

Synthesis, Characterization and Electrostatic Dissipating Ability of Poly(oxyethylene) Block Polyesteramides

J. J. Lin^{1,*}, Y. C. Sheen², F. P. Tseng² and F. C. Chang²

1. *Department of Chemical Engineering, National Chung-Hsing University, Taichung, Taiwan 40227, ROC*

2. *Institute of Applied Chemistry, National Chiao-Tung University, Hsinchu, Taiwan 30050, ROC*

Abstract: Poly(oxyethylene)diamines were included in the copolymerization of ethylene glycol and dicarboxylic acids, such as terephthalic, adipic and sebacic acid, to produce a series of hydrophilic polyether-ester-amides. With the addition of poly(oxyethylene)diamines (average molecular weight of 2,000) to PET in the amounts of 3.2, 6.6, 12 and 16 wt%, melting points of these polymers dropped accordingly, from 240 °C to around 227 °C, and the electronic resistivity decreased from 1×10^{13} to approximately 8×10^8 ohm/sq. For comparison, the introduction of hydrophilic PEG-2000 or a low molecular weight diamine, such as triethyleneglycol diamine, has less effect on electronic resistivity. Molecular weight, polymer rigidity and ageing are other factors affecting the surface resistivity. The degree of hydrophilicity was measured by the moisture absorption of the fibers made from these polyether-ester-amides. A weight gain of 0.96% was observed for 12 wt% poly(oxyethylene)diamine modified polyether-ester-amides in comparison with 0.40% for the unmodified poly(ethylene terephthalate). These results are explained by a mechanism involving moisture absorption on the polymer surface through the formation of hydrogen bonding with amide and $-(OCH_2CH_2)-$ functionalities on the polymer surface.

Keywords: Polyether-ester-amides, Poly(oxyethylene), Hydrophilicity, Electrostatic dissipating.

Introduction

Polymers containing hydrophilic functionalities are versatile and useful for many applications including surfactants, dispersion stabilizers, emulsifiers, thickeners, polymer blend compatibilizers, solid electrolytes [1-4]. Polymeric surfactants, derived from hydrophilic polyethyleneglycol (PEG), are particularly important for usages in the areas of polymer modifiers and pharmaceuticals [5,6]. These functions are accomplished by the introduction of polar poly(oxyethylene) segments into specific polymers [7-9]. As a result, unique properties such as the ability of form complex metal ions [10] or to dissipate electrostatics [11-14], are achieved. For example, the incorporation of poly(oxyethylene) amide segments into poly- ϵ -caprolactam to enhance hydrophilicity as well as the dye-absorbing and static charge dissipating abilities was first reported as early

as 1971 [15].

Terephthalic polyesters such as poly(ethylene terephthalate) (PET), are some of the most common substances used in engineering thermoplastics and textile fibers. It has received a great deal of attention in scientific studies and industrial applications due to its excellent performance with respect to mechanical properties and its good processability. However, one drawback of PET materials is their poor antistatic properties. Copolymers of polyethylene oxide and PET have been studied in an attempt to increase their hydrophilicity [9,16-18]. Recently, a transparent polyether-ester-amide (modified PET) material has been prepared from poly(ethylene glycol), aminocarboxylic acid and carboxylic acid [19] and used for electronic device packaging to prevent of electrostatic charge accumulation. These reports have generally appeared in patent literature. Systematic studies on the synthesis of

*To whom all correspondence should be addressed.
Tel: 886-4-2852591; Fax: 886-4-2871787
E-mail: jjlin@dragon.nchu.edu.tw

J. Polym. Res. is covered in ISI (CD, D, MS, Q, RC, S), CA, EI, and Polymer Contents.

poly(oxyethylene) amide segmented polymers and their corresponding electronic dissipating properties are still limited. In this study, we employed a 2,000 molecular weight of poly(propylene glycol)-block-poly(ethylene glycol)-block-poly(propylene glycol) bis(2-aminopropyl ether) as the comonomer to prepare a series of novel polyether-ester-amides. The unique poly(oxyethylene-oxypropylene)diamine is commercially available product Huntsman Corporation. The chemical structure consists of a middle block of poly(ethylene glycol), two end blocks of poly(propylene glycol) and two terminating primary amines. The average oxyethylene and oxypropylene units are 39.5 and 5.0, respectively. The hydrophilic nature is suitable for modifying PET. The similar M_w of polyethylene glycol, PEG-2000, and low M_w of triethyleneglycol diamine were used for the purpose of comparison; from them the factors affecting electrostatic dissipation were derived. The hydrophilicity of these polymers was characterized by probing the surface resistivity, moisture weight gain and other polymer properties. The influence of hydrophilic poly(oxyethylene)-amide functionality on the surface resistivity is explained by the mechanism involving the moisture absorption through hydrogen bonding. The molecular weight of the poly(oxyethylene) segment, the weight content, amide functionality, and polymer structure are correlated with the surface resistivity.

Experimental

1. Materials

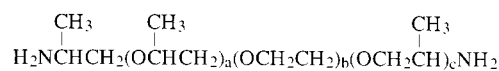
Terephthalic acid (TA), adipic acid (AA), sebacic acid (SA), bis-hydroxyethyl terephthalate (BHET), ethylene glycol (EG), poly(ethylene glycol) at $\sim 2,000 M_w$ (PEG-2000), germanium oxide (GeO_2) and p-toluene sulfonic acid were purchased from Aldrich Chemical Co. Poly(propylene glycol)-block-poly(ethylene glycol)-block-poly(propylene glycol) bis(2-aminopropyl ether) of $\sim 2,000 M_w$ (Jeffamine[®] ED-2001) and triethyleneglycol diamine of $\sim 148 M_w$ (Jeffamine[®] EDR-148) were purchased from Aldrich Chemical Co. or Huntsman Chemical Co. Their chemical structures are described in Figure 1.

2. Preparation of poly(oxyethylene) diamide segmented polyether-ester-amide

Typical procedures for the copolymerization of diacid, ethylene glycol and polyoxyethylene (POE) diamine to produce ca. 6.6 wt% POE-segmented polyether-ester-amide are described below:

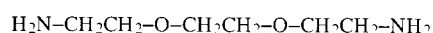
A 1-liter autoclave equipped with a heating device, temperature controller, torque detector,

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



$$b = 39.5, a + c = 5.0, \text{ Mol. Wt. } 2,000$$

Triethyleneglycol Diamine



$$\text{Mol. Wt. } 148$$

Figure 1. Structures of poly(oxyethylene) diamines.

vacuum pump and mechanical stirrer was charged with terephthalic acid (200 g, 1.2 mol), ethylene glycol (148.8 g, 2.4 mol) and 2,000 molecular weight of poly(propylene glycol)-block-poly(ethylene glycol)-block-poly(propylene glycol) bis(2-aminopropyl ether) (Jeffamine[®] ED-2001, 25 g, 12.5 mmol), GeO_2 (1.0 g, 0.5 part) and p-toluene sulfonic acid (1.0 g, 0.5 part). While stirring, the mixtures were slowly heated to 230 °C, held for 4 hours and then subjected to a vacuum gradually to reach 1 torr reduced pressure while the temperature was raised to 260 °C and held until the torque was invariable. During the process, the viscosity of the mixtures increased from 0.009 to 0.024 torque at 60 rpm, and the water (ca. 22 g) was removed. The reaction product was poured into a stainless steel tray. After cooling to room temperature, the sample was maintained in an atmosphere of 50% relative humidity under room temperature, and surface resistivity was measured using ST-3 model tester (Simco Co.) according to the method of ASTM D257-93. The IR spectra showed C=O absorption at 1723 cm^{-1} (–CO–O–), 1578 cm^{-1} (–CO–NH–), and a broad absorption at 1122 cm^{-1} (–C–O–C–). The chemical shifts of ^1H NMR spectra were: δ (ppm) = 3.80-4.10, 4.25-4.40, 4.70-4.85, 4.85-5.05, 8.20-8.40, and $\delta = 11.5$ ppm.

Similarly, polyether-ester-amides with various contents (3.2, 12, and 16 wt%) of polyoxyethylene diamine were produced.

3. Relative reaction rate of diacid

The reaction of the poly(propylene glycol)-block-poly(ethylene glycol)-block-poly(propylene glycol) bis(2-aminopropyl ether) of 2,000 M_w diamine with various diacids, terephthalic acid, adipic acid, and sebacic acid to produce polyamides was carried out in bulk under 250–260 °C. The reaction rates were monitored by the amount of water generated. The relative rates were expressed by plotting the conversion over the reaction time.

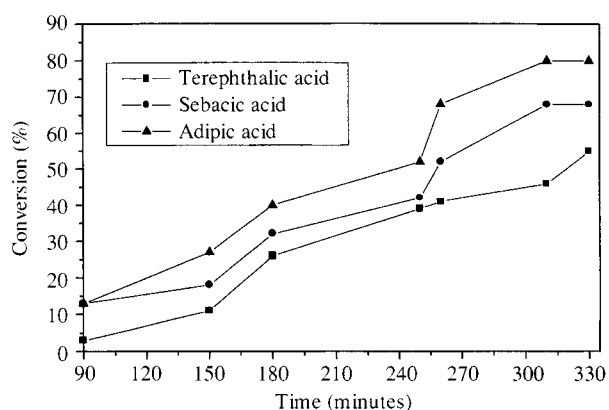


Figure 2. Relative reaction rate of diacid, ethylene glycol, and poly(oxyethylene-oxypropylene) diamine ($M_w \sim 2,000$).

4. Measurements

^1H NMR characterization was performed by a Varrion VXR-300 (300 MHz) NMR spectrometer using trifluoroacetic acid as the solvent. FTIR spectra were obtained through thin film by using a PERKIN ELMER Paragon 500 FT-IR spectrometer with a resolution of 4 cm^{-1} . Surface resistivity was measured by using a ST-3 Model (Simco Co.) tester according to the ASTM method of D257-93. The measurement is in the unit of ohm/square or ohm/sq in which the size of square is immaterial. 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 to 8 mg on a sealed aluminum pan. The analyses were performed under a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ in a 30 mL/min nitrogen atmosphere. The heat of melting (ΔH_m) and crystallization (ΔH_c) was determined by the integration of the peak area under the linear baseline, and the peak values of the thermogram were reported as melting point (T_m) and crystallization temperature (T_c), respectively. The glass transition temperature (T_g) was recorded at the half-height of the corresponding heat capacity jump. The intrinsic viscosities of the copolymers at $30\text{ }^\circ\text{C}$ in a phenol/tetrachloroethane (60/40 w/w) solution were determined by an Ubbelohde viscometer. Water absorption (WS) of the materials was measured on the fiber spun from the polyether-ester-amides (250 d/f, 1 g). The ability to absorb water was calculated on the difference of the weight gains,

$$\text{WS} = [(W_s - W_d)/W_d] \times 100\% \quad (1)$$

where W_s and W_d were the weight of the water-absorbed samples which were maintained in an atmosphere of 50% relative humidity under room temperature and the weight of the dry samples which

Table I. Surface resistivity of various diacid-derived polyether-ester-amides^(a) containing 20 wt% POE segments.

Diacid ^(b)	TPA	AA	SA
Reaction time (hr)	16	4.5	6.5
Catalyst	none	none	none
Conversion (%)	85	>98	>98
Product appearance	milky white	yellow	yellow
Resistivity (ohm/sq)	3×10^9	1×10^9	2×10^9
T_m ($^\circ\text{C}$)	220	46	70

(a) Prepared from copolymerization of Jeffamine[®] ED-2001 (20 wt%), ethylene glycol and diacid.

(b) TPA: terephthalic acid, AA: adipic acid, SA: sebacic acid.

were dried at $110\text{ }^\circ\text{C}$ in a vacuum oven, respectively.

Results and Discussion

1. Synthesis and property of polyether-ester-amides

The general copolymerization of dicarboxylic acids, ethylene glycol and poly(propylene glycol)-block-poly(ethylene glycol)-block-poly(propylene glycol) bis(2-aminopropyl ether) of 2,000 M_w is described by Eq.(1). These reactions were carried out in bulk to generate polyester-ether-amides containing segments of POE diamide block. In comparing the relative reaction rate of terephthalic (TPA), adipic (AA) and sebacic acid (SA), the time-conversion curve based on the rate of water byproduct formation is plotted in Figure 2. Reactions involving aliphatic diacids were faster than those involving aromatic diacids. The rate of adipic acid reaction was faster than that of the higher carbon analog, sebacic acid. Relatively, over 80% of completion was achieved in adipic acid reaction compared with ca. 55% in terephthalic acid reaction, within 330 minutes of reaction time. Less of a rate difference was observed between reactions involving sebacic and adipic acid. The lower reaction rate of aromatic acids, e.g. TPA, may be attributed to the electronic effect of the aromatic functionality in TPA or the higher viscosity increase during the reaction process.

The reaction condition, product appearance, melting point and surface resistivity of polyether-ester-amides containing 20 wt% of POE diamine are summarized in Table I. The product, prepared from TPA and ethylene glycol in the presence of 20 wt% of POE diamine, had a much higher melting point ($220\text{ }^\circ\text{C}$) than those from aliphatic acid derivatives ($46\sim 70\text{ }^\circ\text{C}$) due to the $\pi\text{-}\pi$ interaction between aro-

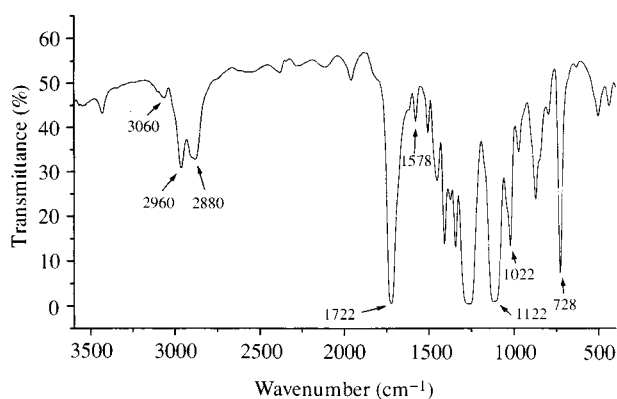


Figure 3. FT-IR spectrum of POE amide (6.6 wt%) segmented poly(ethylene-terephthalate).

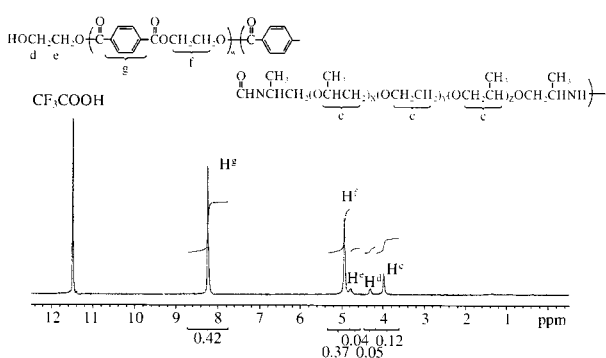


Figure 4. ^1H NMR spectrum of POE amide (6.6 wt%) segmented poly(ethylene-terephthalate).

matic moieties. It was noted that the polyether-ester-amide prepared from TPA was colorless in comparison with the yellowish product prepared from the AA or SA. Their surface resistivities were measured and were in the range of 1×10^9 to 3×10^9 ohm/sq, which was significantly lower than that of unmodified PET ($>10^{13}$ ohm/sq as shown in Table IV). However, there was no significant surface resistivity difference between the aromatic and aliphatic diacid derived products.

In fiber applications, the melting temperature of a fiber must be above 200°C so that its physical integrity can be maintained during cleaning and ironing. Under this consideration, only the polyether-ester-amide prepared from TPA is useful for fiber applications. The FT-IR and ^1H NMR spectra of the POE amide (6.6 wt%) segmented PET are shown in Figures 3 and 4, respectively. The peak absorptions at 2960 and 2880 cm^{-1} (CH_3 stretch) are indicate the methyl groups of POE segments. The FT-IR spectrum showed characteristic absorptions at 1722 cm^{-1} ($-\text{CO}-\text{O}-$, vs), 1578 cm^{-1} ($-\text{CO}-\text{NH}-$, w), and a broad absorption at 1122 cm^{-1} ($-\text{C}-\text{O}-\text{C}-$, vs). However, another possible absorption for amide

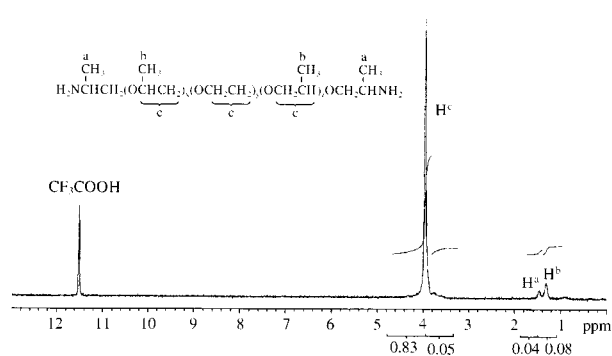


Figure 5. ^1H NMR spectrum of poly(propylene glycol)-block-poly(ethylene glycol)-block-poly(propylene glycol) bis(2-aminopropyl ether) with a M_w of 2,000.

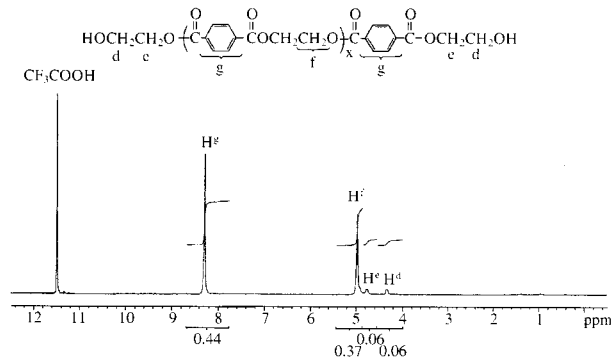


Figure 6. ^1H NMR spectrum of BHET.

at $1650\text{--}1680\text{ cm}^{-1}$ is not observed due to the overlap with the broad absorption of the ester functionality. For comparison, the chemical shifts of ^1H NMR spectra of the starting POE-diamine and bis-hydroxyethyl terephthalate (BHET, PET oligomer) are shown in Figures 5 and 6. Samples were measured using trifluoroacetic acid solvent. In the spectrum of POE-diamine, two types of methyl groups at the integration ratio of 2/1 at $\delta = 1.46$ and 1.32 ppm are assigned to the terminal 2-amino-propyl and the oxypropyl functionalities. This result is roughly consistent with the structure assignment in Figure 1 provided by the manufacturer. However, the molar ratio of oxyethylene to oxypropylene is not in good agreement with the assigned structure, perhaps due to poor integration. The POE-amine modified PETs have ^1H NMR spectra, showing $\delta = 3.80\text{--}4.10$ ppm for methylene and methine in ED-2001 segments, $\delta = 4.25\text{--}4.40$ and $4.70\text{--}4.85$ ppm for terminal oxyethanol, $4.85\text{--}5.05$ ppm for oxyethylene repeating units and $8.20\text{--}8.40$ ppm for aromatic protons. However, the chemical shift of the methyl group ($\delta = 1.30\text{--}1.50$ ppm) is not obvious in the lower content (6.6 wt%) but is observed

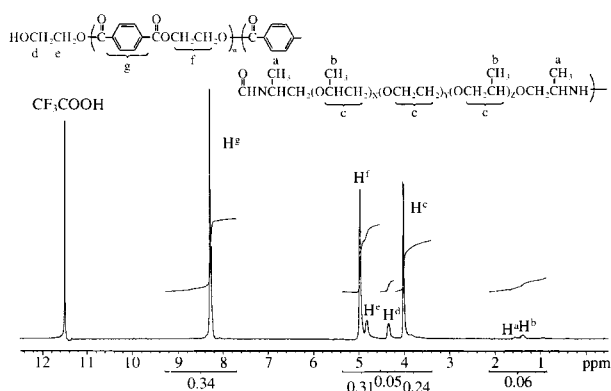


Figure 7. ^1H NMR spectrum of POE amide (16 wt%) segmented poly(ethylene-terephthalate).

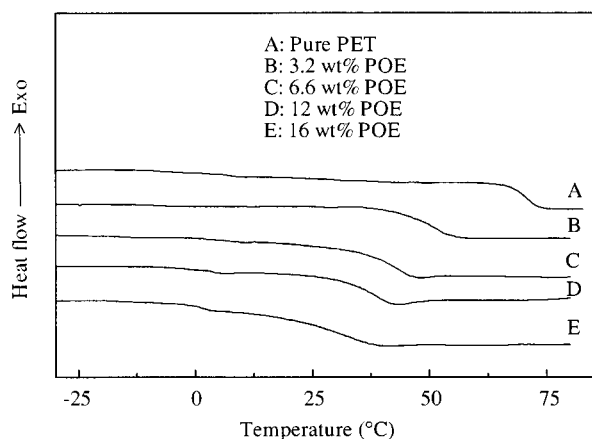


Figure 8. DSC heating scans of PET and polyether-ester-amide copolymers containing various amounts of POE segments.

in the higher content (16 wt%, Figure 7) of POE amide segmented PET. The thermal properties of these polyether-ester-amides are summarized in Table II. With the addition of poly(oxyethylene) (POE) diamine (average molecular weight of 2,000) in the amounts of 3.2, 6.6, 12 and 16 wt%, the melting points of these polymers dropped accordingly, from 240 to around 227 °C, and the melting enthalpy dropped accordingly, from 41.9 to around 33.3 J/g. However, the T_c of these polyether-ester-amides are higher than that of unmodified PET, indicating the fast nucleation caused by the presence of amide functionalities. The T_{gs} of these products were observed clearly by quenching the sample from melt to -120 °C to minimize the crystallinity. The heating thermograms of the polyether-ester-amides are shown in Figure 8. Only one glass transition was found in all the polyether-ester-amides. These results indicate that the large degree of phase separation between the POE soft segment and the PET hard segment in polyether-ester-amides does not occur. With the addition of POE diamines in the

Table II. Thermal properties of polyether-ester-amide^(a) copolymers.

DSC analyses	Hydrophilic component Poly(oxyethylene-oxypropylene)diamine ^(b)				
	0 wt%	3.2 wt%	6.6 wt%	12 wt%	16 wt%
T_c (°C)	159.9	181.0	179.2	168.5	163.0
ΔH_c (J/g)	-45.1	-43.6	-42.9	-38.5	-36.7
T_m (°C)	250.0	240.0	235.6	233.9	226.7
ΔH_m (J/g)	43.1	41.9	40.9	35.6	33.3
T_g (°C)	70.1	50.0	40.8	35.3	30.5

(a) Prepared by copolymerization of terephthalic acid, ethylene glycol and hydrophilic monomer.

(b) Poly(oxyethylene-oxypropylene)diamine of 2,000 M_w : Jeffamine[®] ED-2001.

Table III. Surface resistivity of polyether-ester-amide^(a) at various degrees of copolymerization.

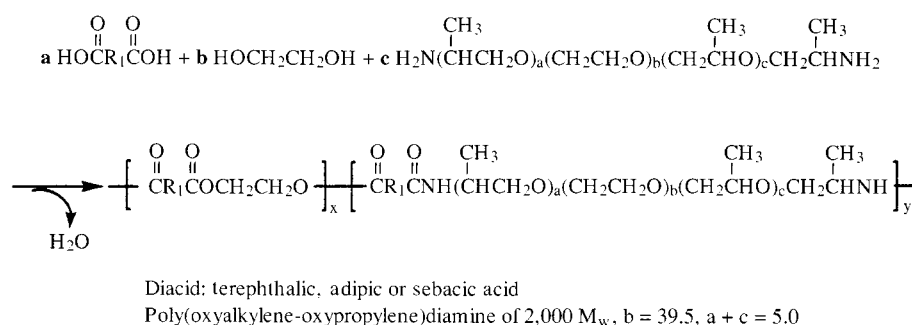
POE amide component (wt%)	Reaction time (hr)	Surface resistivity (ohm/sq)	Intrinsic viscosity (dL/g)
3.2	16	4×10^{10}	0.65
3.2	10	2×10^{10}	0.55
3.2	6	2×10^9	0.32

(a) Prepared from bis-hydroxyethyl terephthalate (BHET)+ethylene glycol+Jeffamine[®] ED-2001 under 250–260 °C, reduced pressure, and varied reaction time.

amounts of 3.2, 6.6, 12 and 16 wt%, their T_{gs} dropped accordingly, from 50.0 to around 30.5 °C. It appears that the incorporation of the flexible POE segment enhances the segmental mobility and lowers the crystallinity of the modified PET.

2. Effect of molecular weight on surface electronic resistivity

The reaction profile during the copolymerization of the POE diamine (i.e., Jeffamine[®] ED-2001), ethylene glycol and BHET produced materials having an intrinsic viscosity ranging from 0.32 to 0.65 (Table III). With the incorporation of 3.2 wt% of POE component in the backbone, the prepared copolymers exhibited decreasing surface resistivities from 4×10^{10} to 2×10^{10} and 2×10^9 ohm/sq according to the behavior of intrinsic viscosity. Apparently, the surface electronic conductivity of a polymer is inversely related to the increase of molecular weight according to the Mark-Houwink-Sakurada equation $[\eta] = KM^\alpha$. This is better explained by the degree of polymer mobility in a molecular level. In other words, the analogous polymer of smaller molecular weight has a higher degree of mobility and hence the freedom of dissipating electrostatics within the structural domain.

**Scheme 1.** Copolymerization of diacid, ethylene glycol and poly(oxyalkylene) diamine.**Table IV.** Surface resistivity of polyether-ester-amide and polyether-ester copolymers^(a).

	Poly(oxyethylene-oxypropylene)diamine ^(b) (2,000 M _w)					PEG-2000 ^(c)		Triethyleneglycol diamine ^(d)
	0 wt%	3.2 wt%	6.6 wt%	12 wt%	16 wt%	16 wt%	25 wt%	20 wt%
Resistivity (ohm/sq)								
After 1 day	> 10 ¹³	3 × 10 ¹¹	2 × 10 ¹¹	2 × 10 ¹¹	2 × 10 ¹⁰	2 × 10 ¹¹	2 × 10 ¹⁰	> 10 ¹³
After 3 months	–	–	–	1 × 10 ¹⁰	1 × 10 ¹⁹	5 × 10 ¹⁰	5 × 10 ¹⁹	6 × 10 ¹¹
After 6 months	–	1 × 10 ¹²	2 × 10 ¹¹	1 × 10 ¹⁰	8 × 10 ⁸	2 × 10 ¹⁰	2 × 10 ⁹	1 × 10 ¹²
Intrinsic viscosity (dL/g)	–	0.65	0.65	0.65	0.65	0.15	0.15	0.15

(a) Prepared by copolymerization of terephthalic acid, ethylene glycol and hydrophilic monomer.

(b) Poly(oxyethylene-oxypropylene)diamine of 2,000 M_w; Jeffamine[®] ED-2001.(c) PEG-2000: Poly(ethylene glycol) of 2,000 M_w.(d) Triethyleneglycol diamine of 148 M_w; Jeffamine[®] EDR-148.

3. Effect of weight content and segmental length of poly(oxyethylene)amine on surface electronic resistivity

In order to understand the effect of a hydrophilic component in block PET on polymer surface resistivity, a series of polyether-ester-amides was prepared. Summarized in Table IV, the hydrophilic components included the monomers of ED-2001, PEG-2000 and EDR-148. The surface resistivity of prepared polyether-ester-amide was actually affected by the presence of the POE amide segment. Poly(ethylene terephthalate), prepared from TPA and ethylene glycol, is considered to be an insulating material, with a surface resistivity of 10¹²~10¹³ ohm/sq. With the addition of a hydrophilic comonomer, such as POE diamines or diol, the resultant polyester-ether-amides had a significantly lower surface resistivity. The drop in resistivity is proportionally correlated to the weight of the incorporated hydrophilic segment, as shown in Table IV. At a similar level of intrinsic viscosity, the surface electronic resistivity dropped accordingly from 1×10¹², 3×10¹¹, 2×10¹¹ to 2×10¹⁰ ohm/sq, with an increase in the amount of incorporated POE diamine, from 3.2, 6.6, 12 to 16 wt%. In comparison, PEG-2000 was less effective in lowering resistivity (2×10¹¹ ohm/sq

for 16 wt%). The difference is attributed to the presence of amide groups which facilitate the hydrogen bonding formed for POE diamine incorporated polymers. For further comparison, the polymer having POE diamide segments at 16 wt% content possesses surface resistivity properties similar to the polymer having 25 wt% PEG composition.

The ineffectiveness of the triethyleneglycol diamine (i.e., Jeffamine[®] EDR-148, M_w at 148) addition was unexpected. This polyether-ester-amide containing as high as 20 wt% of triethyleneglycol diamine had a surface resistivity ranging from 1×10¹³ to 6×10¹¹ ohm/sq, depending on the ageing conditions. In comparison to the polyester-ether-amides prepared from 2,000 molecular weight of POE diamine, the polymers made from 148 molecular weight of diamines had a higher number of amide groups in the polymer strands. The hydrophilicity of a polymer appears to be more related to the intrinsic moisture absorption and the mobility and not necessarily solely related to the total weight of the POE composition. The length of the polyether groups contributes to the polymer segmental mobility. POE diamines that are too short may cause a rigid crystalline structure due to the abundance of amide hydrogen bonds.

Table V. Moisture absorption of polyether-ester-amides^(a) under 50% relative humidity at room temperature.

Duration (Day)	Hydrophilic component Poly(oxyethylene-oxypropylene)diamine ^(b)			
	0 wt%	3.2 wt%	6.6 wt%	12 wt%
	Water absorption (%)			
1	–	0.25	0.44	0.61
2	–	0.27	0.45	0.63
3	–	0.27	0.46	0.65
4	–	0.27	0.46	0.65
30	0.40	0.68	0.70	0.96
60	0.40	0.68	0.70	0.96

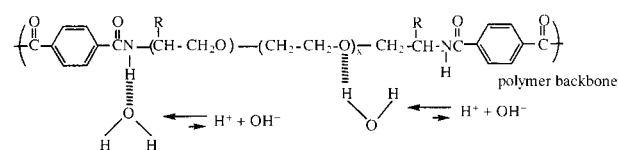
(a) Prepared by copolymerization of terephthalic acid, ethylene glycol and hydrophilic monomer.

(b) Poly(oxyethylene-oxypropylene)diamine of 2,000 M_w ; Jeffamine[®] ED-2001.

4. Effect of poly(oxyethylene)amine on water absorption

As-spun polyether-ester-amide fibers with the same diameter (250 d/f) were made by a conventional melt spinning procedure. The melt-spinning equipment consisted of a single-screw extruder attached to a metering pump. The spinning temperature was 280~290 °C. The spinning dope was homogeneously transferred to a spinneret by a gear pump. The extruded fiber was cooled by quenching with air and then taken up on a godet roll to minimize fiber movement and vibration. The incorporation of POE diamide segments into PET seemed not to influence its spinning ability. The as-spun fibers were cut into identical lengths, subjected to a vacuum oven at 110 °C to remove water and then maintained in an atmosphere of 50% relative humidity under room temperature. The differences in weights were indicated by water absorption (Table V). In general, the moisture weight gains reached equilibrium quickly after 2 days, and then become very slow but reached a constant after 30 days. It appears that water may be absorbed quickly on the fiber surface during the first exposure, after which it gradually penetrates into the inner fiber structures in a much slower manner. The water absorption increased from 0.27, 0.46 to 0.65% after 3 days, in response to the amount of incorporated POE diamine increasing from 3.2, 6.6 to 12 wt% accordingly. Significantly, a weight gain of 0.96% was observed for 12 wt% of poly(oxyethylene)diamine modified polyether-ester-amides in comparison to only 0.40% for the unmodified PET after 30 days. The difference is believed to be significant enough for improving the comfort factor in fibers.

Based on the above observations, the presence of a high molecular weight of POE segments and amide functionalities is responsible for the increased

**Figure 9.** Mechanism for lowering the resistivity of polymer surfaces via H-bonding formed with moisture.

hydrophilicity of polymers, demonstrated by the surface resistivity and also by the ability to absorb moisture from the atmosphere. A mechanism for lowering surface resistivity by moisture absorption on polymer surfaces through hydrogen bonding is suggested and depicted in Figure 9. The partial ionization of water into H^+ and OH^- promotes electronic conductivity. The comparative results of using various POE amines and PEG-2000 as comonomers demonstrated the importance of the poly(oxyethylene)-containing amide segments, facilitating hydrophilicity due to the low energy barrier for C-O bond rotation and its high affinity for water. When these polyether-ester-amides were physically mixed at 5~16 wt% with commercial PET polyester, the resulting materials also possessed moisture absorbing and electrostatic dissipating properties. Incorporation of POE diamide segments into PET generated polyether-ester-amides with relatively low electronic resistivities and low melting points. Practical applications of adding such polyether-ester-amides to PET fibers and other polymers to improve their antistatic and hyroscopic properties are suggested.

Conclusion

Incorporation of poly(oxyethylene) segments into poly(ethylene terephthalate) generated a family of polyether-ester-amides with relatively low electronic resistivities and low melting points. The surface electronic resistivity was generally decreased as the weight of incorporated POE segments increased. Structural variations, such as POE length, crystallinity, and the presence of amide in forming hydrogen bonds, can affect surface hydrophilicity. The presence of hydrophilic poly(oxyethylene) ($-CH_2CH_2O-$) groups in the polymer backbone enhances their moisture affinity and polymer flexibility. The 2000 molecular weight of POE diamine was more effective than the diamine at 148 molecular weight due to the differences in the flexibility of the polymer backbone. Comparing POE diamine and PEG-2000 at 16 wt% in polymers and demonstrating the resistivity difference of 8×10^8 vs. 2×10^{10} ohm/sq (6 month standing samples) show that the

presence of amide groups can enhance the hydrophilic property without affecting the polymer rigidity. A mechanism involving hydrogen bonding is suggested.

References

1. I. Piirma, *Polymeric Surfactant*, Surfactant Science Series 34, Marcel Dekker, Inc., 1992.
2. *Polymer Electrolyte Reviews 1 and 2*, J. R. MacCallum and C. A. Vincent Ed., Elsevier Applied Science, London, 1987 and 1989.
3. *Electrochemical Science and Technology of Polymers I*, R. G. Linford Ed., Elsevier Applied Science, London, 1987.
4. *Application of Electroactive Polymers*, B. Scrosati Ed., Chapman & Hall, London, 1993.
5. *Poly(Ethylene Glycol) Chemistry: Biotechnical and Biomedical Applications*, J. M. Harris Ed., Plenum Press, New York, 1992.
6. *Nonionic Surfactants - Polyoxyalkylene Block Copolymers*, V. M. Nace Ed., Marcel Dekker, Inc., 1996.
7. A. T. Hu, R. S. Tsai and Y. D. Lee, *J. of Appl. Polym. Sci.*, **37**, 1863 (1989).
8. G. P. Speranza and C. S. Henkee, U. S. Pat. 5,324,812 (1993).
9. C. Yang and J. F. Rathman, *Polymer*, **37**, 4621 (1996).
10. D. E. Fenton, J. M. Parker and P. V. Wright, *Polymer*, **14**, 589 (1973).
11. R. Gachter and H. Muller, *Plastics Additives Handbook*, Hanser Publishers, Munich Vienna New York, 1984.
12. L. V. Interrante, L. A. Casper, and A. B. Ellis, *Materials Chemistry, An Emerging Discipline*, Advances in Chemistry Series 245 by The American Chemical Society Publishers Ltd, 1995.
13. B. Lee, U. S. Pat. 5,237,009 (1993).
14. M. Y. Young and J. J. Lin, *Ind. Eng. Chem. Res.*, **37**, 4284 (1998).
15. K. Okazaki, A. Nakagawa and K. Sugii, U. S. Pat. 3, 558,419 (1971).
16. E. Gosselink and F. Diehl, E. P. Pat. No. 24198A2 (1987).
17. H. E. Wixon, E. P. Pat. No. 456569A1 (1991).
18. D. K. Gilding and A. M. Reed, *Polymer*, **20**, 1454 (1979).
19. T. Fukumoto, K. Yano and M. Iwamoto, U. S. Pat. 5, 096,995 (1992).