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Preparation and electrostatic dissipating properties of poly(oxyalkylene)imide grafted polypropylene copolymers

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Abstract

A series of poly(oxyalkylene)imide grafted polypropylenes were prepared from the reaction of maleated polypropylenes and various amines. The amines included crystalline and non-crystalline block poly(oxyethylene–oxypropylene)amines of average molecular weight (M_w) from 1000 to 8000. The reactions afforded comb-like copolymers consisting of a polypropylene backbone, poly(oxyalkylene) pendants and imide linkages. Their electrostatic dissipating properties, probed by measuring surface resistivity, were correlated with the chemical functionalities. Increasing the weight amount or the decreasing crystallinity of the poly(oxyethylene) pendants lowered the polymer surface resistivity significantly from 10^{12} to $10^{6.9}$ $\Omega/\square$. In comparing the structural effect, the polypropylenes modified by low M_w of amines such as 2-aminoethanol, 1,2-ethylenediamine, *N*,*N*-dimethylaminopropylamine and their derivatives were also prepared. Factors including hydrophilicity, the presence of amine functionality or sodium ion in the structure also affected the copolymer electrostatic dissipating ability. A mechanism involving hydrogen bonding with moisture was proposed. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polypropylene; Poly(oxyethylene); Surface resistivity

1. Introduction

To introduce functional groups into polymer backbones generally produces new classes of polymers with different properties and applications [1,2]. Among many commodity polymers, polypropylene (PP) is one of the most inexpensive and widely used materials. However, due to its non-polar nature, PP has inherently poor properties in hydrophilicity, dyeability, etc. Therefore, to modify PP into a value-added product is an important subject industrially and academically. In the past, techniques for converting non-polar polymers through a free radical grafting of maleic anhydride (MA) [3,4] were commercially developed. Further, modifications involving PP-g-MA, SEBS-g-MA and SMA are well documented in Refs. [5–8]. For practical applications, PP-g-MA is commonly used for compatibilizing polymer blends [9–12] including PP/Nylon 6. In the blending process, the MA moieties in PP backbones in situ react with the terminal $-NH_2$ of Nylon 6 to form copolymers consisting of PP and polyamide blocks. The amphiphilic polymer behaves as an organic surfactant which reduces the interfacial tension between two immiscible polymer phases. As a result, a fine microstructure of the polymer blend is obtained and mechanical properties are improved. PP-g-MA was also used to intercalate polar inorganic clays in homogeneously mixing with PPs in nanoscale [13,14]. Through these modifications, the usage of PP has been widened.

Recent advances in the electronics industry require new polymer materials for many different applications [15–18] including ion conducting polymers for solid electrolytes. In literature, there are examples regarding electrostatic dissipating polymers for use in housing, packaging and encapsulation for electronic devices [19–22]. The preparation and the working principle of polymeric antistatic materials were often disclosed in patents [20–22]. For example, a transparent polyether–ester–amide, prepared from the polymerization of polyethylene glycol (PEG), and aminocarboxylic acid, was suggested for such an application [22]. Similarly, the PEG segmented poly-ε-caprolactam was also synthesized [21]. Both examples involved the incorporation of poly(oxyethyene) (POE) segments in the polymers. Recently, we reported the synthesis of modified polyamides through the introduction of hydrophilic poly(oxyethylene)amide segments into hydrophobic polyamide backbones [23]. These amphiphilic

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materials are capable of dissipating electrostatics and potentially useful as antistatic agents, which can be added to commercial plastics to reduce the tendency of accumulating electrostatics. From the viewpoint of structural compatibility, the POE segmented polyamides may be suitable for blending with polyesters and polyamides, but not necessarily being compatible with non-polar PPs or the polymers alike. In order to prepare PP compatible materials, the approach of grafting POE onto MA-g-PP is considered.

In this article, the synthesis of poly(oxyethylene)imide modified polypropylenes and their working principle for electrostatic dissipating are reported. By adopting PP-g-MA as reactive intermediates, copolymers consisting of PP backbone, grafted poly(oxyethylene)/poly(oxypropylene) pendants, and possible quaternary amine or sodium salts were broadly prepared. The preparation involved the uses of a family of crystalline POE and amorphous poly(oxypropylene) (POP) amines. The electrostatic dissipating ability is probed by measuring surface resistivity and correlating to the chemical structures. The purpose is to understand the working principles for electrostatic dissipating polymers and to ultimately tailor a suitable antistatic agent for PP.

2. Experimental

2.1. Materials

The maleated PP (abbrev. PP-g-MA, trade name: Epolene E-43 or MPP-9100) was purchased from Eastman and used without further purification. A titrated acid number of 47 mg KOH/g and average molecular weight of M_w 9100 and M_n 3900 by gel permeation chromatography were recorded. It was calculated to have a MA content of 4 wt.% MA or averaged 3.7 MA units per polymer strain. A low MA content (0.8 wt.%) of PP-g-MA, trade name Polybond® 3150, was obtained from Uniroyal Chemical Co. 2-Aminoethanol (AE), 2-(2-aminoethoxy)ethanol (AEE), 1,2-ethylenediamine (EDA), and *N*,*N*-dimethylaminopropylamine (DAP) were purchased from Aldrich Chemical Co. A series of poly(oxyalkylene)amines were purchased from Aldrich Chemical Co. or Huntsman Chemical Co. They included methoxy-poly(oxyethylene–oxypropylene)-2-propylamines with M_w 1000, 2000 and 3000. These monoamine structures are block ethylene oxide and propylene oxide copolymers with averaged unit EO/PO of 19/3 for Jeffamine® M-1000, 32/10 for M-2070 and 49/8 for M-3000. The difunctional amines include water-insoluble poly(propylene glycol) bis(2-aminopropyl ether) of M_w 2000 (D-2000) and water-soluble poly(propylene glycol)-*block*-poly(ethylene glycol)-*block*-poly(propylene glycol)-bis(2-aminopropyl ether) of average M_w of 2000 and 6000 (ED-2001 and ED-6000). They contain 39/5 and 138/4 units ratios of oxyethylene oxypropylene per mole for ED-2001 and ED-6000, respectively.

2.2. Characterization

FT-IR absorption was recorded by using a Perkin–Elmer Paragon 500 FTIR Spectrometer. Differential scanning calorimeter (DSC) and thermal gravimetric analysis (TGA) were performed on a Seiko SII model SSC/5200. A heating or cooling rate of 10°C/min under nitrogen atmosphere was used for DSC. TGA was measured by heating the samples from 30 to 500°C in air and nitrogen. Gel permeation chromatography (GPC) analyses were performed in a HP 1090M HPLC using THF as eluent, calibrated by polystyrene standards. Surface resistivity was measured by a ST-3 model (Simco Co.) tester, according to the ASTM method D257-93. All samples were conditioned in an atmosphere of 50% relative humidity at room temperature. The measurement of surface resistivity is in the unit of $\Omega/\square$ in which the size of the square is immaterial.

2.3. Preparation of poly(oxyethylene)amide or imide grafted polypropylenes

The representative examples of typical experimental procedures for preparing poly(oxyalkylene) grafted polypropylenes are described below:

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, a thermometer, and a Dean–Stark trap, maleated PP MPP-9100 (48 g, 19.5 mmol of MA) and toluene (100 ml) were placed. While the mixture being heated, stirred and dissolved at 90–100°C, methoxy-poly(oxyethylene–oxypropylene)-2-propylamine of M_w 2000 (i.e. M-2070; 40 g, 19.5 mmol) was added in one portion. The reaction temperature was raised to 120°C and maintained for 2–3 h. During the process, toluene solvent was distilled and removed through Dean–Stark trap. Without cooling, the crude product was poured quickly into a large quantity of deionized water while being vigorously stirred. The product after being quenched by water at ambient temperature appeared as a solid floating on the top of water layer. The solid material was repeatedly extracted by water, collected and grounded. Being dried at 80°C under vacuum, the solid material was recovered as a pale-yellow powder. The analysis by differential scanning calorimeter (DSC) showed a glass transition temperature (T_g) at 5.3°C and a melting point (T_m) at 150°C. The FT-IR (in KBr) showed the characteristic absorption at 1107 cm^{-1} (vs, C–O–C of polyoxyalkylene), 1734 cm^{-1} (vs, imide), 1645 cm^{-1} (w, amide), and 3460 cm^{-1} (s, OH). The powder product was mechanically pressed at high temperature into a sample plaque. The surface resistivity was measured to be $10^{9.6}$ $\Omega/\square$.

PP-g-MA and poly(oxyethylene–oxypropylene)diamine adduct at 1:1 molar ratio: Following the procedures described above, PP-g-MA (37 g, ~15 mmol of MA) in toluene at 120°C was added with poly(propylene glycol)-*block*-poly(ethylene glycol)-*block*-poly(propylene glycol)-bis(2-aminopropyl ether) of M_w 2000 (i.e. ED-2001; 30 g, ~15 mmol). During the process of heating to 120°C, the mixture became a gelatinous material precipitated out from toluene solvent. In another run, the maleated PP (11 g, ~4.5 mmol of MA) in toluene (100 ml) at room temperature was added with ED-2001 (9.0 g, ~4.5 mmol) at ambient temperature. The mixtures were heated slowly and PP-g-MA was gradually dissolved in the presence of the diamine during the process. The homogeneous mixtures were maintained at 110°C without any gel formation. On continuously heating at 120°C to remove toluene, the product became a pale-yellow rubber-like solid. The DSC showed a T_g at -50.5°C and T_m at 21.4 and 141.2°C. The FT-IR (in KBr) showed the characteristic absorption at 1093 cm^{-1} (C–O–C of polyoxyalkylene), 1685 and 1611 cm^{-1} (NHCO– of amide). The surface resistivity was measured to be $10^{6.9}$ Ω/□.

PP-g-MA and poly(oxyalkylene)-monoamine adduct at 1:1 molar ratio in the form of sodium ion. With similar experimental procedures, maleated PP (48 g, 19.5 mmol of MA) and toluene (100 ml) was heated and dissolved at 90–100°C and followed by the addition of methoxy-poly-(oxyethylene–oxypropylene)-2-propylamine of M_w 2000 (i.e. M-2070; 40 g, 19.3 mmol) in one portion. The reactants were further maintained at 120°C for 2–3 h. During the process, toluene solvent was removed. The crude product was poured into a large quantity of 8 wt.% sodium hydroxide in deionized water while vigorously stirring. The solid product was collected and washed by deionized water three times. Being dried at 80°C under vacuum, the solid material was recovered as a pale-yellow powder. The FT-IR (in KBr) showed the characteristic absorption at 1590 cm^{-1} (Na^+ form of carboxylate). The reading of surface resistivity was $10^{8.2}$ Ω/□.

PP-g-MA and poly(oxyethylene–oxypropylene)monoamine/DAP adduct at 2:1:1 molar ratio: With similar experimental procedures, maleated PP (49 g, ~20 mmol of MA) and toluene (100 ml), M-2070 monoamine (21 g, ~10 mmol) and *N*,*N*-dimethylaminopropylamine (i.e. DAP; 1.02 g, ~10 mmol) were added into the reactor in that order. After being heated at 110–140°C for 2–3 h, the crude mixtures were poured into deionized water at room temperature. After the extraction procedures, the powder product was pressed into a flat plaque under pressure and heat. A reading of $10^{9.1}$ Ω/□ was recorded.

PP-g-MA and 1,2-ethylenediamine adduct at 1:8 molar ratio: With similar experimental procedures, the mixtures of maleated PP (49 g, 20 mmol of MA) and toluene (100 ml) were dissolved at 120–130°C, then excess amount of 1,2-ethylenediamine (EDA) (9.6 g, 160 mmol) was added in one portion. The reactants were further maintained at 130°C for 2–3 h. The product mixtures were poured into deionized water at room temperature and worked up according to the above procedures. FT-IR (in KBr) showed the following characteristic absorption: 1646 cm^{-1} (s, NHCO– of amide), 1562 cm^{-1} (vs, NHCO– of amide), 1700 cm^{-1} (COOH), and 3417 cm^{-1} (OH) were observed. The surface resistivity was $10^{10.4}$ Ω/□.

Following these procedures, various molar ratios of amine/PP-g-MA adducts were prepared and their surface resistivities were measured and listed in Tables 1–4. The surface resistivtities of certain starting amine comonomers were indicated in Table 5.

Table 1
Surface resistivity of poly(oxyethylene)-grafted polypropylene (abbreviations: PP, polypropylene; PP-g-MA^2, maleic anhydride-grafted polypropylene (4 wt.% MA), $M_w = \sim 9100$; PP-g-MA^1, maleic anhydride-grafted polypropylene (0.8 wt.% MA); M-2070, methoxy-poly(oxyethylene-oxypropylene)-2-propylamine at M_w ~2000; DAP, *N*,*N*-dimethylaminopropylamine $\mathrm{H_2NCH_2CH_2CH_2N(CH_3)_2}$; M-1000, methoxy-poly(oxyethylene-oxypropylene)-2-propylamine at M_w ~1000; M-3000, methoxy-poly(oxyethylene-oxypropylene)-2-propylamine at M_w ~3000)

Modified PP	Molar ratio	Weight fraction[a] (%)	Surface resistivity (10^x Ω/□)
PP	–	–	>12
PP-g-MA^2	–	–	>12
PP-g-MA^1/M-2070	1:1	14	11.1
PP-g-MA^2/M-2070	3:1	23	10.4
PP-g-MA^2/M-2070	2:1	30	10.4
PP-g-MA^2/M-2070	1:07	38	9.1
PP-g-MA^2/M-2070	1:1	46	9.6
PP-g-MA^2/M-2070/DAP	3:1:2	21:2.1	10.1
PP-g-MA^2/M-2070/DAP	2:1:1	29:1.4	9.1
PP-g-MA^2/M-2070/DAP (no water washed)	2:1:1	29:1.4	7.9
PP-g-MA^2/M-1000	1:1	30	9.5
PP-g-MA^2/M-3000	2.8:1	30	9.6
PP-g-MA^2/M-3000	2:1	38	8.7
PP-g-MA^2/M-3000	1:1	55	7.5

[a] Weight fraction (%): amine/(PP-g-MA + amine).

Table 2
Surface resistivity of low M_w amine-grafted polypropylene (abbreviations: PP, polypropylene (commercial sample); PP-g-MA, maleic anhydride-grafted polypropylene (4 wt.% MA), $M_w = \sim 9100$; AEE, 2-(2-aminoethoxy)ethanol $H_2NCH_2CH_2OCH_2CH_2OH$; AE, 2-aminoethanol $H_2NCH_2CH_2OH$; EDA: 1,2-ethylenediamine $H_2NCH_2CH_2NH_2$; DAP, *N*, *N*-dimethylaminopropylamine $H_2NCH_2CH_2CH_2N(CH_3)_2$)

Modified PP	Molar ratio	Weight fraction[a] (%)	Surface resistivity (10^x $\Omega/\square$)
PP	–	–	>12
PP-g-MA	–	–	>12
PP-g-MA/AEE	1:1	6	11.3
PP-g-MA/AE	1:1	2.5	11.3
PP-g-MA/EDA	1:8	16	10.4
PP-g-MA/DAP	1:1	4.4	10.3

[a] Weight fraction (%): amine/(PP-g-MA + amine).

Table 3
Surface resistivity of poly(oxyethylene)-grafted polypropylene and derivatives (abbreviations: PP, polypropylene; PP-g-MA, maleic anhydride-grafted polypropylene (4 wt% MA), $M_w = \backsim 9100$; H_2O, product was poured into deionized water; Na^+, product was poured into aq. sodium hydroxide; EDA, 1,2-ethylenediamine $H_2NCH_2CH_2NH_2$; Cl^-, product was poured into aq. hydrogen chloride; M-2070, methoxy-poly(oxyethylene-oxypropylene)-2-propylamine at $M_w \backsim 2000$; DAP, *N*, *N*-dimethylaminopropylamine $H_2NCH_2CH_2CH_2N(CH_3)_2$)

Modified PP	Molar ratio	Weight fraction[a] (%)	Surface resistivity (10^x $\Omega/\square$)
PP	–	–	>12
PP-g-MA	–	–	>12
PP-g-MA/H_2O	–	–	10.4
PP-g-MA/H_2O/Na^+	–	–	8.6
PP-g-MA/EDA	1:8	16	10.4
PP-g-MA/EDA/NA^+	1:8	16	10.3
PP-g-MA/EDA/Cl^-	1:8	16	10.4
PP-g-MA/M-2070/H_2O (120°C)	10:1	7.8	10.3
PP-g-MA/M-2070/H_2O (180°C)	10:1	7.8	10.4
PP-g-MA/M-2070/Na^+ (120°C)	10:1	7.8	9.5
PP-g-MA/M-2070/Na^+ (180°C)	10:1	7.8	9.2
PP-g-MA/M-2070/DAP/H_2O	10:1:5	7.6:1.9	10.3
PP-g-MA/M-2070/DAP/Na^+	10:1:5	7.6:1.9	10.2
PP-g-MA/M-2070/DAP/Cl^-	10:1:5	7.6:1.9	10.2
PP-g-MA/M-2070/H_2O	1:1	46	9.6
PP-g-MA/M-2070/Na^+	1:1	46	8.2

[a] Weight fraction (%): amine/(PP-g-MA + amine).

Table 4
Surface resistivity of poly(oxyethylene)-grafted polypropylene (Abbreviations: PP, polypropylene; PP-g-MA^2, maleic anhydride-grafted polypropylene (4 wt.% MA), $M_w = \sim 9100$; PP-g-MA^1, maleic anhydride-grafted polypropylene (0.8 wt.% MA); D-2000, poly(propylene glycol) bis(2-aminopropyl ether) at $M_w \sim 2000$; ED-2001, poly(ethylene glycol) bis(2-aminopropyl ether) at $M_w \sim 2000$; ED-6000, poly(ethylene glycol) bis(2-aminopropyl ether) at $M_w \sim 6000$)

Modified PP	Molar ratio	Weight fraction[a] (%)	Surface resistivity (10^x $\Omega/\square$)
PP	–	–	>12
PP-g-MA^2	–	–	>12
PP-g-MA^1/D-2000	1:1	14	10.6
PP-g-MA^2/D-2000	2:1	29	9.4
PP-g-MA^2/D-2000	1:1	45	8.6
PP-g-MA^2/ED-2001	2:1	29	8.3
PP-g-MA^2/ED-2001	1:1	45	6.9
PP-g-MA^2/ED-6000	2:1	55	8.7

[a] Weight fraction (%): amine/(PP-g-MA + amine).

Table 5
Surface resistivities and melting points of poly(oxyethylene–oxypropylene)amines

Jeffamine[a]	M-1000	M-2070	M-300	ED-2001	ED-6000
10^x (Ωohm/□)	9.4	Liquid	8.4	10.0	9.8
m.p. (°C)[b]	30.4	−2.2	31.0	37.3	54.2
ΔH_m (J/g)[b]	137.4	51.2	98.2	121.8	142.0

[a] Approximate EO/PO units per mole: M1000 (19/3); M2070 (32/10); M3000 (49/8); ED2001 (39/5); ED6000 (138/4).

[b] Melting points (m.p.) and heat of melting (ΔH_m) were measured by DSC.

3. Results and discussion

3.1. Synthesis and structure of PP-g-MA/poly(oxyalkylene)amine adducts

The POE modified polypropylenes were prepared by the grafting reactions of various amines and maleated PP. Two commercially available maleated PP, MPP-9100 (MA 4 wt.%) and Polybond® 3150 (MA 0.8 wt.%) were employed in this study. The pendant succinic anhydride moieties are highly reactive and readily undergo transformations with amines. The FT-IR analyses of these samples showed the characteristic absorption at 1852 cm^{-1} (w) and 1779 cm^{-1} (s) for anhydride carbonyls, and an additional carbonyl absorption at 1710 cm^{-1} (s), revealing the existence of free carboxylic acid (Fig. 1). Relative intensity of the free carboxylic acid absorption depended on the manner of sample preparation. The partial hydrolysis was caused by moisture absorption during the sample preparation. However, the mixtures of anhydride and acid were able to react with the amines smoothly to afford amidoacids and imides. The fundamental reaction pathways is illustrated in Scheme 1, using 1,2-ethylenediamine as the starting amine. The amidation could lead to a variety of possible products. Under basic and acidic conditions, the carboxylate salts and quaternary ammonium salts will be formed, respectively. However, under neutral conditions, the amidoacid can protonate the second amine in the structure to generate a zwitterion functionality. In this study, amines included low M_w of 2-aminoethanol, 2-(2-aminoethoxy)ethanol, 1,2-ethylenediamine, and *N*,*N*-dimethylaminopropylamine, as well as high M_w of poly(oxyalkylene)-monoamines and -diamines. In using *N*,*N*-dimethylaminopropylamine (DAP), the amphoteric structure involving a tertiary amine is formed as shown in Scheme 2. Alternately, Scheme 3 shows that the use of aminoalcohols led to the formation of amidoacid/imide selectively based on IR analyses, rather than to a possible ester product. In general, the conversion of anhydride to amidoacid initially and subsequently cyclized to imides at elevated temperature can be easily monitored by FT-IR. The characteristic IR absorption for 1650 and 1550 cm^{-1} for amide carbonyl and 1730 cm^{-1} for imide were reported previously [5]. The products prepared from PP-g-MA and amines at 120°C was characterized by FT-IR (Figs. 2 and 3). It appeared that the reaction of PP-g-MA and M-2070 afforded the imide predominantly, as indicated by 1734 cm^{-1} (s) and 1645 cm^{-1} (vw). The poly(oxyalkylene) functionality was evidenced by the characteristic 1107 cm^{-1} (s). Other reactions also afforded imide as the major product.

The amidation of methanol-initiated poly(oxyethylene–oxypropylene)-2-propylamines (M-1000, M-2070 and M-3000) formed the corresponding poly(oxyalkylene)-grafted copolymers, as shown in Scheme 4. In the case of diamine, a cross-linked PP can be produced from the multiple succinic anhydride moieties in PP-g-MA (Scheme 5). As a matter of fact, when the bifunctional poly(oxypropylene

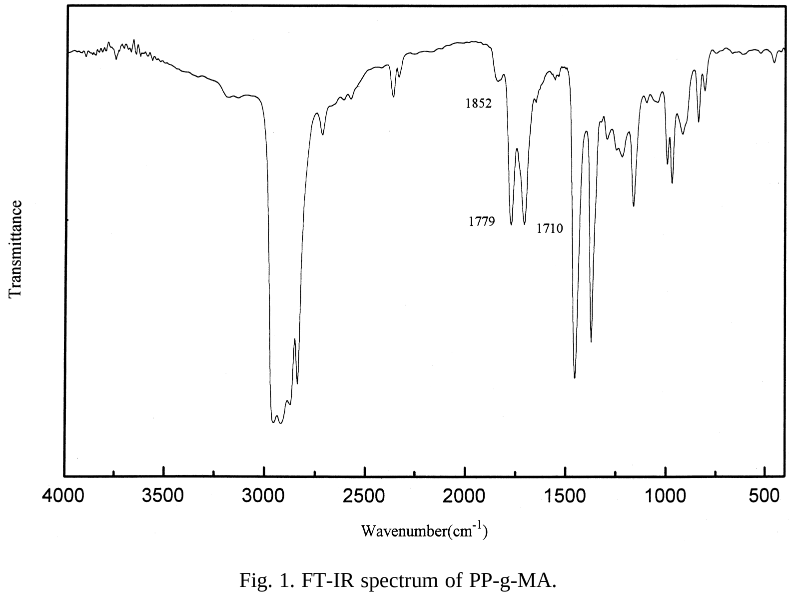
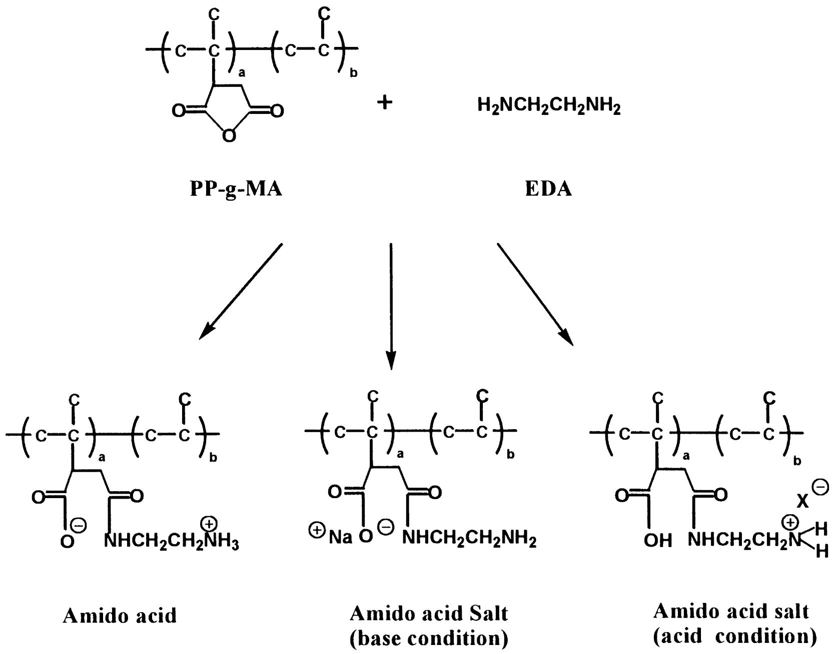
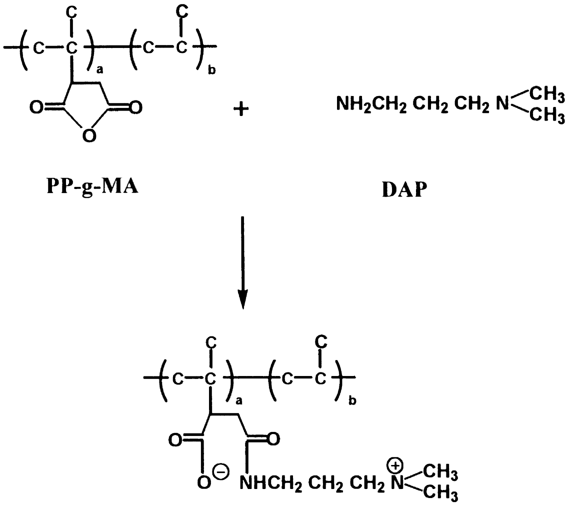


Fig. 1. FT-IR spectrum of PP-g-MA.



Scheme 1. General reaction products of maleate PP and diamine.

glycol)-bis(2-aminopropyl ether) of M_w ~2000 was allowed to react with PP-g-MA (4 wt.% MA or averaged 3.7 MA per polymer strain), a gel or unworkable compound was observed. However, the gel formation can be avoided to some extent by carrying out the reaction at lower temperature. The compound was soluble in hot oxylenes. Presumably, the product was slightly cross-linking mixtures of the poly(oxyethylene–oxypropylene) segmented PP. In appearance, the materials prepared from diamines such as D-2000 and ED-2001 were extremely ductile, in contrast to the brittle polymers made from the monoamine (M-2070), perhaps due to the partial cross-linking structures.

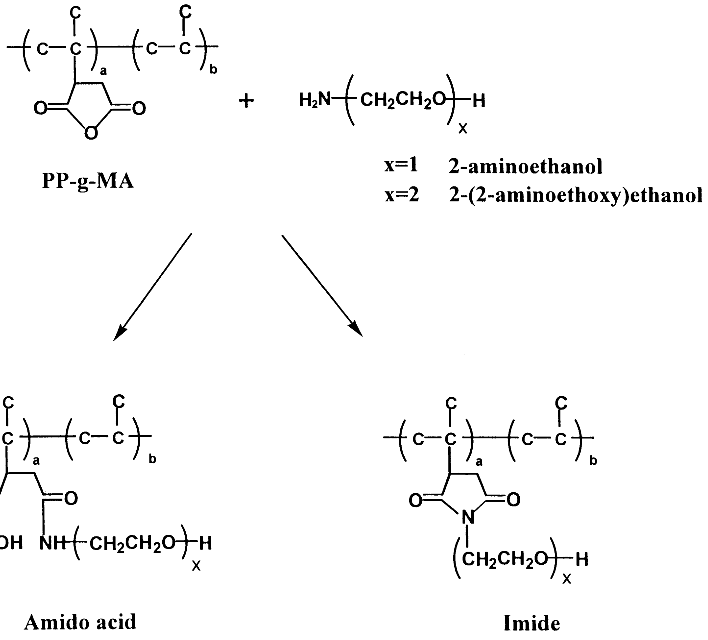


Scheme 2. Amphoteric structure derived from tertiary amine.

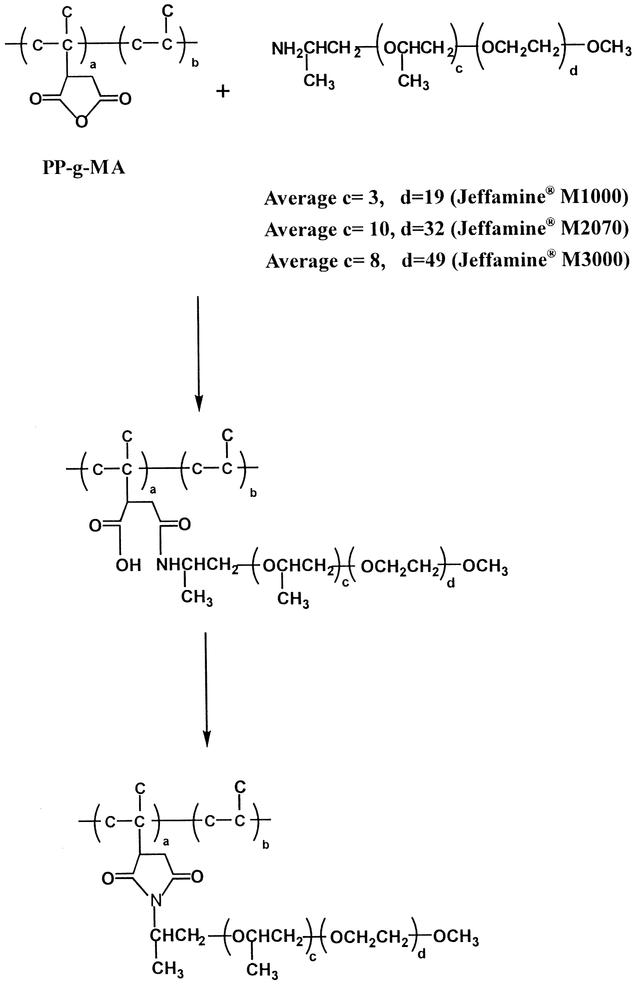
3.2. Thermal analyses of poly(oxyethylene–oxypropylene)imide grafted PP

In order to understand the thermal stability of this family of copolymers, the representative poly(oxyalkylene)imide functionalized PPs were examined by TGA in air and in nitrogen, shown in Figs. 5 and 6, respectively. In comparison with the PP-g-MA starting material, the poly(oxyalkylene)imide grafted PPs were less stable under oxidative degradation condition. As shown in Fig. 5, the PP-g-MA/M2070 and PP-g-MA/D2000 adducts were degraded at a faster rate in air than PP-g-MA. This was expected since the poly(oxyalkylene)amines, M-2070 and D-2000, had lower 50 wt.% retention temperatures at 280°C versus at 340°C for PP-g-MA. Both PP-g-MA/D2000 and PP-g-MA/M2070 had a similar 50 wt.% retention temperature at 320°C, with a slightly more stable decomposition curve for the former. This can be attributed to the presence of $-NH_2$ terminus in PP-g-MA/D2000. This explanation had been further supported by the observation of high stability for PP-g-MA/DAP. This structure consisted of a tertiary amine termination in each pendant group and demonstrated a 50 wt.% retention temperature at 380°C. It appeared that the amine terminus effectively behaved as scavengers for R and ROO radicals in stabilization [26] and contributed greatly to the stability of the whole polymer strain.

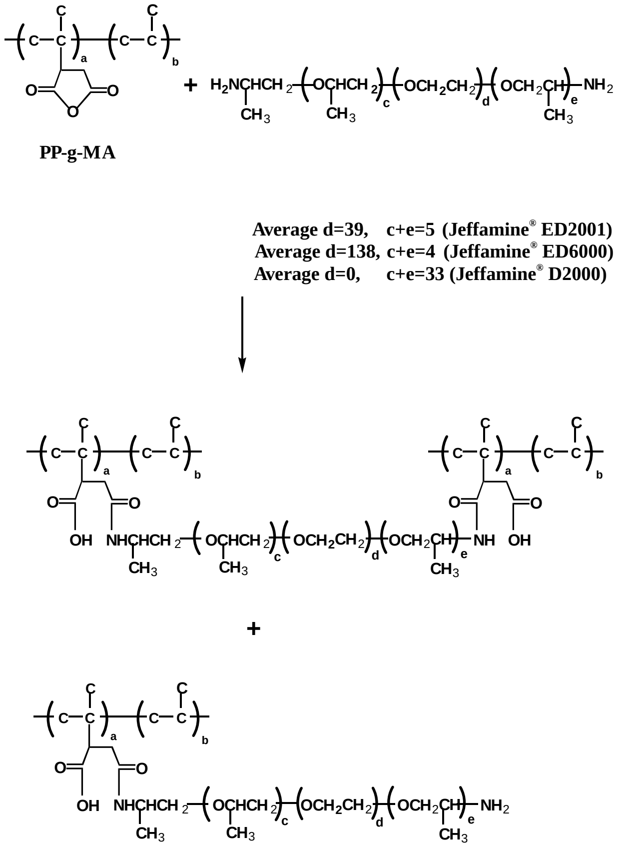
The thermal stability in nitrogen of these compounds was different from their thermal oxidation as indicated in Fig. 6. In nitrogen, the POE functionalized PPs were considerably stable. The compounds containing amine groups displayed a much higher stability than that of PP-g-MA. The PP-g-MA/DAP exhibited a 450°C of 50 wt % retention temperature



Scheme 3. Selective amidation and imidation of aminoalcohol grafting on PP.



Scheme 4. Amidation and imidation of polyether-monoamines on PP-g-MA.



Scheme 5. Poly(oxyethylene) or poly(oxypropylene)diamine cross-linked amphiphilic PP.

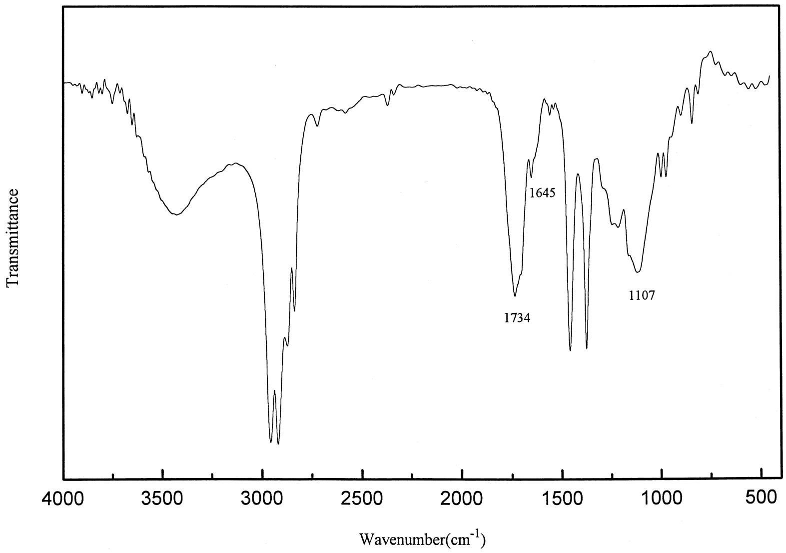


Fig. 2. FT-IR spectrum of PP-g-MA/M-2070 (1:1).

compared to 410°C for PP-g-MA/D2000 and 425°C for PP-g-MA/ED2001.

3.3. Trend of electrostatic dissipating ability

Practically, suitable electrostatic dissipating polymers have surface resistivity in the range of 10^6–10^{12} Ω/□. Resistivity lower than 10^6 Ω/□ may dissipate electrostatics too fast and cause a sudden spark or arcing. It was previously reported [23] that the surface resistivity could be related to the hydrophilicity of polymer materials. By introduction of the tailored hydrophilic POE segments into poly-ether-amides, the materials with such range of resistivity could be prepared. In the following, POE grafted PP via the amidation of poly(oxyethylene)-rich amines were made and compared.

3.3.1. Poly(oxyethylene–oxypropylene)monoamine modified PP

As shown in Table 1, the incorporation of poly(oxyethylene–oxypropylene)monoamines into PP-g-MA rendered polymers with low surface resistivities. The starting material, PP-g-MA, exhibited a surface resistivity of $10^{>12}$ Ω/□, similar to that of the commercial PP based on our measurement. The grafting of polyether backbone amines significantly lowered surface resistivity below 10^{11} Ω/□. In this study, the polyetheramines include the methoxy-poly(oxyethylene–oxypropylene)-2-propylamines of M_w 1000, 2000 and 3000, which are presumably produced via methanol-initiated block ethoxylation and propoxylation and followed by ammonia amination [27,28]. These structures consist of predominantly block POE backbone and a terminal primary amine. The oxyethylene/oxypropylene

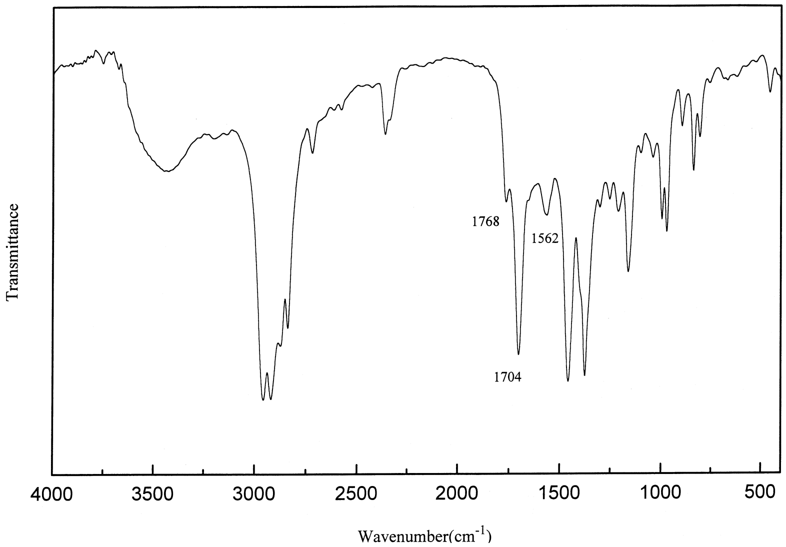


Fig. 3. FT-IR spectrum of PP-g-MA/DAP (1:1).

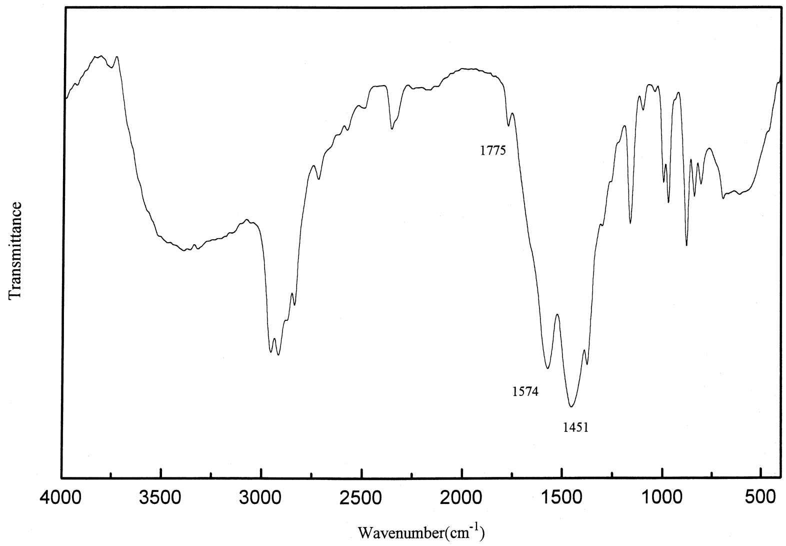


Fig. 4. FT-IR spectrum of PP-g-MA/Na^+.

units of 19/3, 32/10, and 49/8 per mole constitute the poly(oxyalkylene) backbone for Jeffamine® M-1000, M-2070 and M-3000, accordingly. All of these polyether-amimes are oxyethylene-rich structures and soluble in water. When M-2070 was allowed to react with PP-g-MA of 4 and 0.8 wt.%, the resulting materials gave surface resistivity of $10^{10.4}$ and $10^{11.1}$ Ω/□, respectively. By grafting POE onto PP-g-MA, the copolymers exhibited a considerably low surface resistivity proportional to the weight fraction of the POE segments in the pendant polymers. This was further confirmed by using PP-g-MA of 4 wt.%. For example, the increasing weight amount from 14, 23, 30, 38 to 46 wt.% of M-2070 in grafting with PP generated the copolymers with decreasing surface resistivity in the range of 10^{11}–$10^{9.6}$ Ω/□ (Table 1). A similar trend was observed for M-3000, with decreasing resistivities from $10^{9.6}$ to $10^{8.7}$ to $10^{7.5}$ Ω/□. The trend of the resistivity drops against the weight fraction of POE and POP segments is shown in Fig. 7. The POE appeared to be more significant than POP components in contributing to polymer surface resistivities. It is noted that the copolymer of PP-g-MA/M-3000 at 1/1 MA/NH_2 molar ratio gave the lowest resistivity ($10^{7.5}$ Ω/□) in this series. This corresponds to the highest weight fraction (55 wt.%) of POE in the structure among those prepared.

3.3.2. Low M_w amine modified PP

In comparing with the POE–POP-amines as described above, the low M_w amines such as 2-aminoethanol (AE), 2-(2-aminoethoxy)ethanol (AEE), 1,2-ethylenediamine (EDA), and *N*,*N*-dimethylaminopropylamine (DAP) were allowed to react with PP-g-MA to give raise to materials

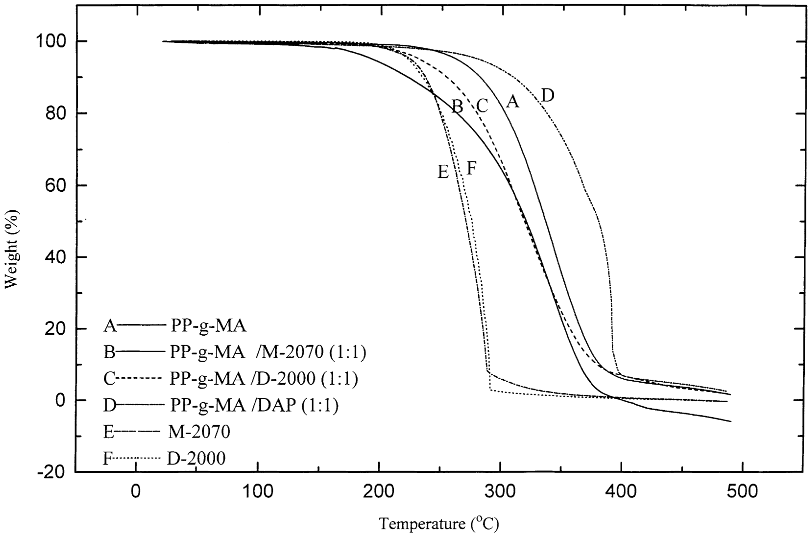


Fig. 5. Relative stability by thermogravimetric analysis (TGA) in air.

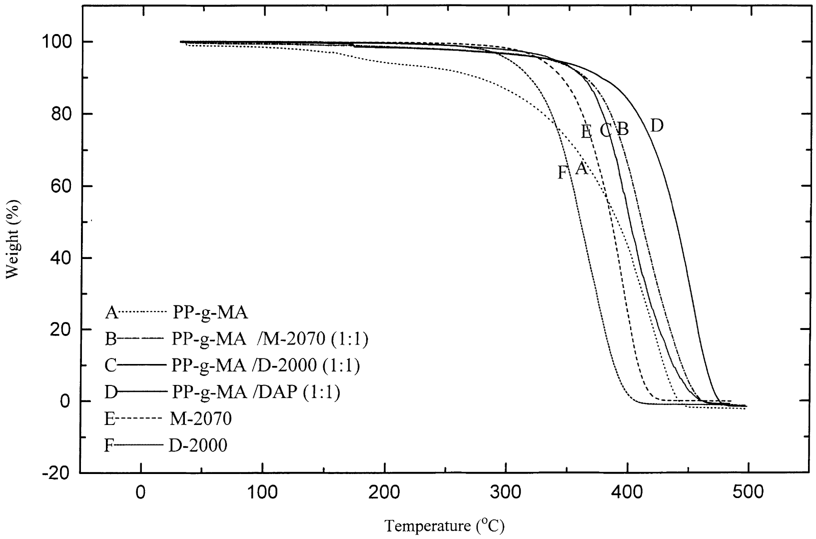


Fig. 6. Relative stability by thermogravimetric analysis (TGA) in nitrogen.

with only a slight decrease in surface resistivity (Table 2). With the monoamines such as 2-aminoethanol or 2-(2-aminoethoxy)ethanol, the surface resistivity dropped to $10^{11.3}$ Ω/□ from $10^{>12}$ Ω/□ of PP-g-MA. This was compared to $10^{10.4}$ ohm/□ for the EDA or DAP modified PP-g-MA. There was roughly one order of magnitude difference between diamines (EDA or DAP) and monoamines (AE or AEE). This may be attributed to the presence of amine groups in the structures of PP-g-MA/EDA or DAP. However, it became obvious that the high M_w of hydrophilic POE segments was required for lowering surface resistivity below the level of 10^{10} Ω/□.

When the mixed DAP and M-2070 was used, the structures involved POE segments and amines. The duel polar groups in PP-g-MA/M-2070/DAP adduct at 2/1/1 molar ratio had a $10^{9.1}$ Ω/□ in comparing with $10^{10.4}$ Ω/□ for PP-g-MA/M-2070 (2/1) and $10^{10.3}$ Ω/□ for PP-g-MA/DAP (1/1). The effectiveness of POE in lowering the resitivity is again realized in this system.

3.3.3. Ionic effect

The complexation of POE block copolymers with alkali, alkaline earth and transition metal salts is well known [16]. The interaction between the ether oxygen of POE segments and the dissociated metal ions was suggested to have a stoichiometric relationship of approximate 3/1 molar ratio for $-CH_2CH_2O-$ to Na^+ or Li^+ ions [29–31]. The ionic conducting polymers have potential uses as solid electrolytes. Recently, the ionic conducting comb polymers involving side chain of $-(CH_2CH_2O)_n-$ grafted vinyl ether/MA copolymers were prepared [25] for such applications. In our synthesis, the generic structures of POE graft PP copolymers are constituted by imide linkages and POE segments which could form complex with metal ions. The

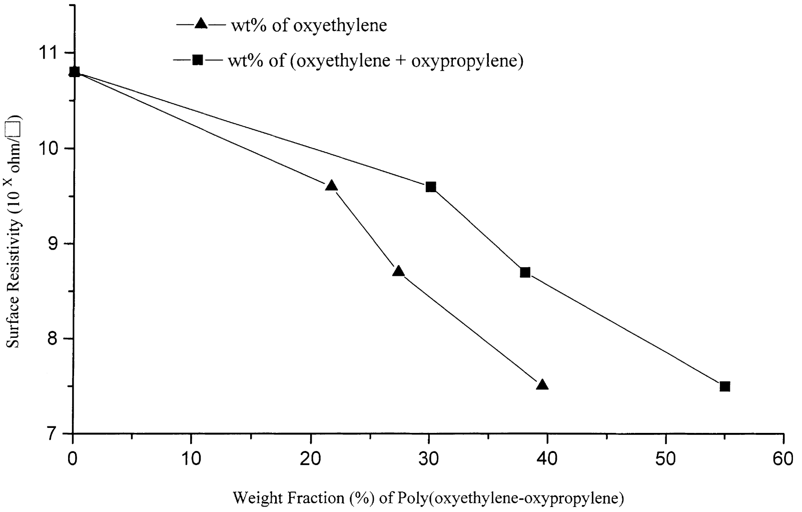


Fig. 7. Decreasing trend of surface resistivity of PP-g-MA/M-3000.

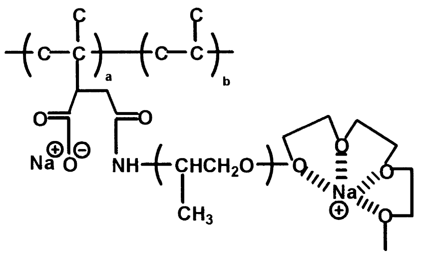


Fig. 8. Metal complexation with POE and carboxylate.

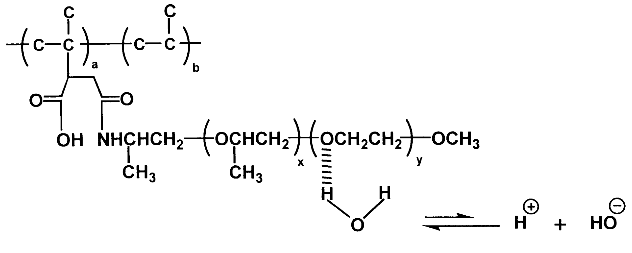


Fig. 9. Mechanism for electrostatic dissipating via hydrogen bonds.

synthesis of PP-g-MA/Na^+ was confirmed by the characteristic FT-IR absorption at 1574 cm^{-1} for the conversion of –COOH into –COONa (Fig. 4). It was noted that the conversion of PP-g-MA into the corresponding sodium salts enhanced the surface conductivity from $10^{>12}$ to $10^{8.6}$ $\Omega/\square$ for the PP-g-MA/Na^+ (Table 3). In the cases of poly(oxyethylene)imide modified PP-g-MA, more alkali metals can be complexed through the oxygen/Na^+ in POE helix (Fig. 8). For PP-g-MA/M-2070 (10/1), the addition of sodium salts significantly lowered the resistivity from $10^{10.3}$ to $10^{9.5}$ $\Omega/\square$. The PP-g-MA/M-2070 adduct of (1/1) molar ratio, which had already a low resistivity of $10^{9.6}$ $\Omega/\square$, further decreased to $10^{8.2}$ $\Omega/\square$ after the sodium ion treatments. The strong effect of Na^+/POE ionic conducting on the electrostatic dissipation was realized in contrast to the hydrogen bonding mechanism through the partial water ionization (Fig. 9). Hence, the $-(CH_2CH_2O)_n-/H_2O$ hydrogen bonding and the $-(CH_2CH_2O)_n-/Na^+$ ionic conduction are two main mechanisms for transferring electrostatic charges in our study. In acidic conditions, the Cl^- ions had no significant promotion effect on either EDA or M-2070 modified PP.

3.3.4. Poly(oxyethylene)- and poly(oxypropylene)-diamine modified PP

The difference between the POE and the POP structures was demonstrated by PP-g-MA/ED-2001 and PP-g-MA/D-2000. To make the direct comparison, poly(propylene glycol) bis(2-aminopropyl ether) of M_w ~2000 (D-2000) and poly(ethylene glycol) bis(2-aminopropyl ether) of M_w ~2000 (ED-2001) were allowed to graft on PP-g-MA. In Table 4, the graft copolymers consisting of M_w 2000 POE pendants (ED-2001) had significantly lower resistivities than those of the POP (D-2000) analogs. A reading of PP-g-MA/ED-2001 (1/1 molar ratio) at $10^{6.9}$ $\Omega/\square$ was compared to PP-g-MA/D-2000 (1/1 molar ratio) at $10^{8.6}$ $\Omega/\square$. At the molar ratio of 2:1, the difference was between $10^{8.3}$ and $10^{9.4}$ $\Omega/\square$. The difference in hydrophilicity between POE and POP was noticed.

It was also realized that the PP-g-MA/ED-2001 had a generally lower resistivity than that of the corresponding PP-g-MA/M-2070. A significant difference between $10^{6.9}$ and $10^{9.6}$ $\Omega/\square$ was compared for the products with similar POE composition. In comparing the difference in the structures, the terminating $-NH_2$ instead of $-OCH_3$ may be the contributing factor.

3.3.5. Crystallinity versus surface resistivity

Increasing weight proportions of the POE incorporated into PP-g-MA is the key factor for lowering resistivity. However, the segmental crystallinity of the POE appeared

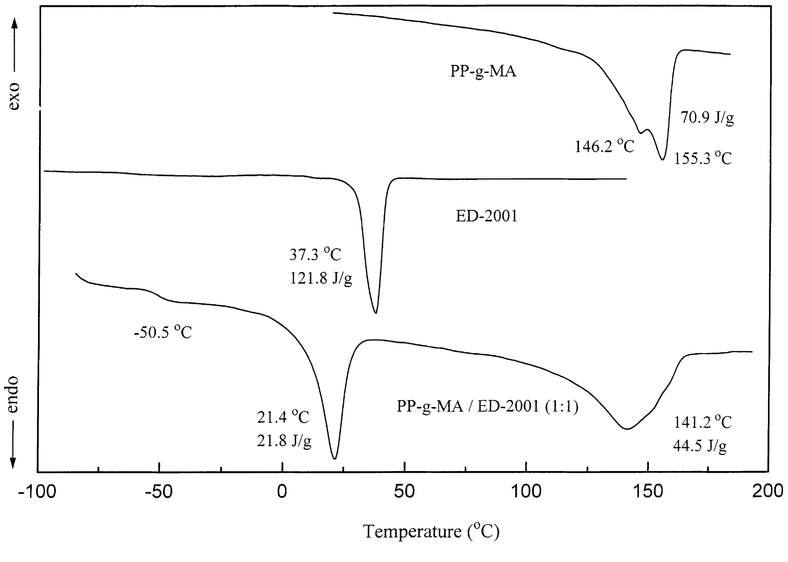


Fig. 10. The DSC heating curves of PP-g-MA/ED-2001.

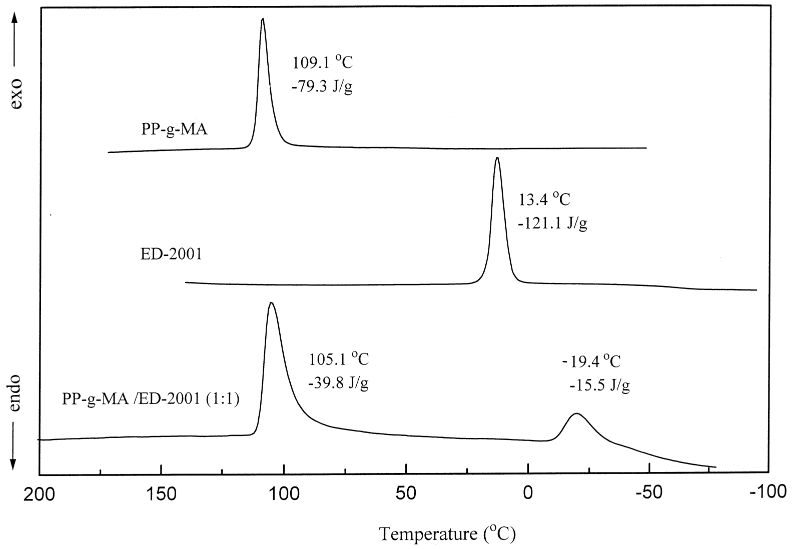


Fig. 11. The DSC cooling curves of PP-g-MA/ED-2001.

to have an adverse effect. It is known that high crystallinity can reduce the flexibility or mobility of the segments in polymer strains, and therefore the ion mobility [32]. Inherently, the high M_w of POE-amines are crystalline due to the high dipole–dipole interaction of C–C–O moieties [24]. The different behavior of the crystallinity may be related to the POE/POP ratio, molecular weight, terminal groups, moisture content and also impurities. For a comparison, surface resistivities and thermal analyses based on DSC of the involved starting POE-amines were measured and listed in Table 5. It was observed that ED-6000, having the highest M_w of POE backbone, had the highest melting point (m.p. 54.2°C) and melting enthalpy (ΔH_m, 142.0 J/g). When incorporated into PP-g-MA at 55 wt.%, the PP-g-MA/ED6000 had a resistivity $10^{8.7}\ \Omega/\square$ which was significantly higher than the analogous ED-2001 ($10^{6.9}\ \Omega/\square$) in Table 4 and M-3000 ($10^{7.5}\ \Omega/\square$) in Table 1. The rigidity due to the high crystallinity of segmental POE (M_w 6000) was the cause.

To further understand the crystallinity effect, several POE-amine grafted PPs were analyzed by DSC. The comparison among PP-g-MA, ED-2001 and PP-g-MA/ED2001 is illustrated in Figs. 10 and 11. Both the PP and POE components in PP-g-MA/ED-2001 had shifted their melting temperatures to lower values. It may be noteworthy that the POE segments had shifted the melting from 37.3 to 21.4°C, below the ambient temperature. Moreover, the melting enthalpy dropped from 121.8 J/g to as low as 21.8 J/g. The significant drops in melting temperature and melting enthalpy were reflected by the decrease of surface resistivity from $10^{10.0}\ \Omega/\square$ of ED-2001(100 wt.%) to $10^{6.9}\ \Omega/\square$ of PP-g-MA/ED-2001(45 wt.%). The phase environment around the hydrophilic POE segments in microstructures seems to play an important role in controlling the electrostatic charge transfer, although the detailed mechanism is not clear.

4. Conclusion

Low surface resistivity of the poly(oxyethylene)imide grafted polypropylenes were prepared by the reaction of PP-g-MA and various hydrophilic POE-amines. The use of 1000–3000 M_w of poly(oxyethylene–oxypropylene)-monoamines and diamines effectively rendered the polymers with surface resistivity as low as $10^{9.6-6.9}\ \Omega/\square$. The weight fraction of the incorporated POE proportionally lowered the surface resistivity of the PP. The electrostatic dissipating ability ($10^{11.3-10.4}\ \Omega/\square$) was not significantly affected by grafting low M_w of DAP, EDA, AE or AEE. The structures consisting of amphoteric quaternary salts or ion conducting sodium salts can further improve the static charge dissipation. On the contrary, the high degree of segmental crystallinity reduced the mobility of transferring electrostatics, as evidenced by the example of using high crystalline ED-6000. A mechanism involving hydrogen bonding between the hydrophilic oxyethylene functionality and moisture water is envisioned. Further investigation on the structural variations and the practical applications will be pursued.

Acknowledgements

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References

[1] Schulz DN, Patil AO. In: Patil AO, Schulz DN, Novak BM, editors. Functional polymers, modern synthetic methods and novel structures, Washington, DC: American Chemical Society, 1998.
[2] Yang C, Rathman JF. Polymer 1996;37:4621.
[3] Sclavons M, Carlier V, Roover BDE, Franquinet P, Devaux J, Legras R. J Appl Polym Sci 1996;62:1205.

[4] Gaylord NG, Mishra MK. J Polym Sci: Polym Lett Ed 1983;21:21.
[5] Perez-Camacho O, Gonzalez-Roa C, Navarro-Rodriguez D, Contreras DZ. J Appl Polym Sci 1997;64:2519.
[6] Duiin MV, Aussems M, Borggreve RJM. J Polym Sci A: Polym Chem 1996;36:179.
[7] Chiang WY, Hu CH. J Appl Polym Sci 1988;68:37.
[8] Kim BK, Park SJ. J Appl Polym Sci 1991;43:357.
[9] Utracki LA. Polymer alloys and blends, thermodynamics and rheology, Munich: Hanser, 1990.
[10] Gaylord NG. Chemtech 1989;July:435.
[11] Chen CC, Fontan E, Min K, White JL. Polym Engng Sci 1988;28:69.
[12] Bonner JG, Hopes PS. In: Folkes MJ, Hope PS, editors. Polymer blends and alloys, Glasgow: Blackie, 1993.
[13] Kawasumi M, Hasegawa N, Kato M, Usuki A, Okada A. Macromolecules 1997;30:6333.
[14] Kato M, Usuki A, Okada A. J Appl Polym Sci 1997;66:1781.
[15] Interrante LV, editor. Materials chemistry, an emerging discipline Advances in Chemistry, vol. 245. New York: American Chemical Society, 1995.
[16] MacCallum JR, Vincent CA, editors. Polymer electrolyte: review 1 London: Elsevier Applied Science, 1987 review 2 (1989).
[17] Linford RG, editor. Electrochemical science and technology of polymers 1, London: Elsevier Applied Science, 1987.
[18] Scrosati B, editor. Application of electroactive polymers London: Chapman & Hall, 1993.
[19] Gachter R, Muller H. Plastics additives handbook, Munich: Hanser, 1984.
[20] Lee B. US Patent 5,237,009, 1993.
[21] Okazaki K, Nakagawa A, Sugii K. US Patent 3,558,419, 1971.
[22] Fukumoto T, Yano K, Iwamoto M. US Patent 5,096,995, 1992.
[23] Young MY, Lin JJ. Ind Engng Chem Res 1998;37:4284.
[24] Harris JM, editor. Poly(ethylene glycol) chemistry, biotechnical and biomedical applications New York: Plenum Press, 1992.
[25] Ding L. Polymer 1997;38:4267.
[26] Pospisil J. In: Clough RL, Billingham NC, Gillen KT, editors. Polymer durability–degradation, stability and lifetime prediction, Washington, DC: American Chemical Society, 1996.
[27] Moss PH. US Patent 3,152,998, 1964.
[28] Yeakey EL. US Patent 3,654,370, 1972.
[29] Fenton DE, Parker JM, Wright PV. Polymer 1973;14:589.
[30] Hibma T. Solid State Ionics 1983;9/11:1101.
[31] Wright PV. Polymer 1975;7:319.
[32] Tsuchida E, Takeoda S. In: Dubin P, Bock J, Davis R, Schulz DN, Thies C, editors. Macromolecular complexes in chemistry and biology, Berlin: Springer, 1994.