leqing, China). Xylene, acetone, propenyl alcohol, deuteroacetone, tetrahydrofuran (THF), and so on were all reagent grade and were used without further purification.

Melt grafting of MAH onto PP

A Haake Rheomix 600 mixer (Thermo Electron Corp., Karlsruhe, Germany) was used to prepare the graft-modified PP. Determined amounts of polymer, monomers, and initiator were premixed by hand in a small container before they were charged into the mixing chamber. The 1-decene/MAH molar ratios were 0.2, 0.3, 0.5, 0.7, and 1.0. The mixing temperature, time, and rotor speed were held constant at 190°C, 3 min, and 90 rpm, respectively, in all runs. The equilibrium torque value at the end of the grafting reaction was used to characterize the degradation degree of PP induced by DCP. The reaction product was removed from the mixing chamber and added to liquid nitrogen to stop any further reaction. For comparison, the PP/DCP samples and the grafted system with SMA molar ratios of 0.3 and 1.0 were also prepared.

Reaction between 1-decene and MAH

MAH was first dissolved in xylene, and then, 1-decene was added to the solution. The mixture was decanted into a three-necked flask, and benzoyl peroxide was added. The flask was evacuated by nitrogen for 15 min before the nitrogen flow was reduced and the system was heated to 95°C. The reaction ran for 6 h, after which the solution was added dropwise into cold propenyl alcohol. The sample was collected and reprecipitated from THF into cold propenyl alcohol and dried in vacuo at 60°C for 24 h. The reactive product was a free-flowing pale yellow powder. Its molecular weight was measured with gel permeation chromatography (GPC; Viscotek model 350, Houston, USA) and with THF as a solvent. Its chemical composition was tested with a Varian Znova ¹H-NMR spectrometer (Palo Alto, USA) operating at 400 MHz. The solid samples were dissolved in deuteroacetone at a concentration of 0.25 g/mL.

Purification of the melt-grafted PP

The MAH-g-PP was xylene soluble and acetone insoluble, whereas the oligomer of MAH, if present, and unreacted MAH monomer dissolved both in xylene and acetone. On the basis of this, the separation of the graft copolymers and other components in the raw grafted samples was performed as follows: several grams of raw MAH-g-PP samples were first

packed into filter paper and were then boiled with refluxing xylene for 0.5 h in a round flask. The solution was precipitated in hot acetone, then filtered by a Buchner funnel, repeatedly washed with fresh acetone, and then dried in a vacuum oven at 60°C to a constant weight. Then, the samples were used to determine the grafting degree of MAH and to laminate with CPP and CPA films.

Characterization of the grafted polymer

Chemical titration

The grafting degree of MAH was defined as the weight percentage of MAH in the MAH-*g*-PP polymers. It was determined by means of acid–alkali titration and carried out by the following procedures. About 1 g of purified sample was first dissolved in 100 mL of refluxing xylene for 0.5 h, in which a few drops of water were added to hydrolyze all of the anhydride functions. Then, the hot solution was titrated immediately with a 0.025 mol/L KOH/C_2H_5OH solution after four drops of 1% phenolphthalein in ethanol were added as an indicator. Titration was stopped when the coloration remained for 30 s. The equation used to calculate the grafting degree of MAH was

$$MAH\% = \frac{(V_2 - V_1)C}{2m} \times 98.06 \times 10^{-3} \times 100\% \quad (1)$$

where V_2 and V_1 represent the volumes of KOH/C_2H_5OH solution used for the titration of the blank and grafted samples (mL), respectively; C is molar concentration of the KOH/C_2H_5OH solution (mol/L); 98.06 is the molecular weight of MAH (g/mol); m is the weight of the grafted sample (g); and the number 2 indicates that one anhydride group could change into two carboxylic acid groups after the anhydride rings were opened. The data presented here is the average of at least three repeated analyses, and its relative mean deviation was less than 5%.

FTIR analysis

The purified graft samples and the 1-decene/MAH reactive product were pressed into 100-μm films by the compression of 0.1–0.2 g of sample between Teflon-covered aluminum sheets under 1 MPa pressure at 190°C for 30 s. The hot-pressed film was submitted to infrared analysis in a PerkinElmer PE 1600 spectrophotometer (Massachusetts, USA) with a resolution of 4 cm^{-1} and 64 scans per spectrum.

DSC analysis

The crystallization behaviors were investigated with a Netzsch DSC 200 differential scanning calorimeter (Selb, Germany) at a heating/cooling rate of 10°C/

min. All operations were carried out under a nitrogen environment. The melting temperature (T_m) and the crystallization temperature (T_c) were determined as the peak maximum and minimum of the melting and crystalline peak, respectively. The samples weights were between 4 and 7 mg.

Application of modified PP in the CPP/CPA laminated films

The purified MAH-modified PP film was prepared with a hydraulic hot press (Jiangsu Mingzhu Testing Machine Co., Ltd., Jiangsu, China) at 200°C and under a pressure of 10 bar. The CPP/modified PP film/CPA three-layer laminated film was bonded with the hot press under a pressure of 10 bar for a heating time of 5 min and at a heating temperature of 160°C. The bonded films were cut into 15 × 140 mm^2 strips (with a peeling length of 100 mm) for the mechanical adhesion tests. The adhesion strength was tested with a T-peel test with a peeling speed of 100 mm/min. Five specimens were tested, and the mean value of the peel force over the width was calculated.

RESULTS AND DISCUSSION

Effect of the DCP and MAH contents on the grafting degree

At a 1-decene/MAH blend ratio of 0.5, the effect of the DCP and MAH contents on the grafting degree was tested, and the results are given in Figures 1 and 2. With increasing DCP and MAH, the grafting degree first increased and then decreased. When the amount of DCP increased, more PP macroradicals were produced by a hydrogen abstraction reaction and more chain ends of PP macroradicals resulted from chain scission. More MAH monomers could react with these macroradicals, and as a result, the grafting degree increased. However, when an excessive content of DCP was used, a severe degradation of the PP backbone was induced, and the grafting degree decreased. Under certain DCP contents, when the MAH content was excessive, because of the
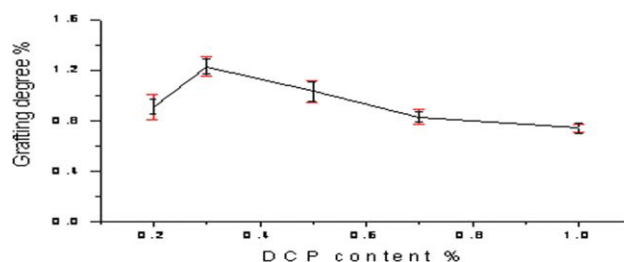

Figure 1 Effect of the DCP content on the grafting degree of MAH onto PP (MAH content = 2%). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
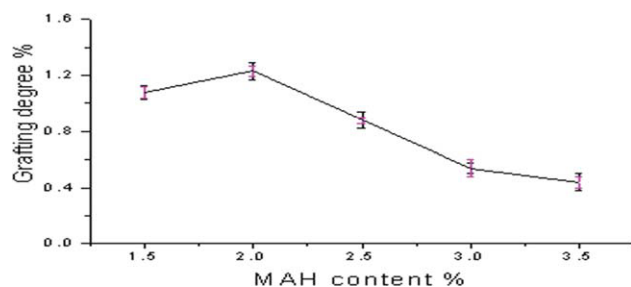
Figure 2 Effect of the MAH content on the grafting degree of MAH onto PP (DCP content = 0.3%). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

worse compatibility between MAH and PP and the better affinity between MAH and DCP, more MAH was homopolymerized; this led to a lower grafting degree. Our results were in agreement with the conclusions given by other researchers.[14,16,20] When the molar ratio of 1-decene to MAH was 0.5, at an MAH content of 2% and a DCP content of 0.3%, the obtained value of the grafting degree was 1.23%.

Effect of the 1-decene/MAH blend ratio on the grafting degree

Figure 3 gives the grafting degree versus 1-decene/MAH ratio curve obtained under an MAH content of 2% and a DCP content of 0.3%. For the pure MAH-g-PP system, the grafting degree was 0.68%. The introduction of 1-decene improved the grafting degree, and at a 1-decene/MAH blend ratio of 0.3, a value of the grafting degree of 1.43% was obtained. Compared with pure MAH system, the grafting degree was improved by 110%. Under a 1-decene/MAH blend ratio of 1.0, the grafting degree value was 0.84%. For comparison, the grafting degrees of MAH with St as the second monomer under the same reaction conditions at blend ratios of 0.3 and 1.0 were measured, and values of 0.87 and 0.98% were obtained, respectively. Li and coworkers[14,15] investigated the effect of St on the grafting behavior of MAH onto PP. In their experiments, the maximum grafting degree of MAH was obtained at a ratio of 1 : 1 (MAH/St), and the maximum reached degree value was about 2.0%, which was higher than ours. This may have been due to the different testing methods used. In their experiments, the relative grafting degree was shown with the absorbance ratio of the areas of the bands at 1782 and 2723 cm^{-1} on the basis of FTIR curves. Zhang et al.[16] observed that under an SMA blend ratio of 1.0, the maximum grafting degree measured with the chemical titration method was 0.75%. Apparently, different testing methods give different results. In our experiments, the chemical titration method was used. Our results, shown in Figure 3, found under the same

reaction condition and with the same testing method, showed that compared with St, 1-decene contributed to a higher grafting efficiency with less content added, and hence, 1-decene was more effective in increasing the grafting degree than St.

FTIR analysis of the grafted PP

The FTIR spectra of the blank and MAH-g-PP samples are shown in Figure 4. As shown in Figure 4(a), compared with pure PP, in MAH-g-PP with and without a second monomer, new absorption bands at 1783 and 1856 cm^{-1} were observed; these were assigned to the absorption of the carbonyl groups (C=O) of cyclic anhydride. We confirmed that MAH was successfully grafted onto the PP backbone. As clearly shown in Figure 4(b) for pure MAH-g-PP, the peak corresponding to the carbonyl groups was divided, with one at 1783 cm^{-1} and the other at 1790 cm^{-1}, whereas for the systems with St or 1-decene as the second monomer, no such peak separation was observed. The one at 1790 cm^{-1} was attributed to a single succinic anhydride attached to the chain end of PP,[10,15] whereas the band at 1783 cm^{-1} was assigned to poly(maleic anhydride) or other forms of MAH.[10] For the pure MAH-grafted system, the existence of a 1790-cm^{-1} band indicated the occurrence of PP chain scission, whereas for the MAH-grafted system with a second monomer, the disappearance of the band indicated that the PP chain scission behavior was inhibited. Both 1-decene and St effectively inhibited PP degradation. To prove the inhibition effect on PP degradation, the equilibrium torque value at the end of the grafting reaction in the torque mixer was recorded. The torque value of MAH-g-PP was 5.4 N/m, whereas that of 1-decene/MAH-g-PP was 6.0 N/m; this indicated that the degradation effect of PP induced by DCP was inhibited to a certain degree by 1-decene. As shown in Figure 4, the difference between 1-decene and St was that the peak height corresponding to the carbonyl groups in the system with 1-decene was higher than that with
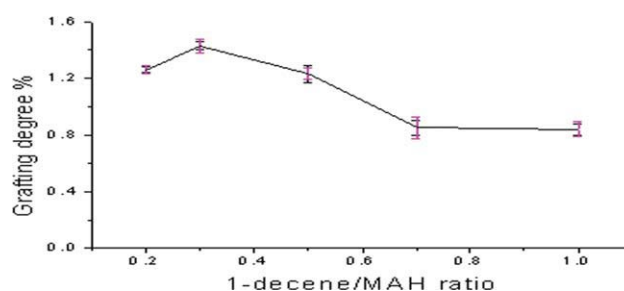

Figure 3 Effect of the 1-decene/MAH blend ratio on the grafting degree of MAH onto PP (MAH content = 2%, DCP content = 0.3%). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]
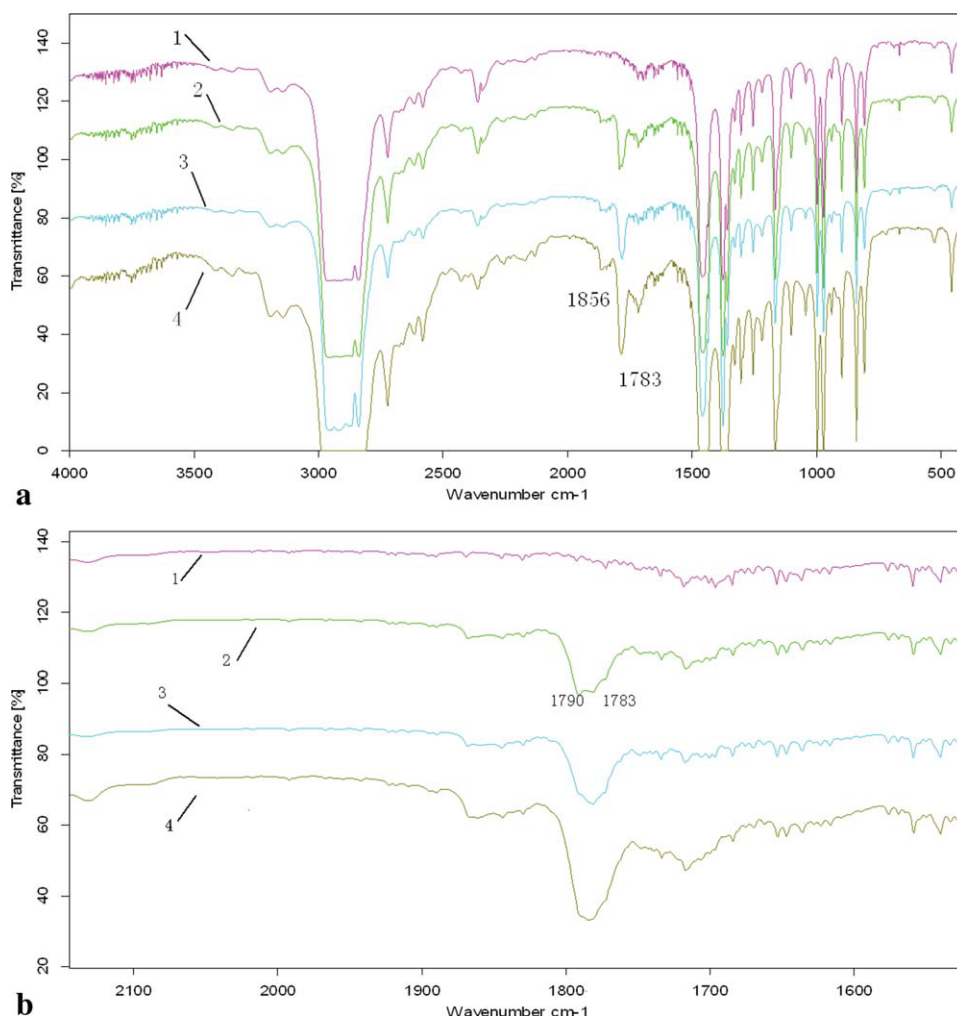
Figure 4 FTIR spectra of blank PP and MAH-*g*-PP: (a) full spectra, (b) partially enlarged spectra, (1) pure PP, (2) MAH-*g*-PP, (3) SMA-*g*-PP with an SMA blend ratio of 0.3, and (4) 1-decene/MAH-*g*-PP with a 1-decene/MAH blend ratio of 0.3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

St; this again proved the higher grafting degree for the system with 1-decene as a second monomer.

Figure 5 shows the FTIR curves of 1-decene/MAH-*g*-PP at 1-decene/MAH ratios of 0.3 and 1.0. Clearly, the band height at 1783 cm^{-1} for a 1-decene/MAH blend ratio of 1.0 apparently decreased. The system with a 1-decene/MAH blend ratio of 0.3 gave a higher grafting degree. When the 1-decene content was lower, its effect was weak, whereas when its content was higher, it tended to homopolymerize; this led to a lower content involved in the grafting reaction and, hence, a lower grafting degree.

DSC analysis of the grafted PP

To characterize the effect of 1-decene on the T_m and T_c values of grafted PP, the DSC curves were tested and are shown in Figure 6. Compared with the endothermic curve of the PP/DCP sample, a small shoulder was observed for the melt-grafted systems. The crystallization ability of the PP molecules with

MAH in the side chain became poor and led to lower T_m values for PP grafted with MAH. However, because of the lower grafting degree, the appearance of the lower T_m values was not a single peak, but only small shoulder was observed. With
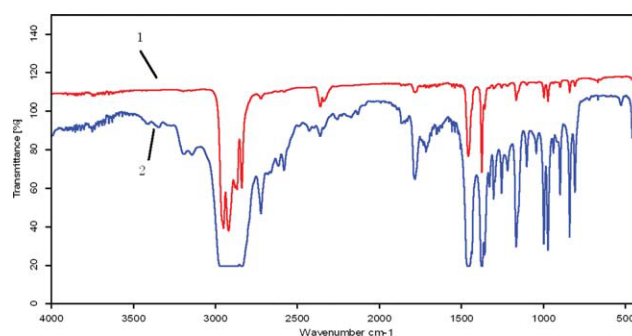

Figure 5 FTIR of 1-decene/MAH-*g*-PP with different 1-decene/MAH blend ratios: (1) 1.0 and (2) 0.3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
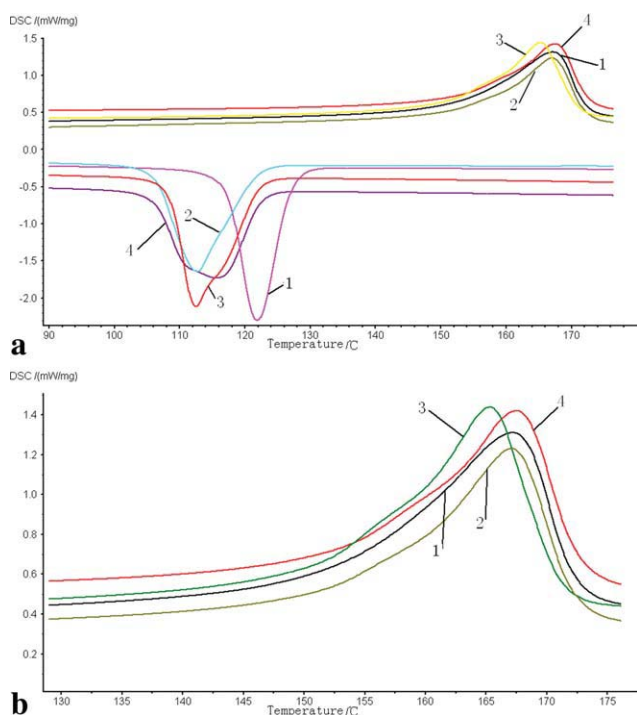
Figure 6 DSC curves of the melt-grafted PP at a heating/ cooling rate of 10°C/min: (a) full spectra, (b) partially enlarged spectra, (1) PP/DCP, (2) MAH-g-PP, (3) 1-decene/MAH-g-PP with a 1-decene/MAH blend ratio of 0.3, and (4) SMA-g-PP with an SMA blend ratio of 0.3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Netzsch peak separation software, the percentage of the shoulder area representing the grafting degree was calculated, and the results are shown in Table I. Apparently, the shoulder percentage of grafted PP with 1-decene as the second monomer was higher than that of the other grafted systems; this was in agreement with the former titration and FTIR results.

As shown in Figure 6, compared with pure PP, the PP/DCP system showed a higher T_c value because of the pronounced degradation induced by DCP, whereas the T_c value of the grafted system was lower; this indicated that the radicals induced

TABLE I
DSC Data of the Melt-Grafted PP

Sample	T_c (°C)	T_m (°C)	Shoulder area percentage/sample weight (%/mg)
Pure PP	114.7	168.5	—
Pure PP/DCP	121.9	167.1	—
MAH-g-PP	112.7	167.0	3.98
1-Decene/MAH-g-PP	112.5/115.9[a]	165.3	4.26
SMA-g-PP	111.2[b]/115.7	167.5	4.03

[a] Corresponding to the right-shoulder temperature in the crystallization curve.
[b] Corresponding to the left-shoulder temperature in the crystallization curve.

by DCP were mainly involved in the grafting reaction. Compared with that of the pure MAH grafted system, the exothermic curves with St and 1-decene as the second monomers were different, with the former exhibiting a small shoulder at the left part and the latter exhibiting a higher peak height in the same position. Some MAH was directly grafted onto PP, whereas some was reacted with St; then, the formed product was grafted onto PP. Under these two circumstance, two different molecular interactions resulted in the existence of the shoulder in the exothermic curve of the St system. As stated earlier, the grafting degree of the system with 1-decene was higher than that with St, and the long chain of 1-decene grafted onto PP resulted in a lower molecular movement ability; this led to a pronounced peak height at a lower position in the exothermic curve.

Application of the MAH-modified PP in the CPP and CPA laminated films

Because of the poor compatibility between PP and PA, the adhesion between the CPP and CPA films was poor. To improve the adhesion strength, the MAH-modified PP was laminated with CPP and CPA films to form a three-layer laminated film. The peeling strength was measured, and the values were 20, 100, 250, and 180 g/15 mm for CPP/CPA, CPP/pure MAH-g-PP film/CPA, CPP/(1-decene/MAH)-g-PP film/CPA, and CPP/SMA-g-PP film/CPA, respectively. The maximum adhesion strength with (1-decene/MAH)-g-PP as the adhesive was obtained because of the maximum grafting degree of the system. Of course, there were other factors influencing the adhesion strength, but those are outside the scope of this article.

Possible grafting mechanism of MAH-g-PP with 1-decene as the second monomer

Figure 7 shows a sketch of the MAH grafting mechanism onto PP with a peroxide initiator. The decomposition of a free-radical initiator, often an organic peroxide of type ROOR, leads to the formation of primary free radicals (RO*'s, step a). In step b, RO*
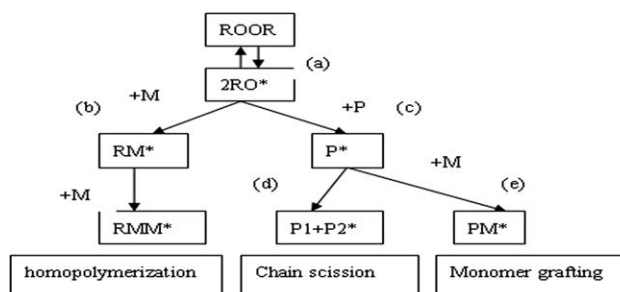

Figure 7 Sketch of the grafting mechanism of MAH onto PP. RMM*: polymer radical from the reaction between RM* and M; P1: the degraded polymer with double bond end group.
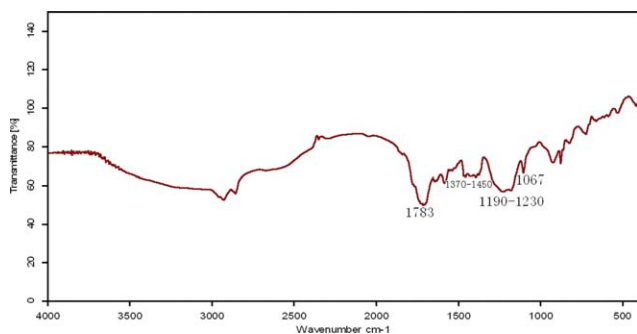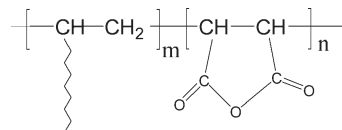
Figure 8 FTIR of the 1-decene/MAH reactive product at a molar ratio of 0.3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reacts with an unsaturated monomer M (e.g., MAH) to form a saturated free-radical species (RM*). If the latter continues to react with M, an oligomer or a polymer of M will be formed. In step c, RO* reacts with hydrogen atoms of the polymer (e.g., PP) and, preferentially, tertiary ones to form the corresponding macroradicals (P*'s). Then, in step d, P* is degraded into two shorter segments (P1 with double bond end group and degraded polymer radical P2*), or in step e, M is grafted onto P*. For MAH-grafted PP, because the reactivity of MAH toward free radicals was very low, step b was negligible. When the MAH was grafted with degraded polymer radical P2*, the grafting reaction was slower than the chain scission reaction, and here, the MAH was a single succinic anhydride connected to the chain end of PP. The previously mentioned FTIR results proved that both 1-decene and St as the second monomers reacted with P* before the occurrence of step d.

Li and coworkers[14,15] and Zhang et al.[16] reported that added St can react with MAH to form an SMA co-

polymer or St can form a charge-transfer complex with MAH; the formed product was grafted onto PP, which resulted in a higher grafting degree. Davis and co-workers[17–19] proved that α-olefins can copolymerize with MAH to form α-olefin/MAH copolymers or has reactivity with MAH through an Alder-ene reaction. To prove the existence of this reaction between 1-decene and MAH, the reaction between 1-decene and MAH was carried out in our laboratory. The FTIR and GPC curves of the product are shown in Figures 8 and 9, respectively. The appearance of the characteristic band of anhydride at 1783 cm^{-1}, the band of C—O at 1230 and 1067 cm^{-1}, and the band of C—H at 1370 cm^{-1} proved the existence of MAH in the formed product. The GPC result shows that the molecular weight of this product was about 4.5 kg/mol. MAH copolymerized with 1-decene to form a copolymer with a lower polymerization degree. To characterize the chemical composition of the copolymer, ^{1}H-NMR was used. The ^{1}H-NMR spectrum of the copolymer in Figure 10 shows the chemical shifts of C—H in MAH around 3.0 ppm, CH$_3$ in 1-decene at 1.0 ppm, and C—H in 1-decene around 1.6 ppm. The chemical shift at 2.05 ppm was attributed to deuteroacetone, due to the existence of part CH$_3$ in its structure. Then, the possible structure of the copolymer is proposed as follows:

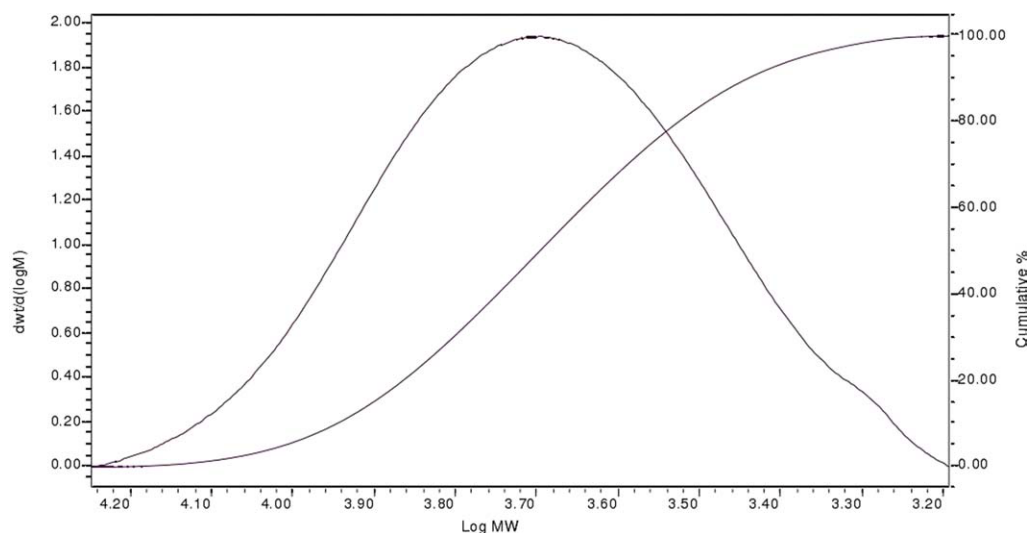As to the reaction between α-olefins and MAH, Davis et al.[18] concluded that the samples

Figure 9 GPC graph of the 1-decene/MAH reactive product at a molar ratio of 0.3. MW: molecular weight; dwt/d(logM): differential weight distribution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

copolymerized by octadecene and MAH had equimolar compositions regardless of the monomer feed, and the product of the values of the monomer reactivity ratios (r_1 and r_2) calculated with the linear method developed by Fineman and Ross[21] and Kelen and Tudors[22] was zero. In Avman and Sabrnal's study,[19] for MAH/octene, values of 2.05 and 0.79 were obtained for r_1 and r_2, respectively, whereas for MAH/tetradecene, values of 0.65 and 2.045 were obtained for r_1 and r_2, respectively. For these two copolymers, the random distribution of chain structure was proven. As shown in Figure 10, the chemical shift corresponding to C—H in the MAH part was very weak compared with that in the 1-decene part. The content of MAH in the copolymer was low. Therefore, the chain structure of the copolymer formed between 1-decene and MAH was more likely to be random.

Figure 11 gives the possible grafting mechanism with 1-decene as the second monomer. One mechanism was that the copolymer (BMA in Figure 11) formed by 1-decene and MAH was grafted onto PP. The other mechanism was that 1-decene was first grafted onto PP, and then, MAH was grafted. Its main problem was that the big size of the 1-decene-grafted PP may have blocked the approach of MAH and the improvement of the grafting degree may have been weak. The third mechanism was that 1-decene reacted with MAH through an Alder-ene reaction, and the formed product was grafted onto PP. The first and third mechanisms were possible for the improvement of the grafting degree by 1-decene. Compared with that of the Alder-ene reaction product, the effect of the copolymer on the grafting degree in the first mechanism may have been more pronounced because of its higher molecular weight and long chain.

The solubility parameters of PP, St, MAH,[23] and 1-decene[24] were 7.4, 9.3, 17.8, and 7.0 cal$^{0.5}$ cm$^{-1.5}$, respectively. The difference in the solubility parameter between 1-decene and PP was smaller than that between St and PP. Hence, compared with St, the affinity between 1-decene and PP was higher, and 1-decene could diffuse into PP molecules easily.
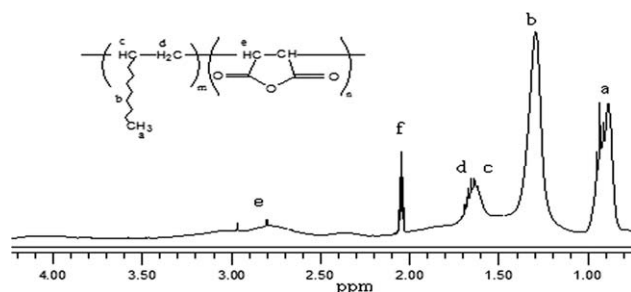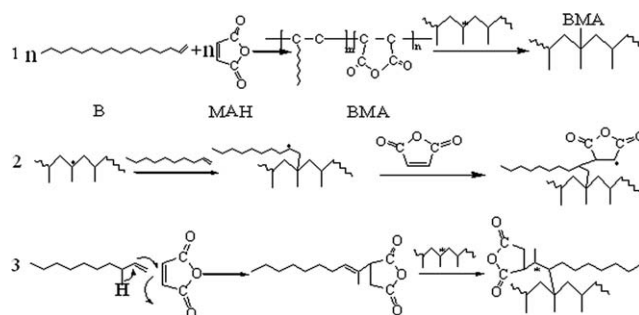

Figure 11 Possible mechanisms of MAH melt grafting under the existence of 1-decene.

Therefore, in the first and third situation in Figure 11, the formed product was more easily grafted onto PP than pure MAH and the system with St as the second monomer; this resulted in a higher grafting degree with less second monomer added.

CONCLUSIONS

In this study, chemical titration, DSC, and FTIR spectroscopy were used to investigate the effect of 1-decene on the grafting behavior of MAH onto PP. The results show that at a 1-decene/MAH blend ratio of 0.3, the grafting degree value was up to 1.43%, which was 110% higher than that of the pure MAH grafting system and 46% higher than that under an SMA blend ratio of 1.0. Similar to the contribution of St, the introduction of 1-decene inhibited the chain scission, and 1-decene can react with MAH. The formed product was grafted onto PP, resulting in a higher grafting efficiency. Compared with St, 1-decene had a higher affinity for PP and, therefore, as the second monomer, was more effective in improving the grafting degree of MAH onto PP.

Figure 10 ^{1}H-NMR spectrum of the 1-decene/MAH reactive product at a molar ratio of 0.3.

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