Phase Behaviors of Poly(oxyethylene)-Grafted Polypropylene Copolymers

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Abstract: A family of amphiphilic graft copolymers were prepared from a maleated polypropylene (PP-*g*-MA) and various crystalline poly(oxyethylene)-segmented amines of 1000 to 3000 molecular weight. Structurally, these copolymers consist of polypropylene (PP) backbone and several crystalline poly(oxyethylene) (POE) pendants in the structure. In the observation of their phase behaviors by using a differential scanning calorimeter (DSC), the interference between the POE segments and PP backbone was found. In a particular case (PP-*g*-MA/ED-2001), the heat of POE crystallization did not show off in the cooling curve of the DSC, but appeared during the consecutive heating process. Generally, heating and cooling patterns of the DSC analyses showed the shifts of melting and crystallizing temperatures, depending on the length and the termini of POE, from those of the starting materials– PP-*g*-MA and POE amines. The TGA and optical microscopy observation further supported the DSC analyses.

Keywords: Polypropylene-*g*-maleic anhydride, poly(oxyethylene), phase behavior, crystallinity.

Introduction

To functionalize the existing polymers into a new class of copolymers has been received a great deal of attention academically and industrially [1]. Particularly, the copolymer consisting of two chemically distinct blocks can exhibit amphiphilic properties and have versatile applications. Among many functional polymers, the polypropylene (PP) derivatives are particularly important mainly due to its availability. However, PP has the nature of non-polarity and low reactivity, which makes the chemical modification rather difficult. Commercially, the free radical grafting of maleic anhydride (MA) on hydrocarbons are known [2,3] to lead the maleated polypropylene, as well as the others such as MA-grafting polyethylene and styrene-(ethylene/butylene)-styrene (SEBS) [4-7]. Particularly, PP-*g*-MA is commonly used as compatibilizers for polymer blends [8,9] including PP/Nylon 6. In the blending process, it is known that the MA moieties in PP backbones are reacted with the terminal -NH_2 of Nylon 6 to form amphiphilic polymers *in situ* [10,11]. However, few studies are reported to derive PP-*g*-MA by using the amidation with poly (oxyethylene)- or poly(oxypropylene)-amines.

Recently, we employed a family of poly (oxyethylene)-block-poly(oxypropylene)amines (i.e., Jeffamine® amine) to prepare the POE-grafted PP copolymers. Composed of the hydrophilic POE-segments and the hydrophobic PP backbone, the amphiphilic copolymers was capable of dissipating electrostatics and suitable for using as permanent antistatics [12]. It was found that the introduction of the poly(oxyethylene) (POE) pendants rendered these PP copolymers with lower surface resistivity. The hydrophilicity and the weight fraction of POE segments are important contributing factors while the segmental crystallinity of the POE pendants adversely affect on lowering the resistivity. The crystalline increases the energy barrier for transferring electrostatics. This phenomenon was particular known in poly(ethylene glycol)/lithium salt complexes in which the electrostatics are conducted through the ionic hopping within the phase matrix [13,14].

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Methoxy poly(oxyethylene-oxypropylene)-2-propylamine

$$CH_3O(CH_2CH_2O)_a(CH_2CHO)_bCH_2CHNH_2$$
$$\qquad\qquad\qquad\quad |\qquad\quad |$$
$$\qquad\qquad\qquad\quad CH_3\qquad CH_3$$

Average a = 19, b = 3 (Approx. M_w = 1,000; Jeffamine® M-1000)
Average a = 32, b = 10 (Approx. M_w = 2,000; Jeffamine® M-2070)
Average a = 49, b = 8 (Approx. M_w = 3,000; Jeffamine® M-3000)

Poly(propylene glycol)-block-poly(ethylene glycol)-block-(propylene glycol) bis(2-aminopropyl ether)

$$H_2NCHCH_2(OCHCH_2)_a(OCH_2CH_2)_b(OCH_2CH)_cNH_2$$
$$\quad |\qquad\quad |\qquad\qquad\qquad\quad |$$
$$\quad CH_3\qquad CH_3\qquad\qquad\qquad CH_3$$

Average a + c = 5.0, b = 39.5 (Approx. M_w = 2,000; Jeffamine® ED-2001)

Figure 1. Chemical structures of poly(oxyalkylene)amines starting materials.

In this paper, we report the phase behaviors and the thermal properties of these amphiphilic copolymer, particularly the micro-structural interaction between the PP backbone and the grafted POE segments. The characteristics revealed by the DSC analyses were further correlated with the polymer textures observed by optical microscopy. The effect of sodium salts in complexing with POE on the crystallinity and thermal stability was also investigated.

Experimental

1. Materials

PP-*g*-MA (maleic anhydride grafted polypropylene, trade name: Epolene E-43 or MPP-9100) was obtained from Eastman. The sample had a titrated acid number of 47 mg KOH/g and average molecular weight of M_w 9,100 and M_n 3,900 by GPC. It was calculated to have a maleic anhydride (MA) content of 4 w% or averaged 3.7 MA units per polymer strain. A series of poly(oxyalkylene)amines, namely Jeffamine® Amines [15,16], was purchased from Huntsman Chemical Co. or Aldrich Chemical Co. They included methoxy-poly(oxyethylene-oxypropylene)-2-propylamines 1,000, 2,000, and 3,000 M_w. These monoamine structures are block ethylene oxide (EO) and propylene oxide (PO) copolymers with averaged unit EO/PO of 19/3 for Jeffamine® M-1000, 32/10 for M-2070, 49/8 for M-3000. The difunctional amine is water-soluble poly(propylene glycol)-block-poly(ethylene glycol)-block-(propylene glycol)bis(2-aminopropyl ether) of average M_w at 2,000 (ED-2001). It contains approximately 39/5 unit ratio of oxyethylene/oxypropylene per mole. The chemical structures of these poly(oxyethylene)-based amines are drawn in Figure 1.

Table I. Chemical compositions of poly(oxyalkylene)-grafted polypropylene.

Modified PP	Molar Ratio	Weight % of poly(oxyalkylene)amine
PP-*g*-MA	–	–
PP-*g*-MA/Na^+	–	–
PP-*g*-MA/M-2070/Na^+	1 / 1	46
PP-*g*-MA/M-1000	1 / 1	30
PP-*g*-MA/M-2070	1 / 1	46
PP-*g*-MA/M-3000	1 / 1	55
PP-*g*-MA/ED-2001	2 / 1	29
PP-*g*-MA/ED-2001	1 / 1	45

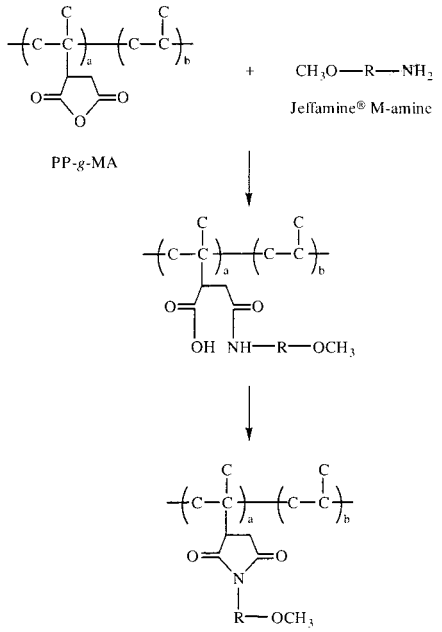
PP-*g*-MA : Maleic Anhydride-grafted Polypropylene (4 wt% MA), M_w = ~ 9,100.
M-1000 : methoxy-poly(oxyethylene-oxypropylene)-2-propylamine at ~1,000 M_w.
M-2070 : methoxy-poly(oxyethylene-oxypropylene)-2-propylamine at ~2,000 M_w.
M-3000 : methoxy-poly(oxyethylene-oxypropylene)-2-propylamine at ~3,000 M_w.
ED-2001 : poly(propylene glycol)-block-poly(ethylene glycol)-block-(propylene glycol)bis(2-aminopropyl ether) at ~2,000 M_w.
Na^+: Product was treated with aqueous sodium hydroxide and dried.

2. Preparation of poly(oxyalkylene)-grafted polypropylene

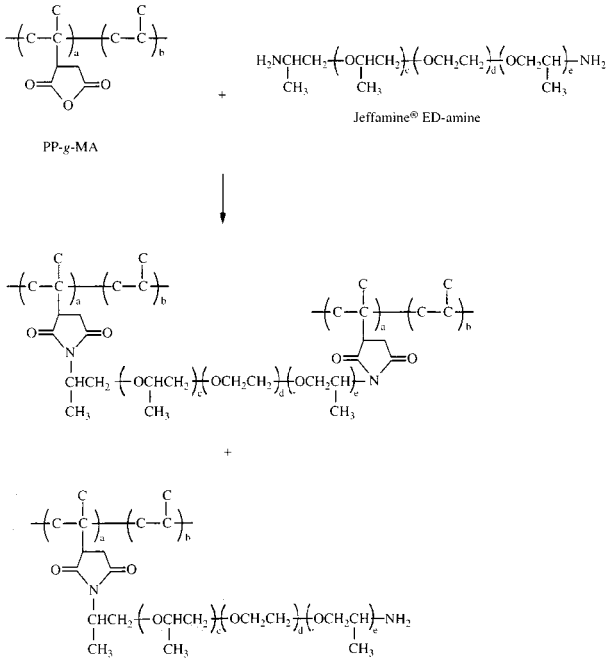
The experimental procedures for preparing poly (oxyalkylene)-grafted polypropylene were reported previously [12]. One example is cited here.

PP-*g*-MA and poly(oxyethylene-oxypropylene) monoamine adduct at 1/1 molar ratio: To a 250 mL three-necked round-bottomed flask, equipped with a mechanical stirrer, nitrogen inlet-outlet lines, thermometer, and Dean-Stark trap, were placed with maleated polypropylene MPP-9100 (48 g, 19.5 mmol of MA) and toluene (100 mL). While the mixture being heated, stirred and dissolved at 90~100 °C, methoxy-poly(oxyethylene-oxypropylene)-2-propylamine of 2,000 M_w (i.e., Jeffamine® M-2070, 40 g, 19.5 mmol) was added in one portion. The reactant temperature was raised to 120 °C and maintained for 2~3 h. During the process, most of toluene solvent was removed through a Dean-Stark trap. Without cooling, the crude product was poured quickly into a large quantity of deionized water while being stirred. The product, quenched by water at ambient temperature appeared to be solid and floated on the top of water layer. The solid material was repeatedly extracted by water, collected and ground. Being dried at ca. 80 °C under vacuum, the solid material was recovered as pale-yellow powder. The FT-IR (in KBr) showed the following characteristic absorptions: 1734 cm^{-1} (vs, imide), 1645 cm^{-1} (w, amide), 1107 cm^{-1} (vs, C–O–C of polyoxyalkylene), and 3460 cm^{-1} (s, OH).

The chemical compositions of these copolymers are calculated summarized in Table I for comparison. The possible reaction pathways and product structures are illustrated in Scheme 1 and 2.



Scheme 1. Amidation and imidation of poly(oxyalkylene)monoamines on PP-*g*-MA.



Scheme 2. Poly(oxyethylene)-based diamine cross-linked amphiphilic PP.

3. Characterization

FTIR spectra were measured on a Perkin Elmer Paragon 500 FT-IR Spectrometer. Gel permeation chromatography (GPC) analyses were performed in a HP 1090M HPLC using THF as eluent, calibrated by polystyrene standards. Optical micrographs were obtained with an Olympus BH2-UMA microscope. The samples were prepared by melt pressing between two glasses at 200 °C, then cooling to room temperature. Differential scanning calorimeter (DSC) measurements and thermogravimetric analysis (TGA) were performed on a Seiko SII model SSC/5200 from Seiko Instruments and Electronics Ltd. The size of the DSC samples was approximately 5 to 8 mg on sealed aluminum pan. The analyses were performed under a heating or cooling rate of 10 °C/min in 40 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 temperatures were reported as melting point (T_m) and crystallization temperature (T_c) during heating and cooling runs, respectively. Each specimen was heated to 200 °C at a rate of 20 °C/min and held for 5 min to remove the residue thermal influence. Different cooling or heating conditions were specified otherwise. TGA was measured from 30 to 500 °C under a heating rate of 10 °C/min and air flow of 100 mL/min.

Results and Discussion

1. Phase behaviors

1.1 Phase behaviors of poly(oxyalkylene)monoamine modified PPs

The thermal properties of starting materials including poly(oxyethylene-oxypropylene) monoamines, -diamine and PP-*g*-MA were measured by a DSC and listed in Table II. The PP-*g*-MA (MPP-9100) had melting temperatures (T_m) at 146.7 and 154.8 °C, and crystallization temperature (T_c) at 109.1 °C (Figures 2 and 3). It appears that the PP-*g*-MA has two endotherms due to its different crystalline structures, similar to that reported for PP [17]. The FT-IR indicated that the PP-*g*-MA is existed in the forms of anhydride (1852 and 1779 cm^{-1}) and free acid (1710 cm^{-1}), which perhaps caused by the hydrolysis. In the family of Jeffamine® amine starting materials, different EO/PO ratios and lengths constitute the polyetheramines. M-2070 has a relatively low oxyethylene composition or EO/PO (32/10) ratio. This reflects its least crystallinity, with the melting point below room temperature (-2.2 °C). In contrast, ED-2001 has a relatively high melting temperature and enthalpy. The first cooling

Table II. Thermal properties of starting materials poly-(oxyethylene-oxypropylene)amines.

	PP-*g*-MA	Jeffamine			
		M-1000	M-2070	M-3000	ED-2001
Apprix. M_w	9,100	1,000	2,000	3,000	2,000
EO/PO (per mole)	–	19/3	32/10	49/8	39/5
Termini	–	$-OCH_3$ $-NH_2$	$-OCH_3$ $-NH_2$	$-OCH_3$ $-NH_2$	$-NH_2$
T_m (°C)[a]	146.7	30.5 154.8	-2.2	30.9	37.3
ΔH_m (J/g)[a]	70.9	136	51.2	98.9	121.8
T_c (°C)[a]	109.1	2.21 4.92	-35.7	1.45	13.4
ΔH_c (J/g)[a]	-79.3	-131.3	-49.9	-89.2	-121.1

(a) Melting point (T_m), crystalline point (T_c), heat of melting (ΔH_m), and heat of crystalline (ΔH_c) were measured by DSC.

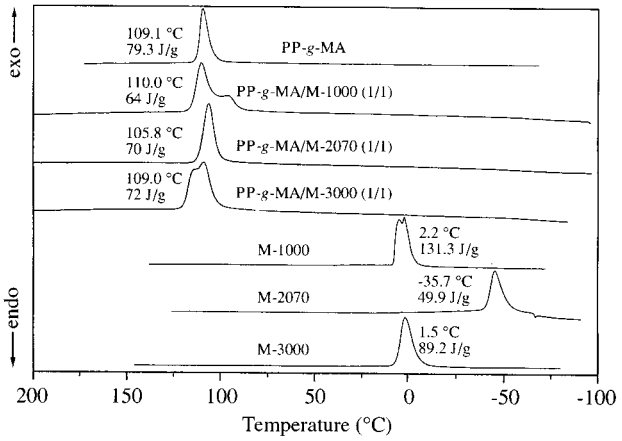


Figure 2. DSC cooling scans of PP-*g*-MA, poly(oxyalkylene) monoamine and poly(oxyalkylene)monoamine modified PPs.

and second DSC scans of poly(oxyalkylene)monoamines modified PP (PP-*g*-MA/M-1000, PP-*g*-MA/M-2070, and PP-*g*-MA/M-3000 at 1/1 molar ratio) are shown in Figures 2 and 3. Since the copolymer is constituted of two distinct types of polypropylene (PP) and polyoxyethylene (POE) blocks, usually more than one crystalline phase is expected. In Figure 2, the T_c of PP backbone is observed, while the T_c with respect to POE segments of poly (oxyalkylene)monoamine in these modified copolymers is not observed. It appears that the POE segments are restricted to self-aligning into crystalline around the PP crystalline domain. The T_m with correspondent to PP in Figure 3 are further confirmed this result. Moreover, the ΔH_m of PP backbone seems to increase by taking account of weight content of PP in these structures, implying the inference of the POE pendants as nuclear agents (Table III).

Table III. Thermal properties of PP-*g*-MA/poly(oxyalkylene) amine adducts.

Modified PP	Molar Ratio	$\Delta H_{m/pp}$	$\Delta H_{m/pp}$ (wt%)	$\Delta H_{m/amine}$	$\Delta H_{m/amine}$ (wt%)
PP-*g*-MA	–	70.9	–	–	–
PP-*g*-MA/Na^+	–	43	–	–	–
PP-*g*-MA/M-2070/Na^+	1/1	32.8	60.74	10.4	22.61
PP-*g*-MA/M-3000/Na^+	1/1	58.7	130.44	4.3	7.82
PP-*g*-MA/M-1000	1/1	55.9	79.86	–	–
PP-*g*-MA/M-2070	1/1	60.4	111.85	–	–
PP-*g*-MA/M-3000	1/1	61.7	137.11	–	–
PP-*g*-MA/ED-2001	1/1	44.5	62.68	21.8	75.17
PP-*g*-MA/ED-2001	2/1	49.6	90.18	10.3	22.88

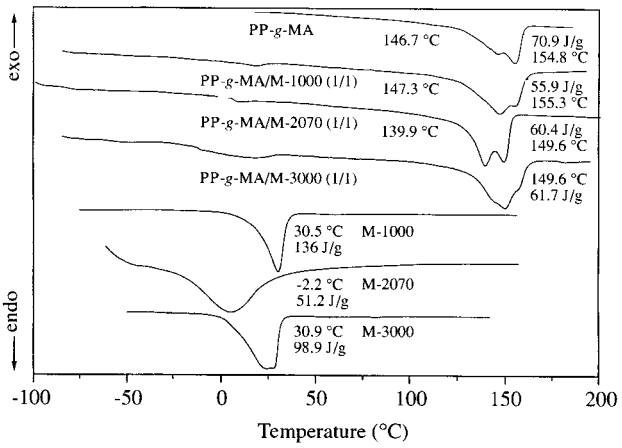


Figure 3. DSC heating scans of PP-*g*-MA, poly(oxyalkylene) monoamine and poly(oxyalkylene)monoamine modified PPs.

1.2 Phase behaviors of poly(oxyalkylene)diamine modified PPs

The use of the ED-2001 diamine had rendered the copolymers with a slightly cross-linking. The relative degree of cross-linking for poly(oxyalkylene) diamine modified PPs could be observed by the solvent test. The PP-*g*-MA/ED-2001 copolymer (1/1 molar adduct) was soluble in hot toluene, however, the PP-*g*-MA/ED-2001 copolymer (2/1 molar adduct) was an insoluble but swelling at this condition. In DSC cooling scans, the exothermal peaks for the PP-*g*-MA/ED-2001 at 1/1 molar ratio were at 105.1 and -19.4 °C, which were assigned to PP and ED-2001 respectively (Figure 4). In the case of the PP-*g*-MA/ED-2001 at 2/1 molar ratio, no crystallization peak was detected for the ED-2001 segments as measuring at a cooling rate of 10 °C/min (Figure 4). However, the crystallization exotherm and melting endotherm of the POE segment were observed at

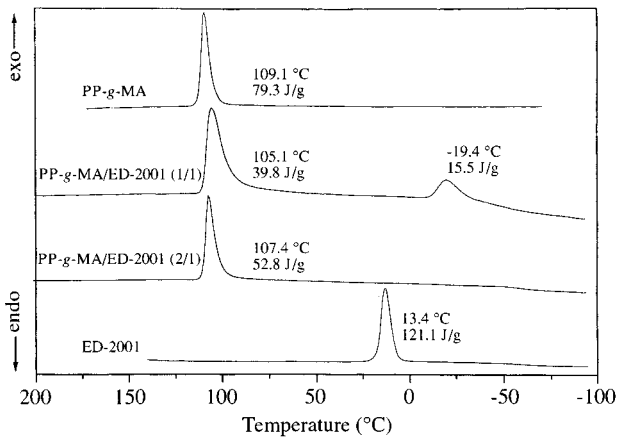


Figure 4. DSC cooling scans of PP-*g*-MA and poly(oxyalkylene) diamine of 2,000 M_w modified PPs.

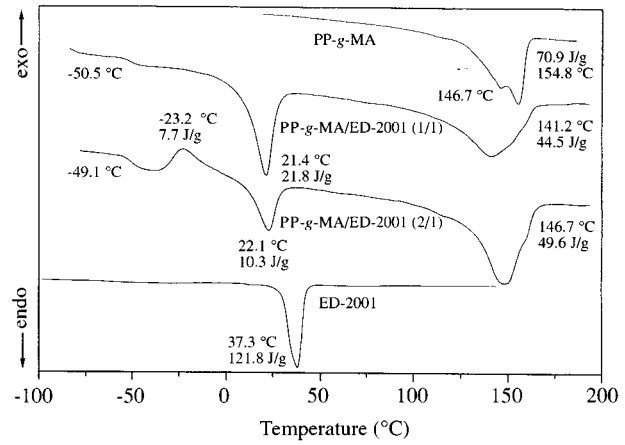


Figure 5. DSC heating scans of PP-*g*-MA and poly(oxyalkylene) diamine of 2,000 M_w modified PPs.

-23.2 and 22.1 °C, respectively (Figure 5). The T_{gs} of POE segments were not obvious, except observed a heat capacity jump around -50 °C for PP-*g*-MA/ED-2001 in Figure 5. During heating, the molecular motions relief the temporally molecular restrictions and cause the crystallization of POE segment. The temporally molecular restriction was avoided by using a very slow cooling rate (1 °C/min in Figure 6(a)), by that, the POE crystallization peak was observed. This means that crystallization of ED-2001 in the PP-*g*-MA/ED-2001 at 2/1 molar ratio was slow due to more crosslinked structures in this sample. This phenomenon occurred in PP-*g*-MA/ED-2001, but not in all cases.

1.3 Sodium effect

The addition of sodium ion gave rise to metal complexation with succinic acid and/or with POE segments. It is clearly observed that thermal natures of the PP-*g*-MA have been altered. An addi-

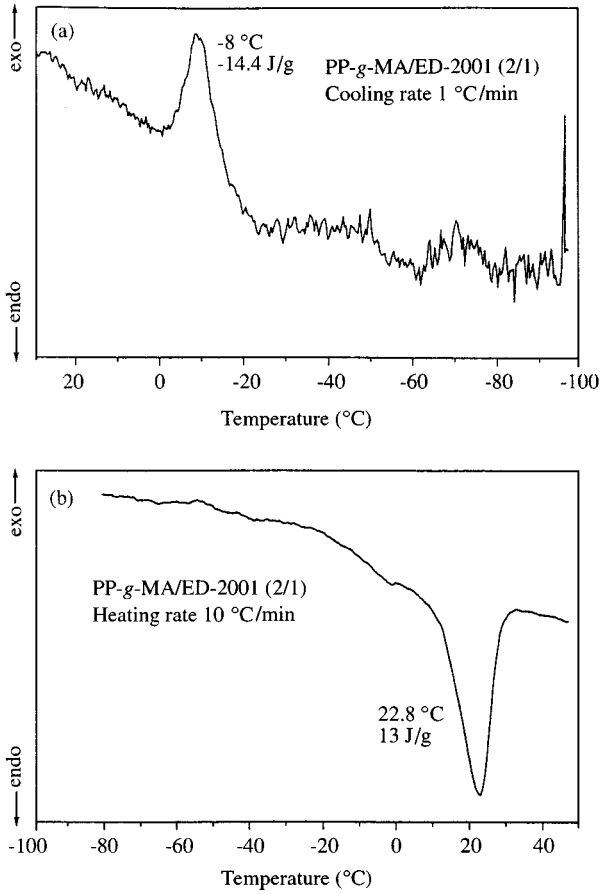


Figure 6. DSC thermograms of poly(oxyalkylene)diamine of 2,000 M_w modified PPs: (a) cooling scans at 1 °C/min.; (b) heating scans at 10 °C/min.

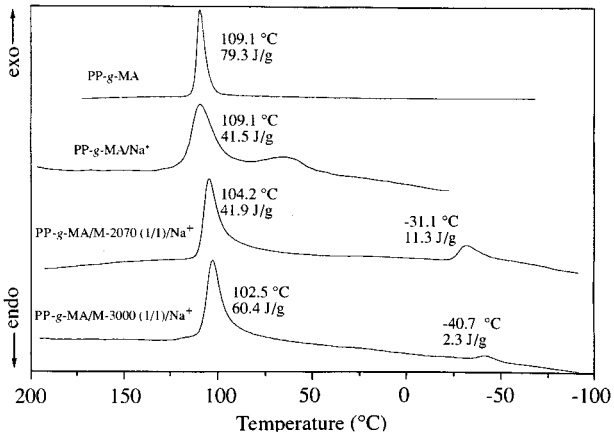


Figure 7. DSC cooling scans of PP-*g*-MA and PP-*g*-MA/Na^+ poly(oxyalkylene) monoamine modified PPs containing sodium ion.

tional crystalline peak at 66.5 °C is detected for PP-*g*-MA/Na^+ (Figure 7), in addition, the melting enthalpy and melting temperature are also lower than the neat PP-*g*-MA (Figure 8). It means that the

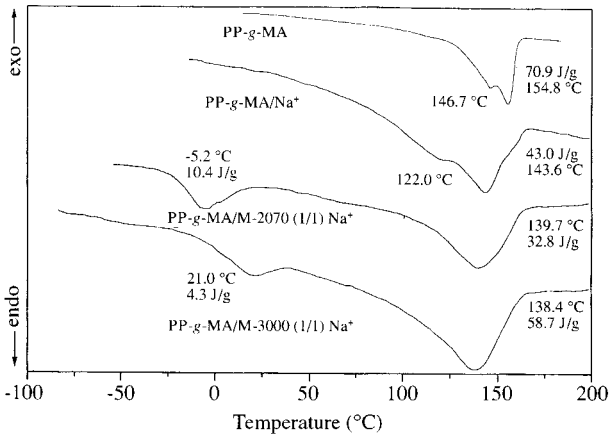


Figure 8. DSC heating scans of PP-*g*-MA and PP-*g*-MA/Na^+ poly (oxyalkylene) monoamine modified PPs containing sodium ion.

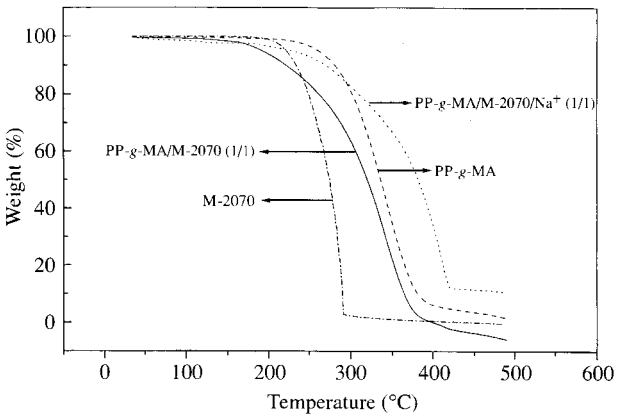


Figure 9. Weight loss curves of PP-*g*-MA, M-2070 and PP-*g*-MA/M-2070 adducts.

mobility of PP backbones is restrained due to the additional ionic bonding from sodium ion.

Poly(oxyalkylene)monoamine-modified PP such as PP-*g*-MA/M-2070 adduct (1/1 molar ratio) is constituted by amide or imide linkages and POE segments which can complex with sodium ions. The DSC cooling and heating scans for sodium-containing poly(oxyalkylene)monoamine modified PPs are shown in Figures 7 and 8. Besides the PP crystalline, it is observed a second peak due to the POE segments in these thermograms. It was known that the additions of metal ion into polyethylene glycol (PEG) was generally increased glass transition temperature, melt viscosities, thermal stability and reduced the melting enthalpy due to the complexation between metal ion and POE segments [18]. However, the metal ion interaction was occurred in the pure form of PEG. In our PP-*g*-MA/poly(oxyethylene)amine copolymer, it can be visualized the presence of a strong ionic interaction between the POE ether oxygen and sodium ion. As a result, the POE aggregation or crystallization was promoted among the PP crystal domains. However, the tendency of such crystallization is still lowered than the starting material as shown by a lower ΔH_m. On the other hand, these POE interactions will decrease the mobility of PP. As the consequence, sodium ions in poly (oxyalkylene)monoamine-modified PPs lowered T_c and ΔH_m for PP components (Figures 2 and 3 *vs.* Figure 7 and 8). Moreover, the melting ranges of PP crystals seem to become broader, implying the presence of different crystal sizes.

2. Thermal stability of poly(oxyalkylene) monoamine modified PPs

The thermal stability of poly(oxyalkylene) monoamine modified PP was evaluated by thermogravimetric analysis (TGA) under air. The TGA thermograms are shown in Figure 9. It was found that the PP-*g*-MA starting material exhibited higher initial decomposition temperature and slower thermal decomposition rate than the Jeffamine® M-2070 amine. The poly(oxyalkylene)monoamine modified PP such as PP-*g*-MA/M-2070 adduct (1/1 molar ratio) showed a stability level between PP-*g*-MA and Jeffamine® M-2070 amine. However, when addition of sodium ion, the initial decomposition temperature and maximum decomposition temperature of the modified PP shifted toward higher temperature. As mentioned, the addition of sodium ion gave rise to the metal complexation with amide or imide linkages and POE segments, which may stabilize the modified PP through the chemical effect. The comparisons of the thermal stability among these copolymers are represented by Figure 9.

3. Crystalline textures of PP-*g*-MA/poly(oxyalkylene)amine

The textures of PP-*g*-MA and the POE-grafting PP-*g*-MA copolymer were investigated by using a polarized optical microscopy. Examples are shown in Figure 10. The crystalline Maltese cross is discernible in all samples, indication the spherulitic crystallization. As shown by DSC analyses, only the PP backbone in these copolymers can be crystallized in the presence of POE segments. Under the same scale, the crystal particles of the PP-*g*-MA/M-2070 (1/1) copolymer were observed to be denser and smaller than PP-*g*-MA, implying the POE pendants may behave as nuclear agents. As a result, the numbers of PP crystalline nuclei increased during the process of crystallization. On the contrary, the crystal particles of PP-*g*-MA/ED-2001 at 2/1 molar ratio are larger but less numbers caused by the crosslinked structures. These results are consistent with the DSC analyses.

(a) PP-*g*-MA

(b) PP-*g*-MA/M-2070 (1/1 molar ratio)

(c) PP-*g*-MA/ED-2001 (2/1 molar ratio)

Figure 10. Optical micrographs (x500) taken with polarized light: (a) PP-g-MA, (b) PP-*g*-MA/M-2070 (1/1 molar ratio) and (c) PP-*g*-MA/ED-2001 (2/1 molar ratio).

Conclusion

The POE-grafted PP copolymers were prepared from the maleated polypropylene and various crystalline block poly(oxyethylene)amines. The DSC demonstrated the interference of these pendant POE segments with PP backbone in crystallization. The POE segments in comb-like copolymer can behave as nuclear agents to promote the PP crystallization, but themselves been restricted. The attachment of the incorporated sodium ion, to the ether oxygen of POE segments enhanced the POE segmental aggregation but reducing the mobility of PP backbone. In a particular case, the disappearance of poly (oxyethylene) (POE) portion, was dormant in crystallization but observable during consecutive heating or using a lower cooling scan rate. The phase behaviors were also depended on the crosslinked structures, as demonstrated by the copolymers of PP-*g*-MA/POE at 1/1 and 2/1 molar ratio. The TGA analysis showed the high thermal stability of the modified PP due to the presence of the Na^+ ionic complexation. The nucleation effect of POE segments on the PP backbones were confirmed and revealed by a microscopy.

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