Electrostatic dissipation and flexibility of poly(oxyalkylene)amine segmented epoxy derivatives

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Abstract: A family of hydrophilic and flexible epoxy polymers was prepared from the reaction of poly(oxyalkylene)amines and diglycidyl ether of bisphenol-A (DGEBA) at 1:1 molar ratio of N—H to epoxide. The use of a high molecular weight ($M_W = 1000$–6000) poly(oxyethylene–oxypropylene)amine and a low M_W amine as curing agents provided epoxy materials with good properties in toughness and hydrophilicity. The hydrophilicity, probed by surface resistivity of these cured materials, was found to be affected by the nature and weight content of poly(oxyethylene) segment in the polymer backbone, and also by the degree of crystallinity. Specifically, in the presence of a water-soluble poly(oxyethylene–oxypropylene)diamine of M_W 2000 the cured epoxies can reach surface resistivity as low as $10^{8.6–9.6}\,\Omega/\square$. In comparison, the water-insoluble poly(oxypropylene)diamine of M_W 2000 afforded a higher surface resistivity of $10^{10.5}\,\Omega/\square$ because of the difference in hydrophilicity between oxyethylene and oxypropylene functionalities. Poly(oxypropylene)diamine of M_W 230 as the sole curing agent generated an epoxy with even higher surface resistivity of $10^{13}\,\Omega/\square$ due to a highly crosslinking structure. With proper selection of mixed poly(oxyethylene–oxypropylene)diamine (25 wt%) and 2-aminoethanol (9 wt%), the DGEBA cured polymer had an appropriate surface resistivity of $10^{9.8}\,\Omega/\square$ for antistatics. Moreover, this material was extremely ductile in appearance and showed over 500% elongation at break during mechanical tests. The high flexibility is rationalized by the balanced chemical structure of poly(oxyalkylene) segments and bisphenol-A distributed in a slightly crosslinked system.
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INTRODUCTION

Epoxy materials are versatile for many industrial applications, including coating, structural decoration and electronic encapsulation.[1–3] In general, epoxy resins are viewed as crosslinked thermosets which have good adhesion and also good resistance to chemicals, moisture, heat and electricity. For some applications that require flexibility, poly(oxypropylene)-backboned epoxy resins or polyetheramine curing agents are generally used in the curing formulations.[3] Previously, we reported a flexible epoxy system using poly(oxypropylene)diamine-derived amindoamines as curing agents.[4] These flexible aromatic poly(oxyalkylene)–amindoamines were prepared from commercially available poly(oxypropylene)diamines and alkyl-substituted aromatic acids such as *t*-butyl isophthalic acid. The structures were designed by taking into consideration the balance between aromatic (rigid) and polyether/alkyl (flexible) functionalities in the molecule. The flexibility can be correlated with the structure and molecular weight of the starting poly(oxyalkylene)amines. Recently, it was found[5] that the nature of poly(oxyalkylene)amines could affect the

hydrophilicity of the resulting polymers. The hydrophilic nature of poly(oxyethylene) segments in polymers together with their segmental length are important factors affecting the surface moisture absorption ability and consequently the surface electric resistivity. These polymers are potentially useful for polymeric electrolytes[6–8] and antistatics.[9–11] Based on these observations, one can design the syntheses of poly(oxyethylene) segmented epoxies which have a wide spectrum of properties in flexibility and hydrophilicity.

Generally, the applications of epoxy materials require high electrical resistivity, in the range of $10^{11–16}\,\Omega$ cm in volume resistivity. Toughening epoxy materials by networking them with rubbers[12–14] or thermoplastics[15–17] has been an important research subject. Epoxy blended with exfoliated inorganic clays to improve thermal and other properties was considered an advanced nanocomposite.[18,19] However, epoxy materials of flexible and low surface resistivity are seldom reported.[5] The materials are predicted to have important applications in coatings for electronic devices. Electrostatic dissipation is required for ad-

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vanced materials, particularly in housing and packaging for electronic devices.[20,21] Polymers with low surface resistivity are capable of preventing the accumulation of electrostatic charges.

In this paper, we report the preparation of a family of novel epoxy materials. Some of the epoxies prepared are extremely ductile, of good structural integrity, and potentially useful for antistatic coatings. Particularly, a series of commercially available poly(oxyethylene–oxypropylene)amines with an average M_W of 2000 were employed as curing components. A second amine of low M_W also had to be added to generate epoxy polymers of both high flexibility and hydrophilicity. The structural variations in the degree of crosslinking, network versus comb-like shapes, together with the length of poly(oxyalkylene) segments are all correlated with electrostatic charge dissipation ability and mechanical properties.

EXPERIMENTAL
Materials
Liquid diglycidyl ether of bisphenol-A (DGEBA, trade name BE-188) with an epoxide equivalent weight (EEW) of 188 was obtained from Nan-Ya Chemical of Taiwan. 2-Aminoethanol (or monoethanol amine, MEA) and 2-(2-aminoethoxy)ethanol (or diethylene glycol amine, DGA) were purchased from Aldrich Chemical Co. A family of commercially available poly(oxyethylene-oxypropylene)amines, namely Jeffamine® Amines,[22,23] was purchased from Huntsman Chemical Co. They included poly(propylene glycol)bis(2-aminopropyl ether) of approximate M_W 230 400 and 2000, poly(ethylene glycol)bis(2-aminopropyl ether) of approximate M_W 2000 and 6000 and methoxypoly(oxyethylene–oxypropylene)-2-propylamine of approximate M_W 1000 and 2000. The chemical structures of these poly(oxyethylene)- and poly(oxypropylene)-based amines are drawn in Fig 1.

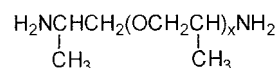## General procedures for the preparation of poly(oxyalkylene)-containing epoxy materials
Network structures
To a mixture of poly(oxyethylene–oxypropylene)-diamine of various approximate M_Ws including 230, 400, 2000 and 6000, in a beaker, was added a stoichiometric amount of DGEBA, based on an epoxide to N—H equivalent ratio of 1.0. The mixture was thoroughly stirred and poured into a flat aluminium-foil mould. placed under vacuum, and heated at 60 °C for 2h, 120 °C for 4h, and in several cases, post-cured at 160 °C for 2h. These samples were cooled to ambient temperature and conditioned overnight in an atmosphere with 50 % relative humidity.

Hybrid network and comb-like structures
To a mixture of methoxy poly(oxyethylene–oxypropylene)-2-propylamine of M_W 1000 or 2000 and a low M_W diamine such as poly(propylene glycol)bis(2-
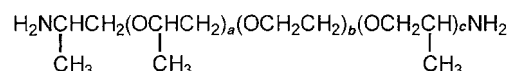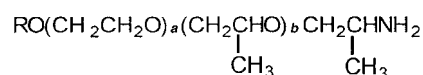
Figure 1. Chemical structures of poly(oxyalkylene)amines.

aminopropyl ether) of M_W 230 or 400, in a beaker, was added a stoichiometric amount of DGEBA based on an epoxide to N-H equivalent ratio of 1.0. The mixture was thoroughly stirred and poured into an aluminium mould, placed under vacuum, and heated at 60 °C for 2h, 120 °C for 4h, and optionally post-cured at 160 °C for 2h. The cured plaque was conditioned overnight in an atmosphere of 50 % relative humidity.

Comb-like structures
A mixture of methoxy poly(oxyethylene–oxypropylene)-2-propylamine of M_W 1000 or 2000 a low M_W monoamine such as 2-aminoethanol or 2-(2-aminoethoxy)ethanol and a stoichiometric amount of DGEBA, in a beaker, was thoroughly stirred. A sample plaque was obtained after being cured and conditioned under the same conditions as described above.

Measurements
Surface resistivity was measured by using a ST-3 Model (Simco Co) tester according to the ASTM method D257-93. The measurement is in the unit of ohm/square or $\Omega/\square$ (the size of square is immaterial). The heat analysis was carried out by a Seiko SII model SSC/5200 differential scanning calorimeter (DSC) from Seiko Instruments and Electronics Ltd. The size of the samples was approximately 5–8 mg on sealed aluminium pans. The analyses were performed at a heating rate of 10 °C min^{-1} in 30 ml min^{-1} flowing nitrogen atmosphere. The heat of melting (ΔH) was determined by integration of the peak area under the
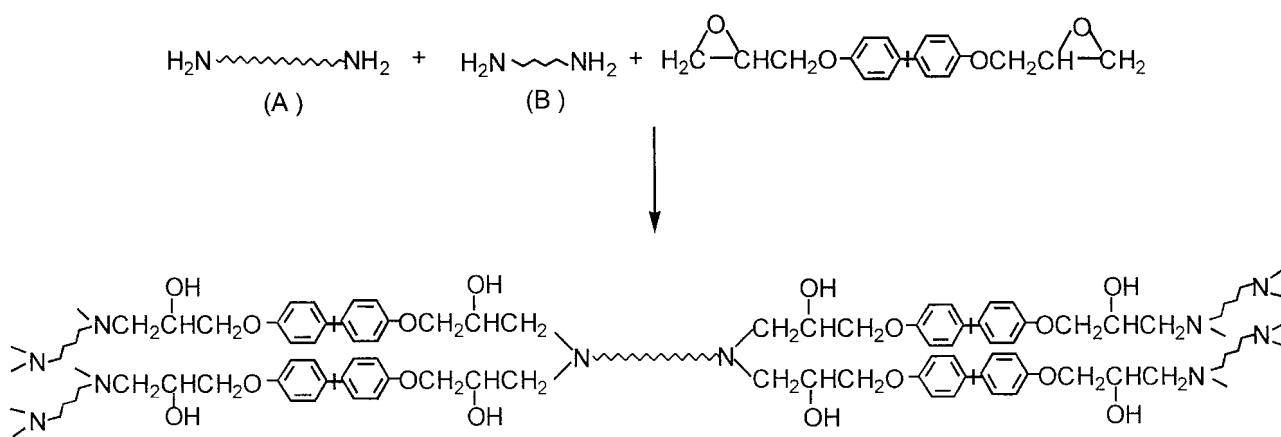
Scheme 1. Crosslinked cured epoxy polymers prepared from poly(oxyalkylene)diamines and DGEBA. (A) poly(oxyethylene)diamine ($M_W \approx 2000$); (B) poly(oxypropylene)diamine ($M_W \approx 230$).

linear baseline, and the peak value of the thermogram was reported as the melting point (T_m). Glass transition temperature (T_g) was recorded at the half-height of the corresponding heat capacity jump. Tensile properties of dog-bone shape specimens were measured using an Instron machine according to the ASTM method D638. These specimens were maintained in an atmosphere with 30% relative humidity for 1 week, and then measured at an average of seven specimen tests.

RESULTS AND DISCUSSION

The representative amine/epoxide reaction and the product structure of poly(oxyalkylene)diamine and DGEBA are described in Scheme 1. These epoxies were prepared by curing DEGBA with a set of amine mixtures. The equivalent of total N—H values to epoxide was always set at 1:1 molar ratio. The curing of epoxy resin with amine may proceed in the following possible reactions: primary amine-epoxy, secondary amine-epoxy, and hydroxyl-epoxy curing processes. The degree of these curing reactions is mainly determined by the molar ratio of amine to epoxy[24] and also the curing conditions.[25] It was reported that primary amine curing could be faster than secondary amine or alcohol curing.[26] In these cured systems, it is assumed that primary and secondary amine curing processes are predominant. Hydroxide curing is considered as a post-curing process with the excess epoxide present in the system.

By varying the structure of the two mixed amines, one can obtain a series of cured epoxy polymers with random or block distribution of poly(oxyalkylene) segments. Crosslinked network structures are obtained by using a poly(oxyalkylene)diamine with four N—H functionalities, while comb-like structures are derived from a monoamine of two N—H groups. By proper selection of different segmental M_W values of the poly(oxyalkylene)amines and a balanced amount of low M_W amines, the relative crosslinked density can be controlled.

Poly(oxyethylene)amines are more hydrophilic than poly(oxypropylene)amines. Poly(oxyethylene)amines are commonly soluble in water while poly(oxypropylene)amines of M_W over 400 are water-insoluble. A series of commercially available poly(oxyethylene–oxypropylene)diamines was allowed to react with DGEBA to prepare electrostatic dissipating and hydrophilic epoxy materials. These epoxies are poly(tertiary-amine)s with bisphenol-A moieties and 2-hydroxypropyl linkages, as shown in Scheme 1.

Poly(oxyalkylene)-segmented epoxies with network structures

Epoxies involving poly(oxypropylene)diamine of approximate M_W 230

When a diamine is employed, the four N—H groups in the molecule tend to form a crosslinked structure, depicted conceptually in Fig 2. Poly(oxypropylene)-diamine with an average M_W of 230 (D-230) afforded an epoxy material of $10^{>12}\Omega/\square$. With the addition of poly(oxyethylene–oxypropylene)diamine of approximate M_W 2000, the cured epoxies had lower surface resistivities due to the increase in hydrophilicity. As shown in Table 1, the hydrophilicity or the surface resistivity is generally correlated with the weight percentage of poly(oxyethylene) segments in the
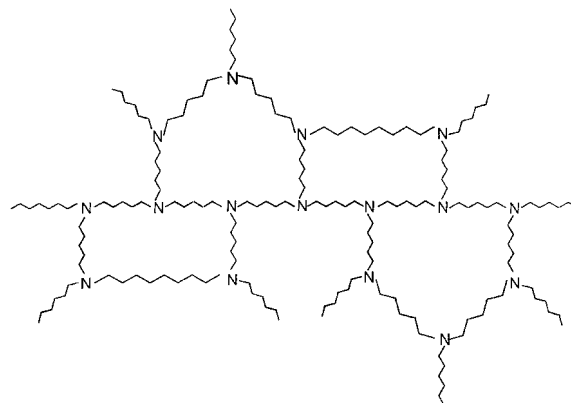

Figure 2. Schematic structure of crosslinked epoxy polymers.

Epoxy resin	Composition (wt %)				$\Omega/\square$
	ED-6000[a]	ED-2001[b]	D-230[c]	D-400[d]	(10^x)
0	100	0	0	0	9.8
11	89	0	0	0	9.4
19	78	0	3	0	9.8
31	62	0	7	0	9.5
39	50	0	11	0	9.7
50	35	0	15	0	9.7
77	0	0	23	0	>12
27	0	73	0	0	8.6
36	0	60	4	0	8.8
43	0	50	7	0	9.6
43	0	50	7	0	9.6 (9.5[e])
43	0	50	7	0	9.6 (9.5[f])
53	0	35	12	0	10.0
60	0	25	15	0	10.4
77	0	0	23	0	>12
32	0	64	0	4	8.6
39	0	51	0	10	8.5
49	0	32	0	20	9.5
52	0	25	0	23	10.5
65	0	0	0	35	>12

[a] Poly(ethylene glycol) bis(2-aminopropyl ether) of $M_w \approx 6000$.
[b] Poly(ethylene glycol) bis(2-aminopropyl ether) of $M_w \approx 2000$.
[c] Poly(propylene glycol) bis(2-aminopropyl ether) of $M_w \approx 230$.
[d] Poly(propylene glycol) bis(2-aminopropyl ether) of $M_w \approx 400$.
All samples were cured at 60 °C for 2 h and 120 °C for 4 h, except that noted [e] which was additionally post-cured at 160 °C for 2 h or [f] at 180 °C for 2 h.

Table 1. Surface resistivity of poly(oxyalkylene)-segmented epoxies with network structures

polymers. For example, the surface resistivity decreased from $10^{>12}$ to $10^{8.6}$, when the proportion of ED-2001 increased from 25 to 73 wt%. However, in the case of 6000 M_W poly(oxyethylene)-rich diamine (ED-6000), for an increase from 35 to 78 wt% the cured polymers have a similar surface resistivity of $10^{9.7}\,\Omega/\square$. The poly(oxyethylene)-rich segments of M_W 6000 crystallize easily and are distributed in low crosslinked density. The DSC demonstrated high melting temperature (T_m, 54 °C) and melting energy (ΔH, 144 J g^{-1}) for pure ED-6000, in comparison with 37 °C (T_m) and 122 J g^{-1} (ΔH) for ED-2001. A T_m of 49 °C was observed in ED-6000 cured epoxy (Fig 3). The degree of crystallinity seems to be another factor controlling the surface hydrophilicity. The high degree of segmental crystallinity could reduce the mobility of polymer chains, and consequently increase the surface resistivity.

Epoxies involving poly(oxypropylene)diamine of approximate M_W 400

Similar to poly(oxypropylene)diamine of approximate M_W 230, an analogue of about 400 M_W also afforded an epoxy material of $10^{>12}\,\Omega/\square$ due to relatively high crosslinked density and hydrophobic nature. When the proportion of poly(oxyethylene)-rich diamine of 2000 M_W increased from 25 to 64 wt%, the surface resistivity of the cured polymers decreased from $10^{10.5}$ to $10^{8.6}\,\Omega/\square$. A similar trend in surface resistivity is observed with epoxies prepared using

poly(oxypropylene)diamine of 400 M_W as the second curing agent. The surface resistivity decreased with the addition of increasing amount of ED-2001 as a curing agent.

Poly(oxyalkylene)-segmented epoxies with hybrid network and comb-like structures
Epoxies involving poly(oxyethylene)diamine and monoamines
Mixtures of poly(ethylene glycol)bis(2-aminopropyl ether) of 2000 M_W, and a second monoamine were allowed to react with DGEBA. Their surface resistivities are summarized in Table 2. In the presence of 2-aminoethanol (MEA) or 2-(2-aminoethoxy)ethanol, a less crosslinked structure was prepared (Fig 4). In comparison with analogous crosslinked polymers, these materials had lower surface resistivities. For example, the polymers consisting of 2000 M_W hydrophilic segments in low crosslinked systems, afforded $10^{8.6}\,\Omega/\square$ for 50 wt% of ED-2001 and $10^{9.8}\,\Omega/\square$ for 25 wt% of ED-2001 in the MEA system. For comparison, the higher resistivities of $10^{9.6}$ and $10^{10.4}\,\Omega/\square$ were observed, respectively, for crosslinked systems using the diamines shown in Table 1. The epoxies prepared from 25 wt% of poly(oxyethylene)amine of 2000 M_W appeared to be extremely ductile; their tensile properties are shown in Table 3. In particular, the cured epoxy polymers involving poly(oxyethylene)-rich diamine (25 wt%) of approximate M_W 2000 and 2-amionethanol (9 wt%) exhibited over 500 %
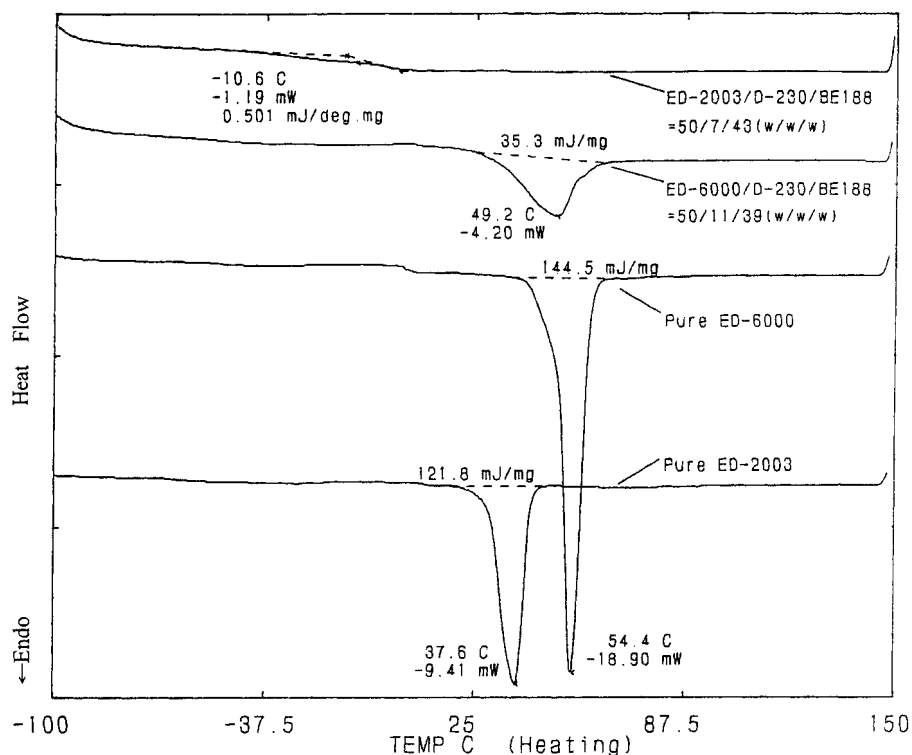
Figure 3. DSC thermograms of poly(oxyethylene)diamines and their derived epoxies.

strain at break under the faster testing rate (50 mm min^{-1}), and at the lower testing rates (5 and 10 mm min^{-1}) this material was not ruptured at all during the test. After being released from the stress,

the material itself rapidly recovered its original length and shape. This epoxy material of high resilience behaved just like an elastomer. The presence of poly(ethylene glycol) bis(2-aminopropyl ether) at a

Epoxy resin	ED-2001	MEA[b]	DGA[c]	D-230	M-2070[d]	M-1000[e]	$\Omega/\square$ (10^x)
27	73	0	0	0	0	0	8.6
46	50	4	0	0	0	0	8.6
66	25	9	0	0	0	0	9.8
86	0	14	0	0	0	0	10.8
43	50	0	7	0	0	0	8.6
61	25	0	14	0	0	0	9.7
77	0	0	23	0	0	0	10.8
16	0	0	0	0	84	0	X[f]
23	0	0	0	3	74	0	X
26	0	0	0	4	70	0	7.7
33	0	0	0	7	60	0	9.3
40	0	0	0	10	50	0	9.7
51	0	0	0	14	35	0	10.5
58	0	0	0	17	25	0	10.2
77	0	0	0	23	0	0	>12
28	0	0	0	0	0	72	X
43	0	0	0	7	0	50	8.1
54	0	0	0	11	0	34	8.9
60	0	0	0	15	0	25	9.0
77	0	0	0	23	0	0	>12

Table title (spanning): *Composition (wt%)*

[a] All samples were cured at 60°C for 2h and 120°C for 4h.

[b] Mono-ethanolamine or 2-aminoethanol.

[c] Diethylene glycol amine or 2-(2-aminoethoxy)ethanol.

[d] Methoxy poly(oxyethylene–oxypropylene)-2-propylamine of $M_w \approx 2000$.

[e] Methoxy poly(oxyethylene–oxypropylene)-2-propylamine of $M_w \approx 1000$.

[f] X, liquid product.

Table 2. Surface resistivity of poly(oxyalkylene)-segmented epoxies[a] with hybrid network and comb-like structures
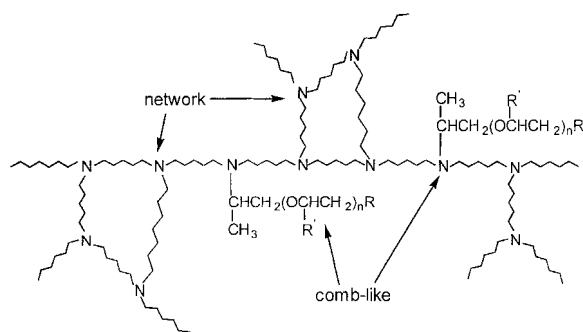
Figure 4. Schematic structure of hybrid network/comb-like epoxy polymers.

Figure 5. Schematic structure of comb-like epoxy polymers.

suitable ratio was required to exhibit this interesting property. The comparative poly(propylene glycol)diamine counterpart compound (D-2000), also at about 2000 M_W (25 wt%) and 2-aminoethanol (9 wt%) failed to produce elastomeric epoxies. This flexibility is rationalized by the balanced chemical structure of poly(oxyethylene) segment and bisphenol-A distribution in a slightly crosslinked system. The crystallinity of M_W 2000 poly(oxyethylene) segments might also be a factor contributing to elasticity. These samples were prepared under the same thermal history.

Epoxies involving poly(oxyethylene)monoamines and poly(oxypropylene) diamine

Two commercially available methoxy poly(oxyethylene–oxypropylene)-2-propylamine of approximate M_W 1000 (M-1000) or 2000 (M-2070) and a poly(oxypropylene)diamine of M_W 230 were allowed to react with DGEBA. The surface resistivities are recorded in Table 2. The epoxies prepared from M-1000 generally had lower surface resistivities than those prepared from M-2070: the difference between $10^{8.1}\,\Omega/\square$ by M-1000 (50 wt%) and $10^{9.7}\,\Omega/\square$ by M-2070 (50 wt%) was due to a higher oxyethylene/oxypropylene ratio in the M-1000 structure. In general, the comb-like structures with pendent poly(oxyethylene) segments had lower surface resistiv-
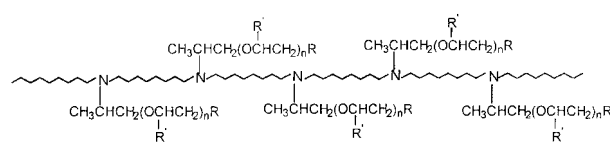
ities than those of the corresponding crosslinked network polymers. For example, in the case of 50 wt% hydrophilic poly(oxyethylene)-rich amine, a trend was observed for lower surface resistivity, from ED-2001/D-230 ($10^{9.6}\,\Omega/\square$) to ED-2001/D-400 ($10^{8.5}\,\Omega/\square$) to M-1000/D-230 ($10^{8.1}\,\Omega/\square$), in accordance with the decrease in crosslinked density.

Poly(oxyalkylene)-segmented epoxies with comb-like structures

The comb-like structures, as shown in Fig 5, can be prepared by using the combination of two monoamines as the curing agents for diepoxide. The surface resistivities (Table 4) are generally lower than those of the corresponding crosslinked materials (in Tables 1 and 2). For example, the results of $10^{8.1}\,\Omega/\square$ for 50 wt%. $10^{8.9}\,\Omega/\square$ for 35 wt% and $10^{9.0}\,\Omega/\square$ for 25 wt% of M_W 1000 methoxy poly(oxyethylene–oxypropylene)-2-propylamine are comparable with the hybrid M-1000/D-230 system and significantly lower than those of ED-2001/MEA or ED-2001/DGA. The use of the corresponding 2000 M_W monoamine afforded epoxies having higher surface resistivities than expected. Again, this is attributed to the difference in the ratio of oxyethylene and oxypropylene segments in the amines. Poly(oxyethylene) is more hydrophilic than poly(oxypropylene) because of affinity to water through hydrogen bonding. The length ratio of oxyethylene/oxypropylene is six for M-1000 and three for M-2070. The overall weight fraction of oxyethylene segment for M-1000 is higher than that for M-2070. It is evidenced again that the weight amount of poly(oxyethylene) segments in polymers is important for lowering surface resistivity.

Table 3. Tensile properties of cured epoxies

			Tensile properties [b]			
Composition [a]	Weight fraction	Speed (mm min^{-1})	Tensile strength (MPa)	Yield strength (MPa)	Strain at break (%)	Surface resistivity ($10^x\,\Omega/\square$)
D-2000/MEA/BE-188	25/9.2/65.8	5	16.3 ± 1.2	15 ± 0.5	117 ± 32	10.5
ED-2001/D-230/BE-188	25/15/60	5	1.3 ± 0.3	0.4 ± 0.0	95 ± 16	10.4
ED-2001/MEA/BE-188	35/7.2/57.8	5	1.4 ± 0.1	0.1 ± 0.0	218 ± 15	9.1
ED-2001/MEA/BE-188	25/9.2/65.8	5	–	0.6 ± 0.1	>500	9.8
ED-2001/MEA/BE-188	25/9.2/65.8	10	–	1.0 ± 0.0	>500	9.8
ED-2001/MEA/BE-188	25/9.2/65.8	50	19.5 ± 0.6	19.5 ± 0.6	656 ± 11	9.8
ED-2001/MEA/BE-188	15/11.1/73.9	5	21.8 ± 3.9	37.8 ± 1.1	100 ± 22	10.4

[a] BE-188, diglycidyl ether of bisphenol-A; D-2000, poly(propylene glycol) bis(2-aminopropyl ether) of $M_W \approx 2000$; ED-2001, poly(ethylene glycol) bis(2-aminopropyl ether) of $M_W \approx 2000$.
[b] Measured on an average of seven specimens.

Table 4. Surface resistivity of poly(oxyalkylene)-segmented epoxies with comb-like structures[a]

	Composition (wt %)				
Epoxy resin	M-2070	M-1000	MEA	DGA	$\Omega/\square$ (10^x)
16	84	0	0	0	X
44	50	0	6	0	X
57	35	0	8	0	9.1
65	25	0	10	0	10.8
76	12	0	12	0	10.5
86	0	0	14	0	10.8
41	50	0	0	9	X
52	35	0	0	13	9.2
60	25	0	0	15	9.8
77	0	0	0	23	10.8
28	0	72	0	0	X
38	0	60	2	0	X
46	0	50	4	0	X
66	0	25	9	0	8.5
43	0	50	0	7	8.1
54	0	35	0	11	8.9
60	0	25	0	15	9.0
77	0	0	0	23	10.8

[a] All samples were cured at 60 °C for 2 h and 120 °C for 4 h; see Table 2 for abbreviations.

Poly(oxyethylene) versus poly(oxypropylene)-segmented epoxies

To differentiate the relative hydrophilicity of poly(oxyethylene) versus poly(oxypropylene), comparative results are summarized in Table 5. Under similar crosslinked densities, the surface resistivities of epoxy materials involving their poly(oxyethylene)-rich diamine of 2000 M_W are generally lower than those of counterpart polymers involving poly(oxypropylene) diamine of M_W 2000. This result is noticeable in low crosslinked systems using MEA as second amine. A

Table 5. Surface resistivities of poly(oxyethylene) versus poly(oxypropylene)-segmented epoxies[a]

	Composition (wt %)				
Epoxy resin	ED-2001[b]	D-2000[c]	D-230	MEA	$\Omega/\square$ (10^x)
53	35	0	12	0	10.0
60	25	0	15	0	10.4
66	15	0	19	0	10.5
53	0	35	12	0	10.4
60	0	25	15	0	10.5
66	0	15	19	0	10.5
58	35	0	0	7	9.1
66	25	0	0	9	9.8
74	15	0	0	11	10.4
58	0	35	0	7	10.4
66	0	25	0	9	10.5
74	0	15	0	11	10.5

[a] All samples were cured at 60 °C for 2 h and 120 °C for 4 h.
[b] Poly(ethylene glycol) bis(2-aminopropyl ether) of $M_W \approx 2000$.
[c] Poly(propylene glycol) bis(2-aminopropyl ether) of $M_W \approx 2000$.

difference in surface resistivity of $10^{9.1}$ versus $10^{10.4} \Omega/\square$ was observed using 35 wt% of 2000 M_W amine and 7 wt% MEA. However, high crosslinking may overcome the nature of hydrophilicity of poly(oxyethylene) segments.
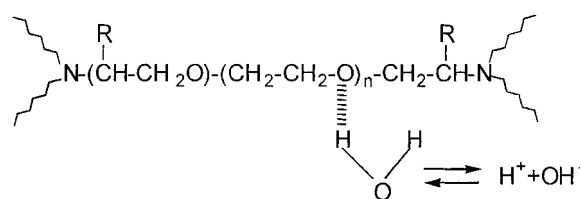
Proposed mechanism

The presence of poly(oxyethylene) segments, capable of absorbing moisture from the atmosphere, is responsible for the hydrophilicity of the polymers.[27] The mechanism for lowering surface resistivity is generally envisioned to be due to moisture absorption on the polymer surface through hydrogen bonding, as schematically depicted in Fig 6. Partial ionization of moisture promotes electronic conductivity. The hydrophilicity of a polymer is also related to the length, nature of poly(oxyalkylene) segments and mobility in crosslinked or comb-like networks.

Thermal properties

DSC thermograms of the cured epoxy polymers are shown in Figs 3 and 7. One can clearly observe the crystalline poly(oxyethylene) segments of ED-6000 amine in crosslinked network structures at $T_m = 49.2$ °C (Fig 3), whereas the poly(oxyethylene) segments of ED-2001 amine are not crystalline in crosslinked network structures. This is compared with T_m values of 54.4 °C for pure ED-6000 and 37.6 °C T_m for pure ED-2001. For the same proportion of poly(oxyethylene) segments, the glass transition temperature (T_g) is higher, according to their crosslinking densities, ie network structures > hybrid network and comb-like structures > comb-like structures (Fig 7). Furthermore, these materials have more than one transition, implying the existence of complicated structures. These data support the crystallinity factor contributing to the observed surface resistivity.

CONCLUSIONS

Three classes of poly(oxyalkylene)-segmented epoxy materials, including network, network/comb-like and comb-like structures, were prepared from the reaction of various poly(oxyalkylene)amines and DGEBA. Their hydrophilicity and electrostatic dissipating ability, measured by their surface resistivity, correlate well with the weight amount and the length of the poly(oxyethylene) segments in the polymers. In general, the epoxies of comb-like structure exhibited lower surface resistivity than that of the networks,

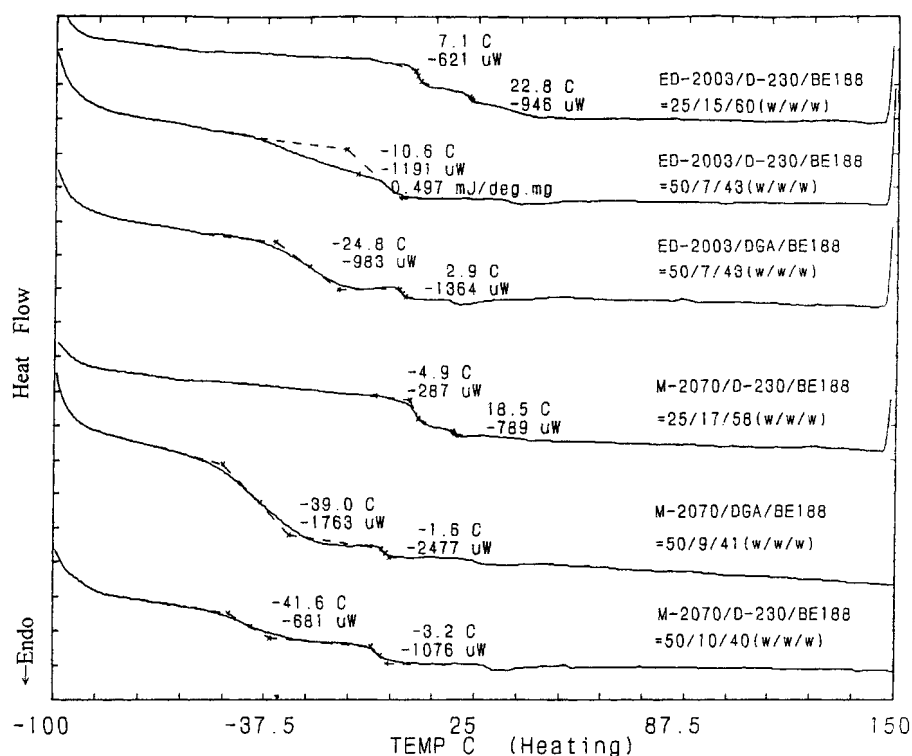**Figure 6.** Proposed mechanism for lowering surface resistivity of polymers.

Figure 7. DSC thermograms of poly(oxyethylene)amine derived epoxies with different degrees of crosslinking.

perhaps due to the ease of poly(oxyethylene) segmental mobility. The high degree of crystallinity adversely affected surface resistivity, as demonstrated by the poly(oxyethylene)amine of M_w 6000. The presence of hydrogen bonding caused by the poly(oxyethylene) groups is rationalized for the lowering of the surface resistivity. With judicial selection of amine compositions involving a proper balance of high M_w (about 2000) of poly(oxyalkylene) diamines (25 wt%) and low M_w of 2-aminoethanol (9 wt%), an extremely ductile epoxy polymer having an unusual mechanical property of 500 % strain at break was prepared.

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