Poly(oxypropylene)-amide grafted polypropylene as novel compatibilizer for PP and PA6 blends

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Abstract

Poly(oxypropylene)-amide grafted polypropylene (PP) was prepared in an extruder by the reaction of poly(oxypropylene) (POP)diamines and maleated PP (PP-*g*-MA). The resulting POP-grafted PP copolymers are confirmed by the FTIR analysis, and used as compatibilizers for polyamide 6 (PA6) and polypropylene blends. These compatibilizers, POP-functionalized PPs (PP-*g*-MA-*co*-POPs), have different amphiphilic properties depending on the content of MA in the starting PP-*g*-MA and the molar ratio of MA/amine. The compatibilization effect is examined in terms of morphologies, thermal and mechanical properties. The morphologies, affected by the molecular weight of POP diamine in PP-*g*-MA-*co*-POP copolymer, show a decreasing size of the dispersed PA6 particles as the molecular weight of POP diamine increasing from 230 to 400 to 2000. Using these PP-*g*-MA-*co*-POP copolymers, the compatibilized blends show improvements in mechanical properties, including Izod impact strength and tensile toughness, over a conventional compatibilizer. The POP and amide functionalities in the compatibilizers can facilitate the formation of hydrogen bonding with PA6 and, therefore, the compatibilizing effect. During the compounding process, the compatibilizers further react with PA6 in situ to afford the mixture of PP-*g*-MA-*co*-POP-PA6, PP-*g*-MA-*co*-POP-*co*-PA6 and PP-*g*-MA-*co*-PA6 copolymers, which further improves the compatibilizing effect. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

It has been well recognized that physical and chemical interactions across the interface can influence the mechanical performance in polymer blends. The interaction between two phases is the key factor for improving adhesive property in polymer blends. Considerable research efforts have been made on methods to reduce interfacial tension and to increase interphase adhesive between two immiscible polymers. In general, an effective compatibilizer is able to function as a surface active agent (surfactant) situating at the interface of two incompatible polymers and to lower its interfacial tension and to promote adhesive between phases.

Compatibilization of polymer blends has been achieved by using various non-reactive and reactive compatibilizers. Recently, the in situ formed copolymer as a compatibilizer in polymer blends has attracted much attention due to its convenience and simplicity. A reactive compatibilizer precursor can produce in situ the graft or block copolymer that contains segments miscible or compatible with both components of the blend. Precursors containing anhydride, carboxylic acid, and epoxide groups are among the most investigated reactive compatibilizing agents. The highly reactive maleic anhydride (MA) functionalized polymers such as polyethylene-MA (PE-*g*-MA), polypropylene-MA (PP-*g*-MA), SEBS-*g*-MA, EPDM-*g*-MA, and poly(styrene-*co*-MA) (SMA) have been widely used in reactive compatibilization [1–27]. These maleated compatibilizing agents are highly active, and readily in reaction with amine terminal groups of polyamides. In general, the effectiveness of the compatibilization depends on the chemical structure, quantity of compatibilizer, reactive group concentration, blending sequence and the final location of the in situ-formed copolymers.

Reactive compatibilization involving polyamide (PA) as the major component has the longest history and probably makes up of over half of the reported literature in the field of reactive compatibilization. Maleic anhydride (MA) and acrylic acid (AA) grafted polyolefins or elastomeric polyolefins are effective precursors of the reactive compatibilizers for various PA/polyolefin blends. The polyolefins grafted with highly electrophilic MA moiety can react readily with the nucleophilic amine end groups of polyamides to

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Table 1
Materials used

	MA content by weight (%)	T_m[a]	T_c[a]	Melt index[b] (g/10 min)	Yield strength[c] (MPa)
PP-g-MA	0.3	164.9	116.2	6.0	–
PP-g-MA	0.8	163.6	114.0	15.3	–
Polypropylene (PP)	0	164.5	115.4	6.6	29.8 ± 0.2
Nylon 6 (PA6)	0	221.5	194.6	36.6	58.0 ± 3.0

[a] Determined by DSC.
[b] Measured at 240°C and 2.16 kg loading.
[c] Measured by Instron machine.

form amic acid, followed by ring closure to form a thermally stable imide at the elevated temperature under normal melt processes [28]. The resulting compatibilizer facilitates the phase interaction with polyamide through multiple hydrogen bonding predominantly [28]. From this viewpoint, increasing the hydrogen bonding formation is also expected to improve the miscibility of PA/polyolefin blends.

Polymers containing ether groups are known to be miscible with PAs. For example, poly(oxyethylene) (POE) and other ether group containing polymers have found to interact with different PAs through hydrogen bonding [29,30]. In the present work, the commercially available poly(oxypropylene)diamines, trade name as Jeffamine® D-series amines, and the PP-g-MAs are used to produce POE-functionalized PPs as the compatibilizer for the PP/Polyamide-6 (PA6) blends. In this study, our investigations focus on the effect of hydrogen bonding to the miscibility, morphology, thermal behavior and mechanical properties of the resulting blends.

2. Experimental

2.1. Materials

The polymers used in this work are described in Table 1. Polypropylene (PP), a general purpose grade 366-3, was obtained from Taiwan Polypropylene Company. Polyamide-6 (PA6), Novamide 1010C2, a general purpose grade from the Mitsubishi Kasei Co. Ltd of Japan. PP-g-MAs with various MA contents (0.3 and 0.8 wt.%) were purchased from the BP Chemicals of USA. Poly(propylene glycol)-bis-(2-propylamine) at M_w 230, 400, and 2000 or

trade name Jeffamine® amines, D-230, D-400, and D-2000 were purchased from the Huntsman Co. of USA. The chemical structures are drawn below.

$$H_2NCHCH_2(OCH_2CH)_xNH_2$$
$$CH_3 \qquad CH_3$$
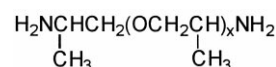
x = 2–3 (Approximately M_w = 230; Jeffamine® D-230)
x = 5–6 (Approximately M_w = 400; Jeffamine® D-400)
x = 33 (Approximately M_w = 2000; Jeffamine® D-2000)

2.2. Extrusion and injection molding

All blends and the POP-functionalized PPs were prepared by a co-rotating 30 mm twin-screw extruder (L/D = 36, Sino Alloy Machinery Inc. of Taiwan) with a decompression zone. The rotating speed of the screw was 250 rpm. Standard ASTM specimens (tensile and flexural) were prepared by an Arburg 3 oz injection-molding machine of Germany. Before melt blending and injection molding, all pellets were dried in an oven at 80°C for 24 h. The detailed processing conditions for extrusion and injection molding are listed in Table 2.

2.3. Extraction of PA6/PP-g-MA-co-POP binary blend

Ten grams of a binary blend (PA/PP-g-MA-co-POP = 30/5) were extracted in 140 ml formic acid for 1 h. The formation of milky stable emulsion was an indication of the surfactant structure formed by POP grafting on PP [31]. The precipitate was formed when the acetone was added into the emulsion solution. The solid was filtered and

Table 2
Processing conditions for extrusion and injection molding

Stage	1	2	3	4	5	6	7	8	9	Die	Nozzle	Mold
(A) Extrusion condition for modified PP-g-MA:												
Temp. (°C)	150	200	200	200	200	200	200	200	200	185		
(B) Extrusion condition for all blends:												
Temp. (°C)	180	230	235	240	240	240	240	240	240	230		
(C) Injection condition:												
Temp. (°C)	240	250	260								260	70
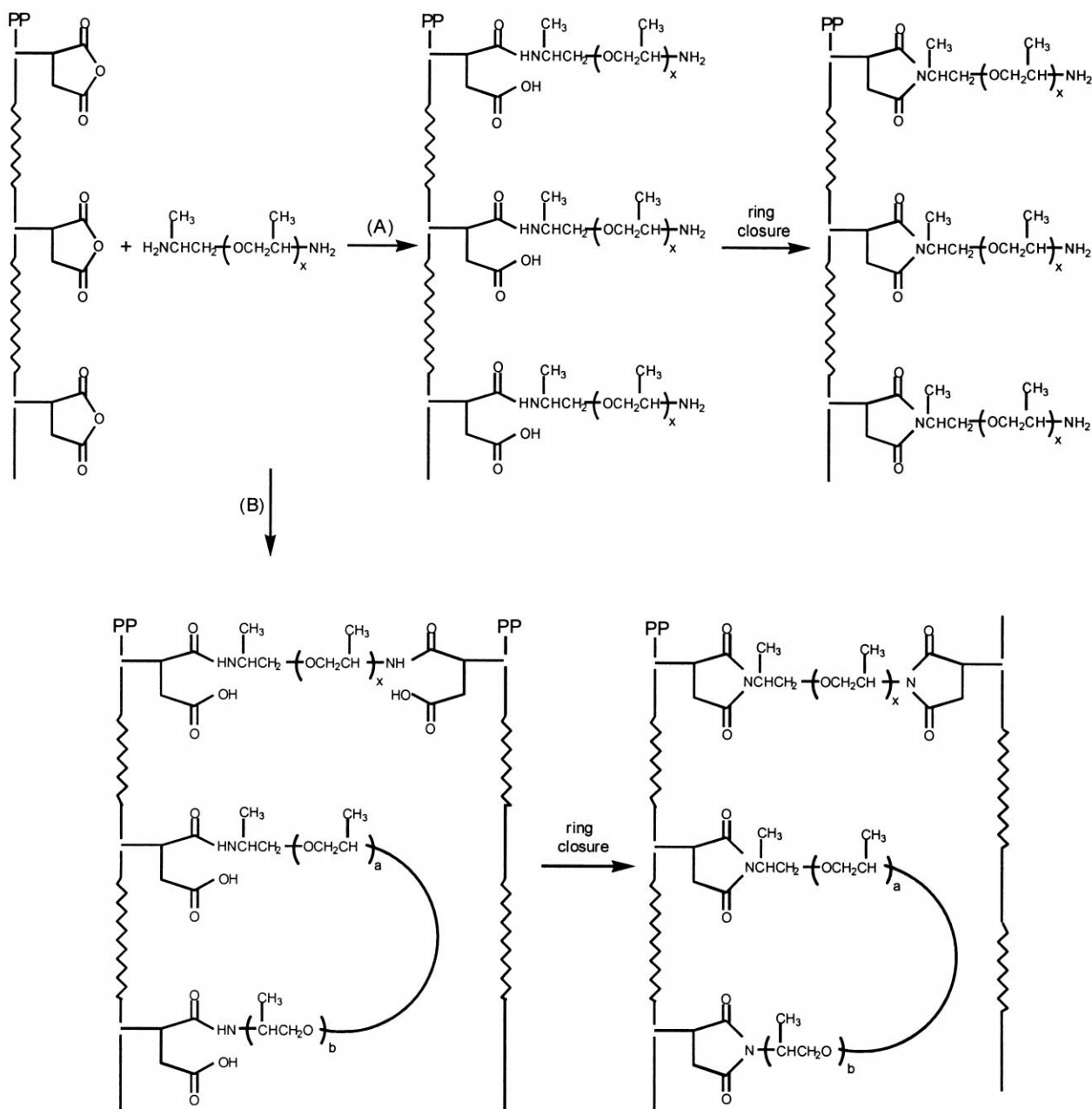
Scheme 1. Proposed synthesis of POP-functionalized PPs.

extracted again with formic acid. The same procedure was repeated for five times. The resulting solid was finally washed with water and dried overnight at 80°C in a vacuum oven.

2.4. Characterizations

FTIR spectra were recorded by a Perkin Elmer Paragon 500 FTIR Spectrometer with a resolution of 4 cm^{-1}. Samples are ground with KBr powder, then compressed into pellets. The heat analysis was carried out by a Seiko SII model SSC/5200 differential scanning calorimeter

(DSC) from Seiko Instruments and Electronics Ltd. The size of the samples was approximately 5–8 mg on sealed aluminum pan. The analyses were performed under a heating rate of 10°C/min in 30 ml/min nitrogen atmosphere. The heat of melting (ΔH_m) and crystallization (ΔH_c) was determined by integration of the peak area under linear baseline, and peak values of the thermogram were reported as melting point (T_m) and crystallization temperature (T_c), respectively. Each specimen was heated to 300°C at a rate of 30°C/min and held for 5 min to remove the residue thermal influence. Melt Index (MI) of the blends was measured at 240°C and 2.16 kg loading according to the ASTM-D1238 method.
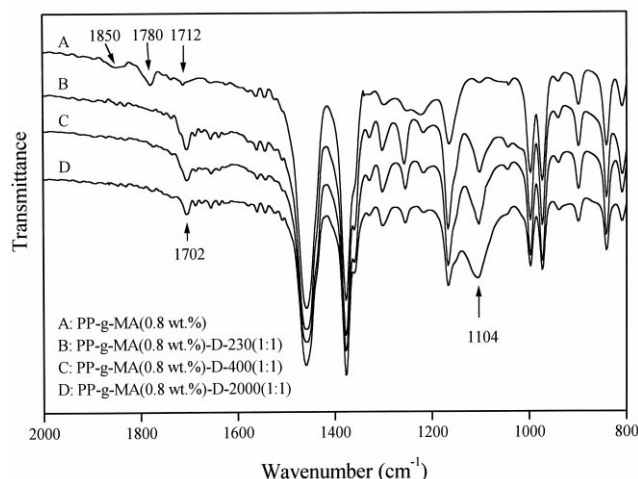
Fig. 1. FTIR spectra of modified and unmodified PP-*g*-MA.

Tensile tests were measured according to the ASTM D638-86 method at a testing rate of 5 mm/min using an Instron Universal Testing Machine Model 4201 under ambient condition. Izod impact tests were carried out at ambient conditions according to the ASTM D256 method. These specimens were maintained in an atmosphere having 30% relative humidity for one week and then measured at an average of seven specimen tests. Scanning electron microscopy (SEM) of the fractured surfaces were examined by a Hitachi S-570 SEM at an accelerating voltage 20 kV. The morphologies were examined from fractured specimens in the plane perpendicular to flow direction of injection molding. Samples were etched with formic acid to dissolve the PA6 phase out of the blends. The fractured surfaces of specimens were coated with thin film of gold to prevent charging.

3. Results and discussion

3.1. In situ synthesis of POP-functionalized PPs

Melt reaction of the commercially available POP diamines, i.e. Jeffamine® D-series amines, and PP-*g*-MA in an extruder was carried out to yield the amide linked POP-functionalized PPs (PP-*g*-MA-*co*-POPs) as shown in Scheme 1. A similar procedure was reported by Evans et al. in a recent US Patent [32]. Two major types of products can be envisioned — comb-like graft copolymers (Scheme 1A) and inter-or intra-cross-linking block copolymers (Scheme 1B). However, there may be other hybrid graft and cross-linked block copolymers, free POP diamines and unreactive MA functionalities in the product. The graft copolymers will be formed predominantly when the molar ratio of MA/Amine = 1/1 while inter-and/or intra-cross-linked block copolymers may be formed predominantly when the molar ratio of MA/Amine = 2/1. The FTIR spectra are shown in Fig. 1. The FTIR indicated that the PP-*g*-MA exists in the forms of anhydride (1850 and 1780 cm^{-1}) and hydrolyzed free acid (1712 cm^{-1}). After reaction, a decrease in intensity for the absorption peaks of the MA group at 1850 and 1780 cm^{-1} (Fig. 1A) is observed with the appearance of new peak at 1702 cm^{-1} (Fig. 1B–D). In the fingerprint region, the peaks at 1104 cm^{-1} with an increasing intensity depending on the POP chain length are attributed to the C–O–C stretching of the POP diamines. The absorption peak at 1702 cm^{-1} may be corresponding to the carbonyl group of the amide-acid or imide. The relative degree of cross-linking for POP diamine modified PPs could be detected by the solvent test. All of the PP-*g*-MA-*co*-POP copolymers (derived from PP-*g*-MA precursor with 0.3 wt.% MA) were soluble in hot toluene, however, all of PP-*g*-MA-*co*-POP copolymers (derived from PP-*g*-MA

Table 3
DSC data with modified (modified PP-*g*-MA: 1:1 or 2:1 molar ratio of MA to diamine D-230, D-400 or D-2000) and unmodified PP-*g*-MA

Composition	Weight fraction	T_c (°C)	ΔH_c^a (J/g)	T_m (°C)	ΔH_m^a (J/g)
PP-*g*-MA[b]	100	116.2	98.0	164.9	95.9
PP-*g*-MA[b]/D-230 (1:1)	100/0.7	115.9	97.6	165.0	95.5
PP-*g*-MA[b]/D-230 (2:1)	100/0.35	116.0	97.9	164.7	96.0
PP-*g*-MA[b]/D-400 (1:1)	100/1.2	115.6	97.0	164.9	95.2
PP-*g*-MA[b]/D-400 (2:1)	100/0.6	115.8	97.5	164.9	95.4
PP-*g*-MA[b]/D-2000 (1:1)	100/6	115.4	96.5	165.0	94.5
PP-*g*-Ma[b]/D-2000 (2:1)	100/3	115.8	96.9	164.7	95.0
PP-*g*-MA[c]	100	114.0	96.3	163.6	96.1
PP-*g*-MA[c]/D-230 (1:1)	100/1.8	111.0	90.6	163.1	89.0
PP-*g*-MA[c]/D-230 (2:1)	100/0.9	111.0	87.8	163.1	88.0
PP-*g*-MA[c]/D-400 (1:1)	100/3.2	112.3	94.8	163.5	93.5
PP-*g*-MA[c]/D-400 (2:1)	100/1.6	112.9	93.5	163.5	93.2
PP-*g*-MA[c]/D-2000 (1:1)	100/16	114.3	97.4	164.2	98.1
PP-*g*-MA[c]/D-2000 (2:1)	100/8	114.0	92.5	163.5	92.8

[a] The enthalpy has been corrected by weight fraction.
[b] 0.3 wt.% of maleic anhydride in PP-*g*-MA.
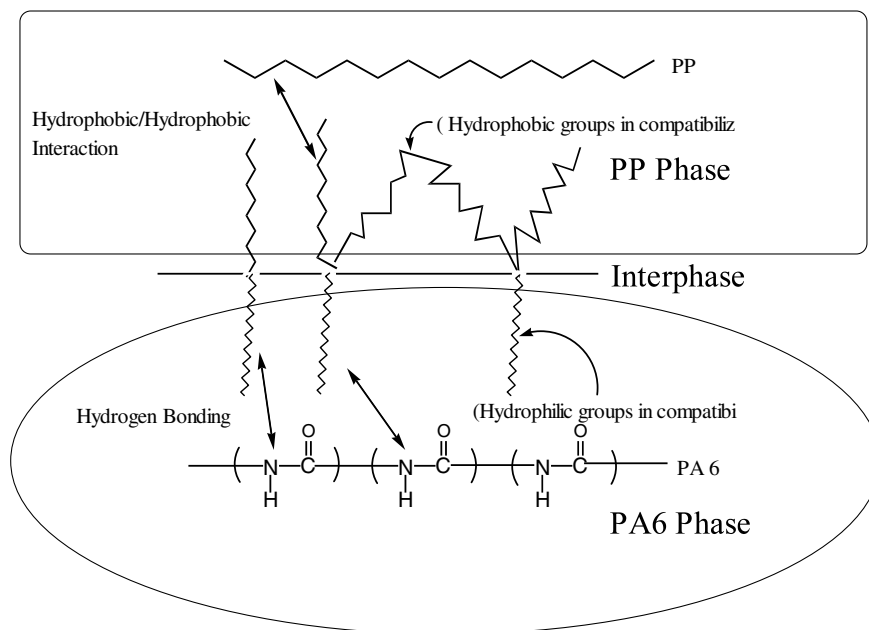[c] 0.8 wt.% of maleic anhydride in PP-*g*-MA.

Fig. 2. Conceptual structure of compatibilization of PA6/PP blend.

precursor with 0.8 wt.% MA) showed some swelled gelation in solution. The higher molar ratio of MA/Amine and the shorter POP diamine chain length resulted in the product with higher cross-linking or swelling in solvent. DSC results are summarized in Table 3. No significant difference is observed for the thermal properties of the PP-*g*-MA-*co*-POP copolymers (derived from PP-*g*-MA precursor with 0.3 wt.% MA) relative to the origin PP-*g*-MA. However, the slightly lower of crystallization temperature (T_c) and enthalpy of the copolymers derived from PP-*g*-MA precursor with 0.8 wt.% MA were observed. This may be due to the formation of the cross-linked products.

These copolymers, comprised of hydrophobic PP backbone and hydrophilic POP pendants, have amphipathic properties for compatibilizing PP/PA6 blends. Enhanced compatibilization induced by these copolymers is presumably developed from the hydrophobic interaction with PP and the hydrophilic hydrogen bonding with PA6 conceptually illustrated in Fig. 2. In addition, the unreacted MA groups in PP-*g*-MA are still able to react with PA6 amine terminal group competitively to form a PP-*g*-MA-*co*-PA6 copolymer.

3.2. SEM morphologies

Interfacial tension, interaction between two phases, melt viscosities of the blended constituents, volume fraction, and processing conditions are key factors governing the degree of dispersion and stability against coalescence. Pieces of one polymer may be drawn into filaments which may remain as filaments, break up into smaller droplets, or connect with each other to give an interconnected network. The SEM photomicrography is the most convenient

approach to differentiate the morphologies between the compatibilized and the uncompatibilized blends. The incompatible blend possesses higher interfacial tension and usually results in coarser morphology compared to that of the corresponding compatibilized blend.

Morphology changes of the fracture surfaces with solvent etching for various PA6/PP = 30/70 blends are shown in Fig. 3. The residue holes were caused by removing the dispersed PA6 component. The sections were taken at right angle to the flow direction. The large domain size of the dispersed PA6 phase with different dimensions can be easily identified from the non-compatibilized blend (Fig. 3A). Incorporating 5 phr PP-*g*-MA (0.3 wt.% MA) failed to reduce noticeably the dispersed PA6 domain size (Fig. 3B). Lower content of the MA unit is expected to produce only limited number of the desired copolymer, PP-*g*-MA-*co*-PA6. When 5 phr of the PP-*g*-MA-*co*-POP copolymer (derived from PP-*g*-MA precursor with 0.3 wt.% MA) is added, the average domain size of the dispersed phase decreases depending on the chain length of the POP diamine modifier (Fig. 3C–E). The hole sizes of the dispersed PA6 phase become smaller and uniform as the molecular weight of the POP diamine is increased from D-230 to D-2000. This suggests that the modifier with longer chain length of the POP diamine is more effective in reducing the interfacial tension of the blend. Conceptually shown in Fig. 2, the compatibilizer has two distinct blocks of PP backbone and the POP pendants. While interacting with PP through the hydrophobic effect, hydrogen bonds formed between POP ether oxygens and PA6 amide groups resulting in high compatibilizing efficiency. This interaction may cause the compatibilizer residing along the interface to function as an effective compatibilizer. The resultant morphologies
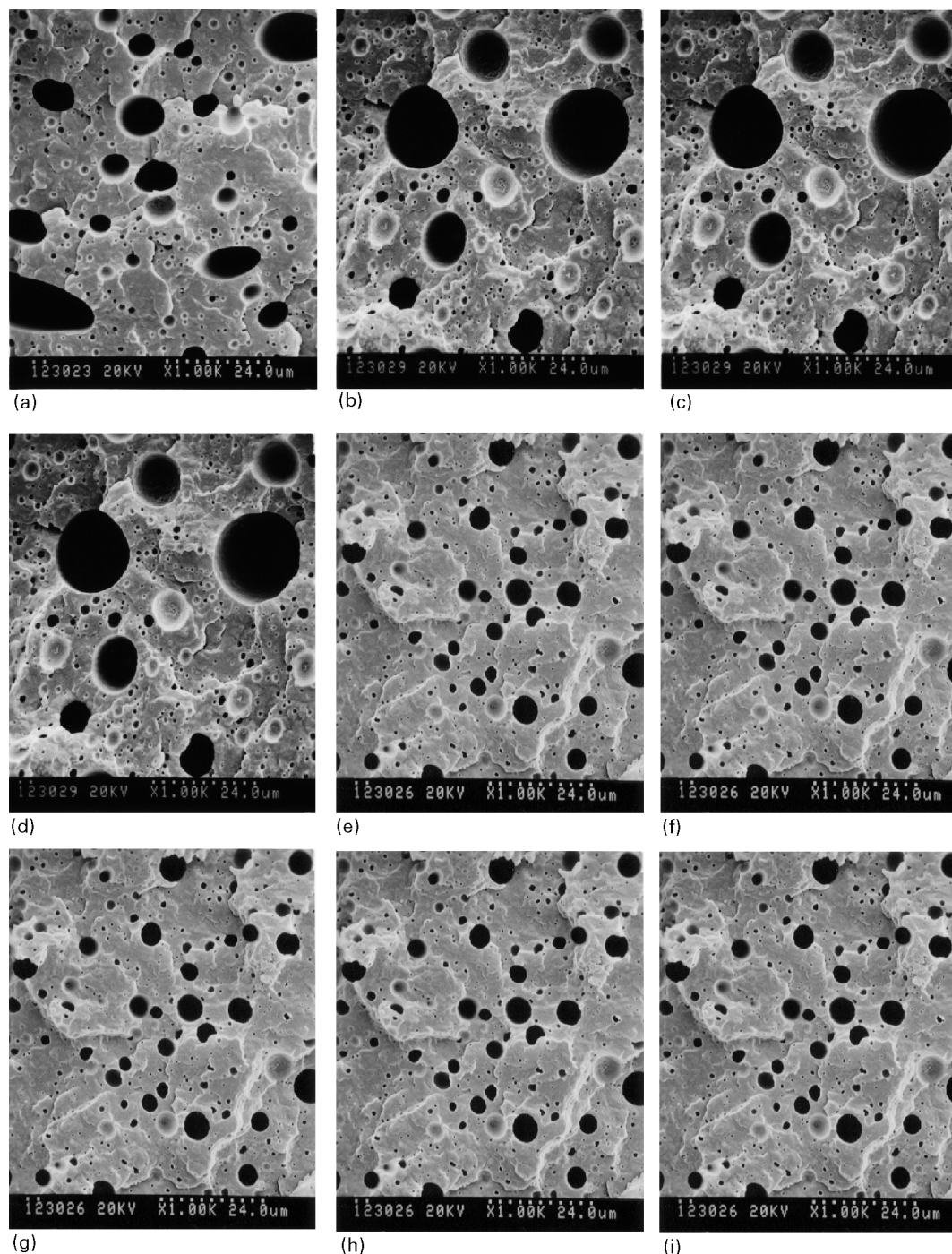
Fig. 3. SEM micrographs of the uncompatibilized and compatibilized PA6/PP = 30/70 blends.

exhibited an effective compatibilization by involving a high molecular weight POP diamine. The compatibilizers, PP-*g*-MA (0.8 wt.% MA) and the derived PP-*g*-MA-*co*-POP copolymers have a pronounced effect on reducing the dispersed domain size (Fig. 3F–I). The finest dispersion is observed with the copolymer derived from the POP diamine modifier having 2000 M_w. The high M_w of POP grafting resulted in a proper balance between the PP and the POP blocks in bonding with PP/PA6, respectively.

From these morphological observations these PP-*g*-MA-*co*-POPs copolymers are proven to be effective compatibilizers for PA6/PP blends.

3.3. Thermal properties

DSC results are summarized in Table 4 and Fig. 4. For comparison, the enthalpy (fusion or crystallization) had been corrected by the weight fraction. Fig. 3 shows the

Table 4
DSC data of polyamide (PA6)/polypropylene (PP) (30/70) with modified (modified PP-g-MA: 1:1 or 2:1 molar ratio of MA to diamine D-230, D-400 or D-2000) and unmodified PP-g-MA

Composition	Weight fraction	T_c PP (°C)	ΔH_c^a PP (J/g)	T_c PA6 (°C)	ΔH_c^a PA6 (J/g)	T_m PP (°C)	ΔH_m^a PP (J/g)	T_m PA6 (°C)	ΔH_m^a PA6 (J/g)
PA6	100	–	–	194.6	−69.9	–	–	221.5	72.1
PP	100	115.4	−88.7	–	–	164.5	89.6	–	–
PP-g-MA[b]	100	116.2	−98.0	–	–	164.9	95.9	–	–
PP-g-MA[c]	100	114.0	−96.3	–	–	163.6	96.1	–	–
PA6/PP	30/70	122.8	−86.9	193.9	−66.6	167.2	87.7	222.2	68.9
PA6/PP/PP-g-MA[b]	30/70/5	124.1	−88.9	192.6	−68.4	165.8	89.3	221.5	70.2
PA6/PP/PP-g-MA[b]-D-230 (1:1)	30/70/5	123.5	−88.8	192.6	−69.1	165.8	92.3	222.2	70.0
PA6/PP/PP-g-MA[b]-D2000 (1:1)	30/70/5	122.1	−87.6	191.9	−65.5	165.8	89.3	222.2	67.4
PA6/PP/PP-g-MA[c]	30/70/5	123.4	−92.8	190.5	−45.6	165.8	90.9	222.2	59.6
PA6/PP/PP-g-MA[c]-D-230 (1:1)	30/70/5	122.8	−89.2	191.9	−67.0	165.8	90.0	222.2	70.0
PA6/PP/PP-g-MA[c]-D-400 (1:1)	30/70/5	122.1	−88.6	191.9	−64.2	165.8	89.3	222.2	67.7
PA6/PP/PP-g-MA[c]-D2000 (1:1)	30/70/5	121.4	−88.7	190.5	−57.8	165.8	89.6	222.2	64.3

[a] The enthalpy has been corrected by weight fraction.
[b] 0.3 wt.% of maleic anhydride in PP-g-MA.
[c] 0.8 wt.% of maleic anhydride in PP-g-MA.

DSC cooling scans of PA6, PP and the PA6/PP = 30/70 blends. The cooling scanning crystallization temperatures (T_cs) of the PA6 component in these compatibilized blends are about 2–3°C lower than that of the neat PA6, an indication of slower nucleation. The presence of the in situ formed PP-g-MA-co-PA6 copolymer tends to interfere with the PA6 crystallization [33,34]. Polymers containing ether groups have known to interact with "amorphous" PAs through hydrogen bonding [29,30] and hinder PA6 crystallization as expected. The T_c of the PA6 component in the compatibilized blends is depressed slightly with increasing POP chain length. However, T_cs of the PP component are substantially higher than that of the virgin PP (6–9°C), an indication of fast nucleation due to the crystalline PA6 as nucleating agent across PP–PA interface to promote PP crystallization in these compatibilized PA6/PP blends. The glass transition temperature of PA6 and PP cannot be detected in these heating thermograms. PA6 and PP are semicrystalline polymers with melting temperature (T_m) at 221.5 and 164.5°C, respectively. No marked change is observed for the melting points of the two phases in these uncompatibilized and compatibilized blends. However, crystallinity of PA6 component in these compatibilized blends is lower than that of the pure PA6. Again, the copolymer molecules situated at the interface are able to prohibit the crystal formation. According to Duvall et al. [35] and Paul et al. [16], PP and PP-g-MA could co-crystallize when PP-g-MA containing low content of maleic anhydride. Under this consideration, the enthalpy (fusion or crystallization) had been corrected by the weight fraction involving PP and PP-g-MA. The crystallinity of the PP component in the compatibilized PA6/PP blend is close to pure PP but still lower than that of co-crystallized PP and PP-g-MA. The compatibilizers may interfere with the co-crystallization.

The presence of the PP-g-MA-co-PA6 and PP-g-MA-co-POP copolymers results in slower crystallization and lower crystallinity of the PA6 component in the compatibilized blends. However, two factors, nucleating agent (crystalline PA6) and compatibilizer (PP-g-MA-co-PA6 and PP-g-MA-co-POP copolymers), dictate the crystalline behavior of the PP component.

3.4. Mechanical properties

The material mechanical properties can be roughly classified into two categories: strength and toughness. Tensile strength and modulus can be considered as the material strength while tensile toughness and Izod impact strength are the material toughness. In general, modification of a polymeric material seldom results in improving both properties simultaneously. It usually results in improvement of one property but suffers the other. Fortunately, improvement in both strength and toughness properties can be achieved in these compatibilized PA6/PP blends.

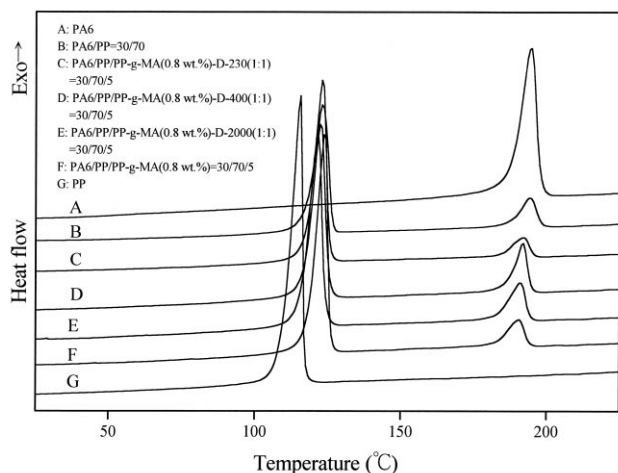Melt Index (MI) and mechanical properties including tensile and Izod impact are summarized in Table 5 and

Fig. 4. DSC cooling scans of PA6, PP and PA6/PP = 30/70 blends.

Figs. 5–7. Essentially all of the compatibilized blends have relatively lower MI than the corresponding uncompatibilized counterpart. All these PA6/PP blends, uncompatibilized and compatibilized, are brittle with low notched impact strength because both PA6 and PP are notch sensitive. Unnotched Izod impact strength is commonly used to differentiate toughness change resulting from compatibilization. A general trend of improved impact strength is observed in the compatibilized blends relative to the uncompatibilized one as shown in Fig. 5. The blends with PP-*g*-MA derived compatibilizers having higher MA content

(0.8 wt.%) give higher unnotch Izod impact strength than those counterparts using lower MA content (0.3 wt.%) of PP-*g*-MA. The improvement of impact strength by the 0.8 wt.% MA derived compatibilizer with the D-2000 is dramatic; the impact strength increases about 300%. The impact strength improvement of these compatibilized blends indicates that the interphase between PP and PA6 adheres strongly to both phases and results in toughness improvement [36]. Strong adhesion is needed for immiscible blends due to effective stress transfer under stress.

A substantial improvement in tensile toughness of all blends is demonstrated in Fig. 6 where the trend of the tensile toughness improvement is similar to that of the impact strength. The greatest improvement is also obtained by using the compatibilizers involving the highest molecular weight of the POP diamine (D-2000).

Fig. 7 illustrates the effect of the compatibilizer on the tensile strength. The improvement in tensile strength shows similar trend as the tensile toughness that can be attributed to the change of their morphologies (Fig. 3) and the improved interfacial adhesion. Tensile properties of immiscible and partially miscible blends depend on two interrelated factors; the adhesion between two phases and the domain size of the dispersed component, both are controlled mainly by the interfacial tension [37,38].

A compatibilized polyblend, in general, has finer phase domain size, greater interfacial contact area and higher interfacial adhesion than that of the corresponding uncompatibilized blend. An effective compatibilizer preferably resides along the interface.

Table 5
Mechanical properties and melt index (MI) of polyamide (PA6)/polypropylene (PP) with modified (modified PP-*g*-MA: 1:1 or 2:1 molar ratio of MA to diamine D-230, D-400 or D-2000) and unmodified PP-*g*-MA

Composition	Weight fraction	Izod impact		Tensile properties		Melt index (MI) (g/10 min)
		Notch (J/M)	Unnotch (J/M)	Tensile strength (MPa)	Toughness (MPa)	
PA6/PP	30/70	35	119	25.0 ± 0.4	2.2 ± 0.1	19.6
PA6/PP/PP-*g*-MA[a]	30/70/5	27	138	30.2 ± 0.4	2.5 ± 0.2	9.3
PA6/PP/PP-*g*-MA[a]-D-230 (1:1)	30/70/5	32	138	30.3 ± 0.1	2.7 ± 0.1	9.3
PA6/PP/PP-*g*-MA[a]-D-230 (2:1)	30/70/5	32	140	29.0 ± 0.8	2.0 ± 0.1	8.9
PA6/PP/PP-*g*-MA[a]-D-400 (1:1)	30/70/5	27	153	31.3 ± 0.2	3.3 ± 0.4	10.0
PA6/PP/PP-*g*-MA[a]-D-400 (2:1)	30/70/5	24	138	31.9 ± 0.4	3.4 ± 0.2	8.0
PA6/PP/PP-*g*-MA[a]-D-2000 (1:1)	30/70/5	27	190	32.2 ± 0.2	3.9 ± 0.2	7.0
PA6/PP/PP-*g*-MA[a]-D-2000 (2:1)	30/70/5	41	194	32.3 ± 1.2	3.8 ± 0.5	6.7
PA6/PP/PP-*g*-MA[b]	30/70/5	19	256	34.1 ± 0.4	7.7 ± 0.9	6.7
PA6/PP/PP-*g*-MA[b]-D-230 (1:1)	30/70/5	21	208	34.0 ± 0.3	7.1 ± 0.8	8.8
PA6/PP/PP-*g*-MA[b]-D-230 (2:1)	30/70/5	18	213	34.7 ± 0.3	5.4 ± 0.3	7.1
PA6/PP/PP-*g*-MA[b]-D-400 (1:1)	30/70/5	22	214	34.4 ± 0.2	8.0 ± 0.7	9.6
PA6/PP/PP-*g*-MA[b]-D-400 (2:1)	30/70/5	19	232	34.0 ± 0.3	9.6 ± 1.0	8.7
PA6/PP/PP-*g*-MA[b]-D-2000 (1:1)	30/70/5	27	386	35.6 ± 0.4	11.5 ± 0.6	6.4
PA6/PP/PP-*g*-MA[b]-D-2000 (2:1)	30/70/5	27	372	35.7 ± 0.6	8.3 ± 0.2	7.1

[a] 0.3 wt.% of maleic anhydride in PP-*g*-MA.
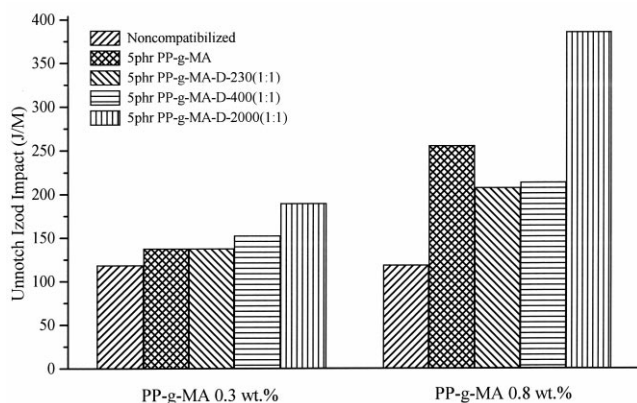[b] 0.8 wt.% of maleic anhydride in PP-*g*-MA.

Fig. 5. Unnotch Izod impact strength of PA6/PP = 30/70 blends with various compatibilizers.

The blends with POP modified PP-*g*-MA compatibilizer give better mechanical properties in general than that of the unmodified PP-*g*-MA, the POP diamine of 2000 M_w results in the best improvement. It is noteworthy once again that the formation of hydrogen bonding is the predominant factor for the compatibilization of polyolefins/polyamide blends [28]. Therefore, for the PP-*g*-MA-*co*-POPs as compatibilizer, this interaction is higher with POP diamine at 2000 M_w.

3.5. Compatibilization mechanism

The mechanism of a reactive compatibilizer is much more complicated because the chemical structure, quantity, and the final location of the in situ-formed copolymer vary with processing condition, reactive group concentration and blending sequence. The PA6/PP blend compatibilized by PP-*g*-MA is a conventional type of reactive compatibilization. From the structural viewpoint, the PP-*g*-MA polymer itself cannot act as an interfacial compatibilizer for the PP/ PA6 blends. The grafted polymers, PP-*g*-MA-*co*-PA6, can act as compatibilizers only if they are distributed along the interface with branched PA6 chains protruding into PA6 phase while the PP segments dissolving in PP phase. During melt blending of PP/PA6/PP-*g*-MA blend, the PP-*g*-MA
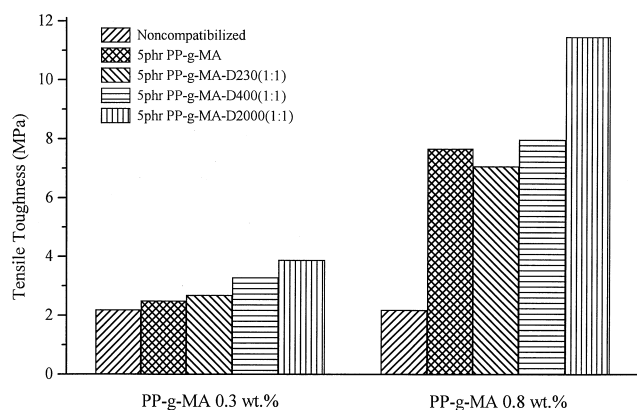

Fig. 6. Tensile toughness of PA6/PP = 30/70 blends with various compatibilizers.

will be completely dissolved in PP phase because they are totally miscible and PP has lower T_m. Only those PP-*g*-MA molecules in the vicinity of the interface have the opportunity for MA units to make contact and to react with the PA6 terminal amine group to form the desirable PP-*g*-MA-*co*-PA6 copolymer during vigorous melt blending. As soon as the graft reaction takes place, most of the in situ-formed PP-*g*-MA-*co*-PA6 copolymer molecules at the interface are believed to be only lightly grafted because the PP-*g*-MA segment is miscible with PP and tends to mix intimately with the PP phase. Lightly grafted copolymer, with one or two grafts per main chain, has been demonstrated to be the most efficient compatibilizer [39,40]. As reported previously [39,41], reactive group concentration is an important factor in designing an optimized compatibilization system. The key factor in determining the efficiency of a reactive compatibilizer is the fraction of the added copolymer turning into lightly grafted copolymers and anchors along the interface. The chance of these MA units from the PP-*g*-MA with 0.3 wt.% MA to make contact and react with the PA6 is considerably low and the formation of the desired copolymer, PP-*g*-MA-*co*-PA, is insignificant. Relatively, the numbers of grafted copolymers formed and the numbers of the branched PA6 chain per molecule produced will be higher and better compatibilized when the PP-*g*-MA with 0.8 wt.% MA is employed in the blend.

According to Paul et al. [16] and Carlier et al. [42], the PP-*g*-MA with 0.3 wt.% MA possesses approximately one maleic anhydride unit on a PP molecular chain end. Reaction of this material with amine end group of the PA6 is expected to produce a diblock copolymer. Therefore, the numbers of the PP-*g*-MA-*co*-PA6 grafted molecules formed will also be less in the one-step PA6/PP/PP-*g*-MA blending process. However, the in situ formation of the PP-*g*-MA-*co*-POPs copolymers should be significant by preblending the PP-*g*-MA and the POP diamines in an extruder. For the PP-*g*-MA-*co*-POPs as compatibilizer, the POP segments tend to reside along the interface due to strong hydrogen bond interaction with PA6. The POP segments will protrude and penetrate into PA6 phase by H-bonding interaction and the degree of penetration depends on the length of the POP segment. This degree of penetration is expected to increase with increasing POP segmental length. The interfacial anchorage of these grafted copolymers with shorter POP segment is expected to be less stable due to shorter penetration of the POP segments and may be forced back into the PP phase under vigorous melt mixing and results in less number of the copolymer residing along the interface. Therefore, the POP length in the PP-*g*-MA-*co*-POP copolymers is an important factor in determining the compatibilizer distribution. The PP-*g*-MA-*co*-POP molecules anchoring along the interface may contain some unreacted amine (–NH2) functionalities which are still able to react with PA6 by an amide exchange reaction (interchange reaction) to form PP-*g*-MA-*co*-POP-PA6 (Scheme 2A) and/or PP-*g*-MA-*co*-PA6 (Scheme 2B) copolymers as shown in
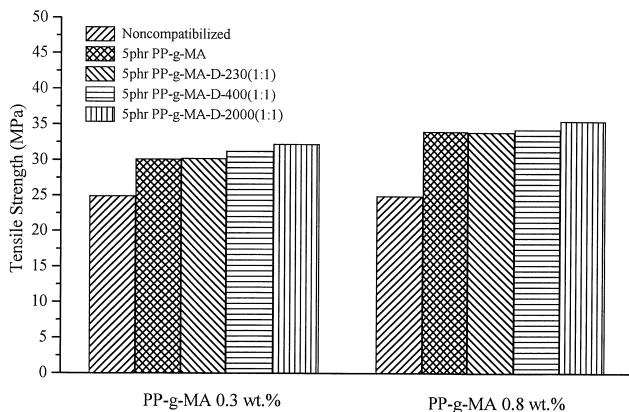
Fig. 7. Tensile strength of PA6/PP = 30/70 blends with various compatibilizers.

Scheme 2. The reaction (Scheme 2B) will not take place for these PP-*g*-MA-*co*-POP molecules via the ring closure reaction. However, the PP-*g*-MA-*co*-PA6 copolymer may also come from the unreactive PP-*g*-MA during preblending process reacts with the PA6 amine terminal group under second stage of blending. Interchange reaction may involve reactions between the terminal functional group of one polymer molecule with the interunit repeating linkage of another polymer molecule, such as the terminal –NH2 and the interunit –CONH– group of the polyamide molecule. The extent of such interchange reaction increases with increasing POP segmental length (the degree of penetration). The PP-*g*-MA-*co*-POP-PA6 copolymer is considered more effective compatibilizer than the PP-*g*-MA-*co*-POP copolymer due to additional PA6 segment in the copolymer. All these mixed copolymers, PP-*g*-MA-*co*-POP, PP-*g*-MA-*co*-POP-PA6 and/or PP-*g*-MA-*co*-PA6, are able to interact with PP through van der Waals bonding and hydrogen bonding with amide of PA6. This is the reason that the observed compatibility using PP-*g*-MA-*co*-POPs as compatibilizers is better than that of PP-*g*-MA with 0.3 wt.%

MA, especially for the one involving the highest M_w POP diamine (D-2000).

The numbers of the PP-*g*-MA-*co*-PA6 grafted copolymers are expected to be higher when the PP-*g*-MA with 0.8 wt.% MA than that with 0.3 wt.% MA. However, the PP-*g*-MA-*co*-POPs are still more effective than PP-*g*-MA in compatibilizing the PP/PA6 blend since the melt reaction is not required. In addition, the PP-*g*-MA-*co*-POP-PA6 and PP-*g*-MA-*co*-POP-*co*-PA6 (Scheme 3B) copolymers will also be formed through the unreacted amine (–NH2) and MA units in the PP-*g*-MA-*co*-POPs by reacting with PA6 as shown in Scheme 3. The probability of such interchange reaction increases with increasing POP segmental length. Shorter POP segment tends to form an inter- and/or intra-cross-linking block copolymer. Moreover, the unreactive PP-*g*-MA during preblending process still has an opportunity during the second stage of blending to react with the PA6 amine terminal group to form the conventional compatibilizer, PP-*g*-MA-*co*-PA6 copolymer. Therefore, the numbers of the grafted molecules formed and the numbers of the protruding PA6 branched molecules formed will also be more. This result explains the observed compatibility of the PA6/PP = 30/70 blend using PP-*g*-MA-*co*-POP with higher molecular weight POP is better than that of the blend when PP-*g*-MA with 0.8 wt.% MA is employed.

3.6. Extraction of compatibilizer

As mentioned above, it was proposed that PP-*g*-MA-*co*-POP copolymer was the major compatibilizer while PP-*g*-MA-*co*-POP-PA6 and/or PP-*g*-MA-*co*-POP-*co*-PA6 copolymers co-existed through the exchange reaction. However, there is no method to show their relative compositions among these compatibilizers. In order to study the formation of these graft copolymers, the most efficient compatibilizer was allowed to react with PA6. Binary blend in a PP-*g*-MA-*co*-POP/PA6 = 5/30 composition was prepared by an extruder under the same processing conditions of ternary blend as listed in Table 2. With the addition of formic acid to binary
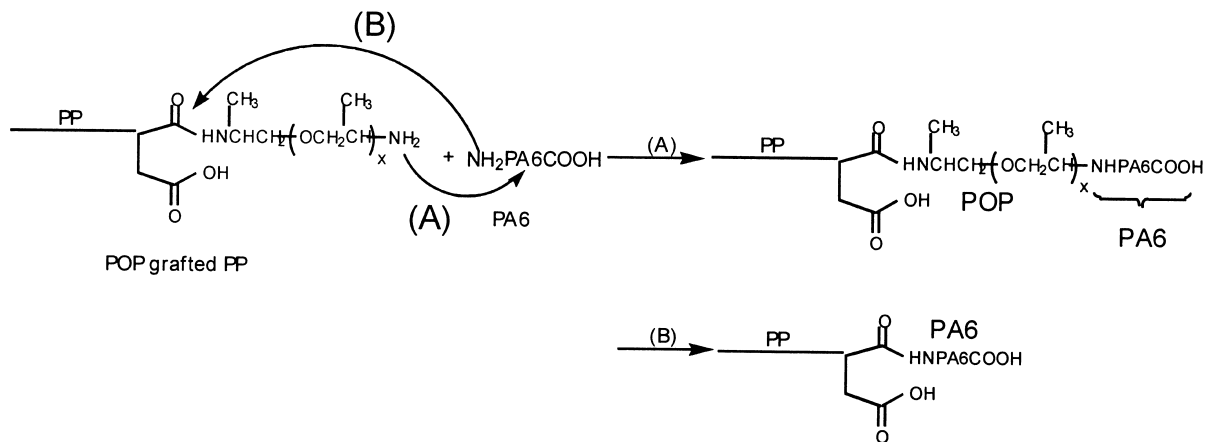
Scheme 2. Proposed reactions of POP-functionalized PPs with PA6.
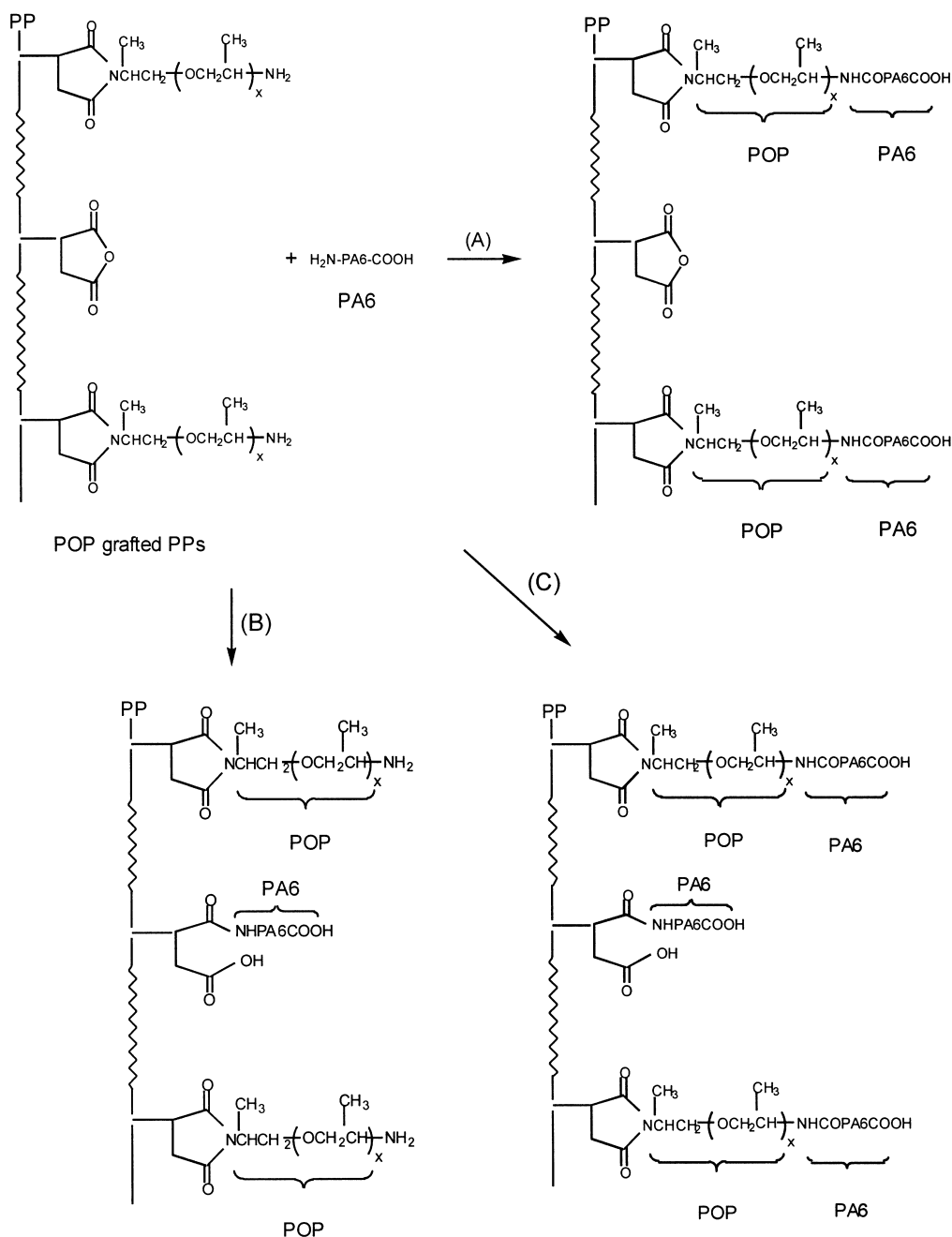
Scheme 3. Proposed reactions of POP-functionalized PPs with PA6.

uncompatibilized PP/PA6 blend, the PA6 was completely dissolved and PP was separated out as floating on the surface. But when formic acid was added to binary PP-*g*-MA-*co*-POP/PA6 blend, stable emulsion was obtained, indicating the existence of graft copolymers acting as interfacial agents [31]. However, when acetone was added, this stable emulsion was gradually divided into colloid solid and emulsion parts, which could be separated through filtration. The colloid residue was extracted again with formic acid. The same procedure was repeated five times to ensure complete

extraction. At the last extraction, the residue was floating up to the surface rapidly. The thermal properties of the extraction residue are shown in Figs. 8 and 9. In DSC cooling scan, the exothermal peaks for the extraction residue were at 184.9 and 118.7°C, which were assigned to PA6 and PP, respectively (Fig. 8). The T_c of the PA6 component in this copolymer is about 10°C lower than that of the neat PA6, indicating that the molten PP backbone is able to hinder or retard the PA6 crystallization. However, T_c of the PP component are higher than that of the virgin PP-*g*-MA
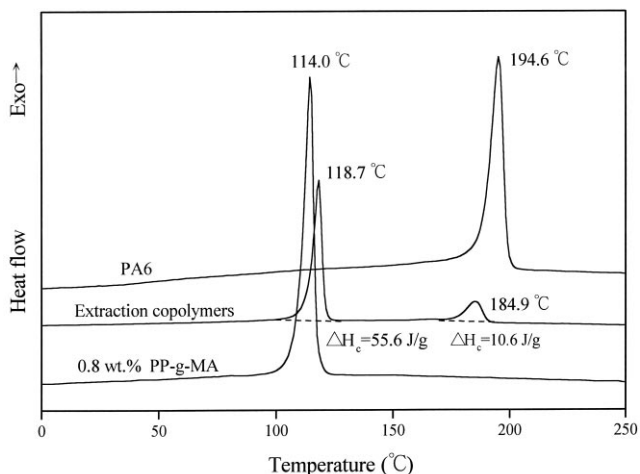
Fig. 8. DSC cooling scans of PA6, PP-*g*-MA and extraction copolymers.

(5°C), an indication of fast nucleation due to the crystalline PA6 as nucleating agent to promote PP crystallization. Moreover, the T_{ms} of the PA6 and PP component in the copolymer are also depressed relative to the starting materials, indicating the crystal imperfection, caused by the interference of both components with each other as shown in Fig. 9. It is evident from the DSC analysis that the PP-*g*-MA-*co*-POP compatibilizer actually reacted with PA6 to form mixed PP-*g*-MA-*co*-POP-PA6 and/or PP-*g*-MA-*co*-POP-*co*-PA6 and/or PP-*g*-MA-*co*-PA6 copolymers.

4. Conclusions

The in situ reaction of the commercially available POP diamine and PP-*g*-MA in an extruder yields the POP-functionalized PPs that is a more effective compatibilizer than the conventional PP-*g*-MA in compatibilizing PA6/PP blends. The compatibilizers, POP-functionalized PPs (PP-*g*-MA-*co*-POPs), are confirmed by the FTIR analysis. These
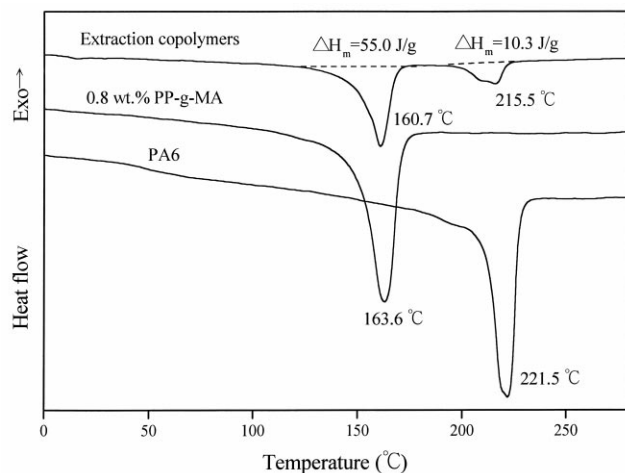
PP-*g*-MA-*co*-POP copolymers have different amphiphilic properties depending on the amine structure and the starting PP-*g*-MA. The cross-linked copolymers of PP-*g*-MA-*co*-POPs are formed with the uses of higher MA content in PP-*g*-MA. The blending morphologies, affected by the molecular weight of POP diamine in PP-*g*-MA-*co*-POP copolymer, show a decreasing size of the dispersed PA6 particles as the molecular weight of POP diamine increases from 230 to 400 to 2000. More regular and finer dispersion is observed upon the addition of the PP-*g*-MA-*co*-POP copolymer to the PA6/PP blends because of lower interfacial tension between these two phases. The presence of the PP-*g*-MA-*co*-PA6 and PP-*g*-MA-*co*-POP copolymers results in slow crystallization and low crystallinity of the PA6 component in compatibilized blends. Two factors, nucleating agent and compatibilizer, dictate the crystalline behavior of the PP component. The POP-grafted PPs is able to react with PA6 to form mixed PP-*g*-MA-*co*-POP-PA6, PP-*g*-MA-*co*-POP-*co*-PA6 and PP-*g*-MA-*co*-PA6 copolymers during melt blending that are confirmed by the solvent extraction. These copolymers function as effective compatibilizers through the formation of hydrogen bonding with the amide of the PA6. As a result, the mechanical properties in PA6/PP (30/70) blend have been significantly improved. The suitable molecular weight of the POP diamines in the range of 230–2000 is the key factor to act as an effective compatibilizer. Particularly, the POP amine at 2000 M_w in the PP-*g*-MA-*co*-POP copolymer results in the most efficient compatibilizer with respect to improving mechanical properties and morphologies.

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Fig. 9. DSC heating scans of PA6, PP-*g*-MA and extraction copolymers.

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