

Morphologies and Properties of Cured Epoxy/Brominated-phenoxy Blends

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ABSTRACT: Morphologies of cured epoxy/brominated-phenoxy blends were observed by scanning transmission electron microscopy (STEM) and energy dispersive X-ray fluorescence spectroscopy (EDX). When brominated-phenoxy content was 30 wt %, cocontinuous phase structures between cured epoxy and brominated-phenoxy were found. Since every loss tangent ($\tan \delta$) curve as a function of temperature on dynamic mechanical analysis (DMA) showed 2 peaks at 128°C and 155°C respectively, cured epoxy phases and brominated-phenoxy phases were incompatible together and T_g s of cured epoxy phases were not

decreased. Tensile strength and tensile elongation of the cured blends were increased together. T-peel adhesion strength and the lap-shear adhesion strength were also increased together. These phenomena could be due to the cocontinuous structures consisted by the rigid cured epoxy phases of thermosets and ductile the brominated-phenoxy phases of thermoplastics. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1702–1713, 2007

Key words: epoxy; phenoxy; morphology; polymer blends; adhesives; flexible printed circuits

INTRODUCTION

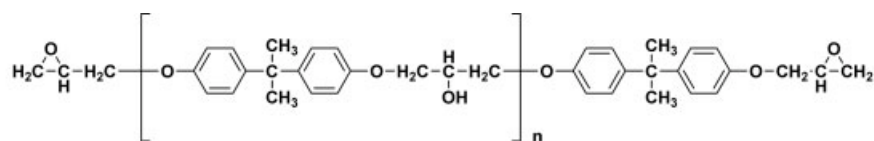
Epoxy resins have been used widely as matrices for composite materials and as structural adhesives.^{1–7} However, since cured epoxy resins are brittle, poor toughness and low T-peel adhesion strength have been pointed out as disadvantages. The addition of rubbers to epoxy resins has been investigated to enhance the above disadvantages.^{8–16} Rubber-added epoxy resins usually result in lowering glass transition temperature (T_g) and thermal stability.

Recently, cured epoxy-containing phenoxy as one of thermoplastics has been investigated by a lot of researchers because phenoxy is a thermoplastic with a chemical structure very similar to that of high molecular-weight epoxy resins.^{17–27} For the relationships between morphologies and properties, it was found that the toughness of the cured epoxy matrix will increase on increasing the amount of dissolved phenoxy. A homogeneous blend, which has the highest content of dissolved phenoxy in the epoxy matrix, also possesses the highest fracture toughness. But the homogeneous blend suffers the disadvan-

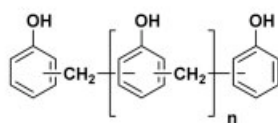
tages of having lower T_g , modulus, and yield stress.²² On the other hand, it was also found that the diamino-diphenyl-sulfon (DDS)-cured epoxy/phenoxy blends having a two-phase morphology showed improved ductility and toughness without significantly losing other mechanical and thermal properties such as modulus, tensile-strength, T_g and heat deflection temperature.²³

We have also investigated the morphologies and the properties of epoxy/brominated-phenoxy blends to apply them to adhesives for flexible printed circuits (FPCs). Brominated-phenoxy was used for incombustibility. The morphologies were analyzed by scanning transmission electron microscopy (STEM) and energy dispersive X-ray fluorescence spectroscopy (EDX). For thermal properties, dynamic mechanical analysis (DMA) was measured. Storage modulus (E') and loss tangent ($\tan \delta$) as a function of temperature were measured with DMA. For mechanical properties, tensile properties (tensile strength and elongation) and adhesion properties (lap-shear adhesion strength and T-peel adhesion strength) were measured. Recently, adhesives for FPCs have required high tensile strength and high T-peel adhesion strength without significantly decreasing elongation, lap-shear adhesion strength and T_g to maintain the reliability of FPCs. But, since a lot of previous adhesives for FPCs have been composed of epoxy/

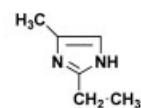
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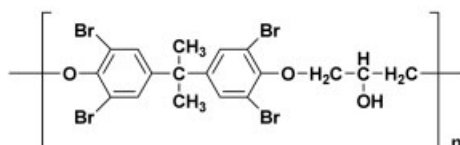
Bis-phenol A type epoxy resin (equipment weight of epoxy groups; 186g/mol)



Novolac phenolic resin (equipment weight of hydroxyl groups; 105g/mol)



2-ethyl-4-methylimidazole

Brominated-phenoxy ($M_w=35,000$, Br content; 25% by weight)**Figure 1** Molecular structures of materials.

rubber blends, the rubber domains invariably resulted in significant reduction in the tensile strength, the modulus, and the T_g .²⁴⁻²⁷ Then, the reliability has not been sufficient.

The aim of this study was to develop cured epoxy composites that have high tensile strength and high T-peel adhesion strength without decreasing elongation, lap-shear adhesion strength and T_g .

EXPERIMENTAL

Materials

Epoxy

As epoxy, phenol, 4,4'-(1-methylethylidene) bis-, polymer with chloromethyl oxirane (diglycidylether-bisphenol A), "Epotohto YD-128" produced by Tohto Kasei, Japan, was used. The epoxide equivalent weight (EEW) is 185 g/mol and the molecular structure is presented in Figure 1.

Brominated phenoxy

As brominated-phenoxy, oxirane, 2,2'-[(1-methylethylidene) bis(2,6-dibromo-4-1-phenylene) oxymethylene]-bis-, homopolymer, "Phenotohto YPB-40" produced by Tohto Kasei, Japan, was used. The M_w determined by gel permeation chromatography with polystyrene standards is 50,000 and the bromine content is 25 wt %. Molecular structure is also presented in Figure 1.

Curing agent

As a curing agent, novolac type phenol-formaldehyde resin "Shownol BRG-557" produced by Showa High-polymer, Japan, was used. The hydroxyl equivalent weight is 105 g/mol and the molecular structure is presented in Figure 1.

Curing promoter

As a curing promoter, 2-ethyl-4-methylimidazole "Curezole 2E4MZ" produced by Shikoku, Japan, was used. Molecular structure is presented in Figure 1.

Formulations

Formulations for this study are presented in Table I. Every one was prepared to be a 50 wt % varnish. For a solvent, methylethylketone (MEK) was used. Equivalent weight ratio between epoxy and novolac phenolic resin (curing agent) is 1 : 1.

Measurements

Scanning transmission electron microscopy

A method for morphological analyses of the cured epoxy/phenoxy blends was performed by STEM. S-4700 produced by Hitachi, Japan, was used as STEM instrument. The accelerated voltage was 27 kV. Specimens were prepared as follows. First, the varnish formulations presented in Table I were coated on two teflon sheets with a size of 45 × 150 mm²

TABLE I
Formulations and Properties of Cured Epoxy/Brominated-phenoxy Blends

	Run-0	Run-1	Run-2	Run-3	Run-4	Run-5
Epoxy resin : bis-phenol A type epoxy resin (YD-128)	63.6	59.3	54.8	49.9	44.6	38.9
Curing agen : Novolac type phenolic resin (BRG-557)	35.8	33.5	30.9	28.2	25.2	21.9
Curing pron : 2-ethyl-4-methylimidazole (2E4MZ)	0.6	0.6	0.5	0.5	0.5	0.4
Modifier : Br-phenoxy (YPB-40)	0	6.6	13.8	21.4	29.7	38.8
Total (% with a weight)	100	100	100	100	100	100
Equivalent weight ratio between epoxy resin and curing agent	1 : 1	1 : 1	1 : 1	1 : 1	1 : 1	1 : 1
Component ratio with a weight between epoxy resin and Br-phenoxy	100 : 0	90 : 10	80 : 20	70 : 30	60 : 40	50 : 50
Storage modulus E' at 23°C ($\times 10^9$ Pa)	2.90	3.32	2.51	2.49	2.60	2.32
at 190°C ($\times 10^7$ Pa)	2.60	2.52	2.26	1.91	1.41	0.88
Glass transition temperature: T_g (°C)	154	156	152	152	154	154
Coefficient of thermal expansion at $<T_g$: α_1 (ppm)	55	56	48	50	84	61
$>T_g$: α_2 (ppm)	172	186	170	188	182	160
Tensile strength (MPa)	33.3	56.6	37.8	61.0	61.7	63.8
Elongation (%)	2.1	3.9	2.7	4.0	5.3	6.9
T-peel adhesion strength (N/25 mm)	3.4	3.7	3.8	4.0	5.3	7.5
Lap-shear adhesion strength (MPa)	7.0	6.2	8.7	7.6	10.4	9.1

and a thickness of 1 mm. The coated teflon sheets were heated in an oven at 150°C for 3 min to dry MEK of a solvent. Then the dried coated teflon sheets were stuck together through other teflon sheets for spacers with a size of 10 × 30 mm² and a thickness of 0.1 mm. They were pressed at 0.98 MPa and 170°C for 2 h *in vacuo* as precuring. The precured epoxy/brominated-phenoxy blends were revealed from the teflon sheets. Finally, the revealed precured epoxy/brominated-phenoxy blends sheets were heated at 190°C for 1 h in an oven to be postcured. The postcured epoxy/brominated-phenoxy blends sheets were implanted in another liquid epoxy for a package and cured at 23°C for 24 h. Finally, the packaged postcured epoxy/brominated-phenoxy blends were cut by the ultramicrotome (Ultratome III LKB) to be thin films for the specimens of STEM.

Energy dispersive X-ray fluorescence spectroscopy

Another morphological analysis was performed by EDX. EDX is a method to perform qualitative and quantitative analyses for elements comprising a material by measuring re-emitted characteristic X-ray from elements. For an EDX instrument, EMAX400 produced by Hitachi, Japan, was used. The distribution of bromine in brominated-phenoxy was mapped with EDX. The accelerated voltage was also 20 kV. Specimens were used the same of STEM.

Dynamic mechanical analysis

For a DMA test machine, DMS 6100 produced by Seiko Instrument, Japan, was used. E' and $\tan \delta$ as a

function of temperature was measured from -150°C to 200°C respectively. The measurements were performed at a constant frequency of 10 Hz and a constant heating rate of 2°C/min. E' at rubbery plateau regions gives information on crosslinking densities of the cured epoxy/brominated-phenoxy blends and $\tan \delta$ gives information on T_g . For specimens, the above postcured epoxy/brominated-phenoxy blends sheets, which were described in STEM, were used. The size was 5 × 30 mm² and the thickness was 0.1 mm.

Thermal mechanical analyses

TMA was performed to determine coefficients of thermal expansion (α_1 and α_2) of the cured epoxy/brominated-phenoxy at a constant heating rate of 2°C/min. α_1 is a coefficient of thermal expansion at temperature below T_g ; α_2 is that at temperature over T_g . Specimens were prepared with the same way described in DMA. For a TMA machine, DMS 6100 produced by Seiko Instrument, Japan, was also used.

Tensile tests

Tensile tests were performed to measure tensile strength and elongation of cured epoxy/brominated-phenoxy blends. For specimens, above cured blends shaped into type 1 dog-bones described in JIS K 6251 (equal to ISO 37 : 77) were used. The specimens were set to chucks of a tensile tester (Autograph AGS-500 produced by Shimadzu, Japan), and the tensile tests were performed in accordance with JIS

K 7161 (equal to ISO 527-1) at 23°C-65RH% and at a crosshead speed of 1 mm/min.

Lap-shear adhesion strength

Copper plates (C1100P), having a size of $25 \times 100 \text{ mm}^2$ and a thickness of 5 mm, sanded with no. 200 sandpapers, were used for adherents. Specimens were prepared as follows. First, the varnish formulations presented in Table I were coated on the two adherents with an area of $25 \times 12.5 \text{ mm}^2$ respectively. Next, the coated adherents were heated in an oven at 135°C for 5 min to dry MEK of a solvent. Then, the dried coated adherents were stuck together with a thickness of 0.1 mm and they were pressed and precured at 0.98 MPa and at 170°C for 2 h. Finally, they were postcured at 190°C for 1 h in an oven.

Lap-shear adhesion strength was measured in accordance with JIS K 6850 (equal to ISO 4587 : 95). Specimens were set to chucks of the above tension test machine. The test machine was run at a crosshead speed of 2 mm/min in a controlled environment of 23°C-65RH%. Measurements were performed 4 times at least and the averages were adopted as lap-shear adhesion strength.

T-peel adhesion strength

Copper plates (C1100P), having a size of $25 \times 150 \text{ mm}^2$ and a thickness of 0.25 mm, sanded with no. 200 sandpapers were used for adherents. Specimens were prepared as follows. First, the varnish formulations presented in Table I were coated on the two adherents with an area of $25 \times 100 \text{ mm}^2$ respectively. Next, the coated adherents were heated in an oven at 135°C for 5 min to dry MEK of a solvent. Then, the dried coated adherents were stuck together through 3 stainless wires of 0.1 mm ϕ diameter for spacers and they were pressed and precured at 0.98 MPa and 170°C for 2 h in an oven. Finally, they were postcured at 190°C for 1 h in an oven.

T-peel adhesion strength was measured in accordance with JIS K 6854 that is equal to ISO 8510-1 : 90. Specimens were set to chucks of the above tension test machine. The tension test machine was run at a crosshead speed of 100 mm/min in a controlled environment of 23°C-65RH%. Measurements were performed 4 times at least and the averages were adopted as T-peel adhesion strength.

SEM for fractured surfaces of T-peel adhesion specimens

Fractured surfaces of T-peel adhesion specimens were observed with SEM. For a SEM machine, S-4300 produced by Hitachi, Japan, was used and the accelerated voltage was 27 kV.

RESULTS AND DISCUSSION

Morphologies of cured epoxy/brominated-phenoxy blends

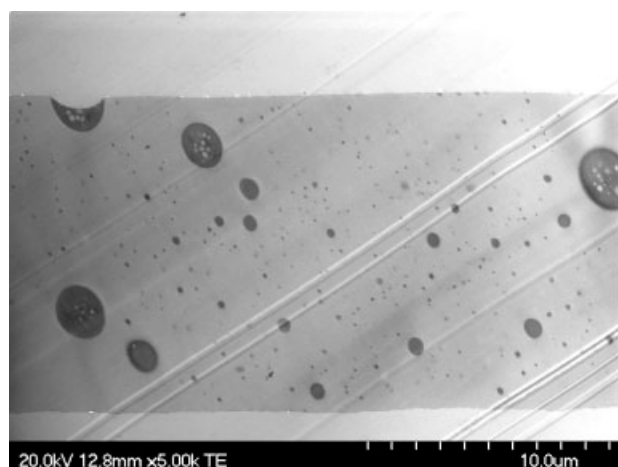
STEM

STEM micrographs of cured epoxy/brominated-phenoxy blends are presented in Figure 2. Since transmittance of electron beams at the place where bromine exists is lower than the other places, dark places showed in the micrographs would correspond to brominated-phenoxy domains. When a content of brominated-phenoxy is <14 wt % (Run-2), cured epoxy forms continuous phases; whereas, when a content of brominated-phenoxy is 30 wt % (Run4), cured epoxy and brominated-phenoxy form cocontinuous phases. When a content of brominated-phenoxy is 40 wt % (Run5), brominated-phenoxy forms a continuous phases, i.e., phase transportation could take place when a content of brominated-phenoxy is 30–40 wt %. Shiddhamalli and Kyu²³ reported that, at higher phenoxy content of 30 wt %, a cocontinuous morphology was observed in SEM micrographs of fracture surfaces of diamino diphenyl sulfone(DDS)-cured epoxy(diglycidyletherbisphenol A, "Epon-828" supplied by Shell Chemical, USA; EEW = 185–192 g)/phenoxy("PKHM-30" supplied by Phenoy Associates, USA) blend compositions and the cured epoxy phases are segregated into spherical domains. Furthermore, Yamanaka and Inoue²⁸ reported that the interconnected spinodal decomposition (SD) domains, which were observed in optical microscopic investigations, tend to transform into droplets driven by surface tension. Since the results of the above previous studies are very close to our results, the spherical domains observed in our cured epoxy in Run-5 would be also interconnected SD.

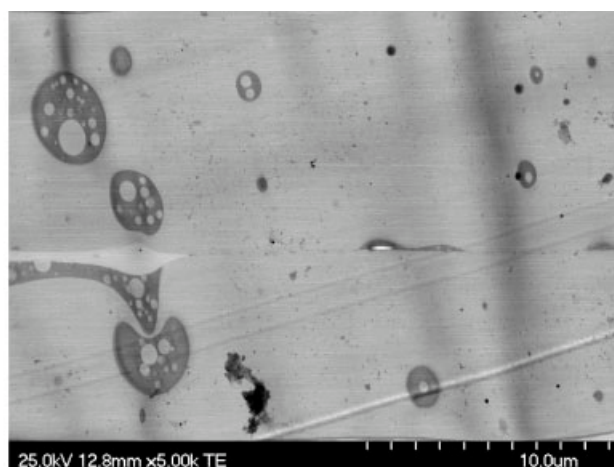
EDX

The results of bromine mapping with EDX are presented in Figure 3. Since brighter places could correspond to brominated-phenoxy phases, it was found that the morphologies analyzed by EDX are very similar to those observed by STEM.

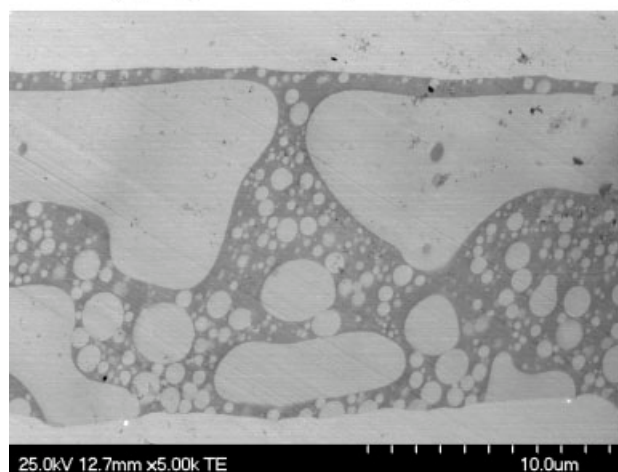
Previously, it was found that the morphologies of epoxy/phenoxy blends are dependent on the choice of curing agents, that is, for the blends cured with 4,4'-diaminodiphenylmethane (DDM) and aliphatic anhydride such as maleic anhydride (MA) and hexahydrophthalic anhydride (HHPA) show no phase separation, while for the blends cured with 4,4'-diaminodiphenylsulfone (DDS) and phthalic anhydride (PA) show the evidences of phase separation, as indicated by DMA and SEM respectively.²⁰ Homogeneous and inhomogeneous epoxy/phenoxy blends can be also prepared by kinetic control of the curing



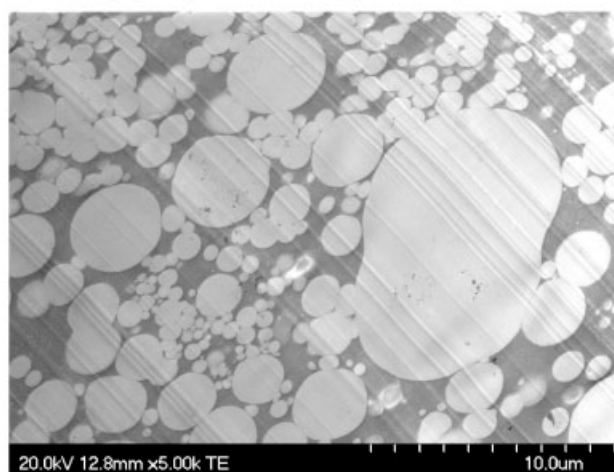
Run-1 Brominated-phenoxy 6.6%
(Epoxy:Br-Phenoxy=90:10)



Run-2 Brominated-phenoxy 13.8%
(Epoxy:Br-Phenoxy=80:20)



Run-4 Brominated-phenoxy 29.7%
(Epoxy:Br-Phenoxy=60:40)



Run-5 Brominated-phenoxy 38.8%
(Epoxy:Br-Phenoxy=50:50)

Figure 2 STEM micrographs of cured epoxy/brominated-phenoxy blends.

rate, that is, in the mixture of epoxy/phenoxy/1-cyanoethyl-4-methylimidazole (CEMI) as an accelerator, when the mixture contains 0.3 or 0.5 phr CEMI, the final cured product is transparent and morphologically homogeneous, while when the mixture contains 0.15 phr or less CEMI, the resultant product is translucent to opaque.^{21,22} It was explained by kinetic and thermodynamics, that is, when the curing rate is relatively high, the dissolved phenoxy molecules are completely locked within the epoxy networks even though the thermodynamics favor phase separation of the phenoxy, while when the curing rate is relatively low, the resultant immiscibility owing to the epoxy molecular weight increase still allows the phenoxy to diffuse and coalesce to form a separate phase.²¹

In our study, since cured epoxy and brominated-phenoxy did not dissolve together, brominated-

phenoxy molecules could not be locked within the cured epoxy networks and phase separation could proceed. It may be also that, since the curing rate is relatively low and the compatibility between cured epoxy phases and brominated-phenoxy phases is not stable thermodynamically, phase separation could be favored.

Thermal properties

DMA

Storage modulus (E'). E' data as a function of temperature are presented in Figure 4 and E' data at 23°C and 190°C are presented in Table I. Once E' at 23°C increased as shown in Run-1, thereafter they decreased. The phenomena of the increase would be described afterward in terms of "antiplasti-

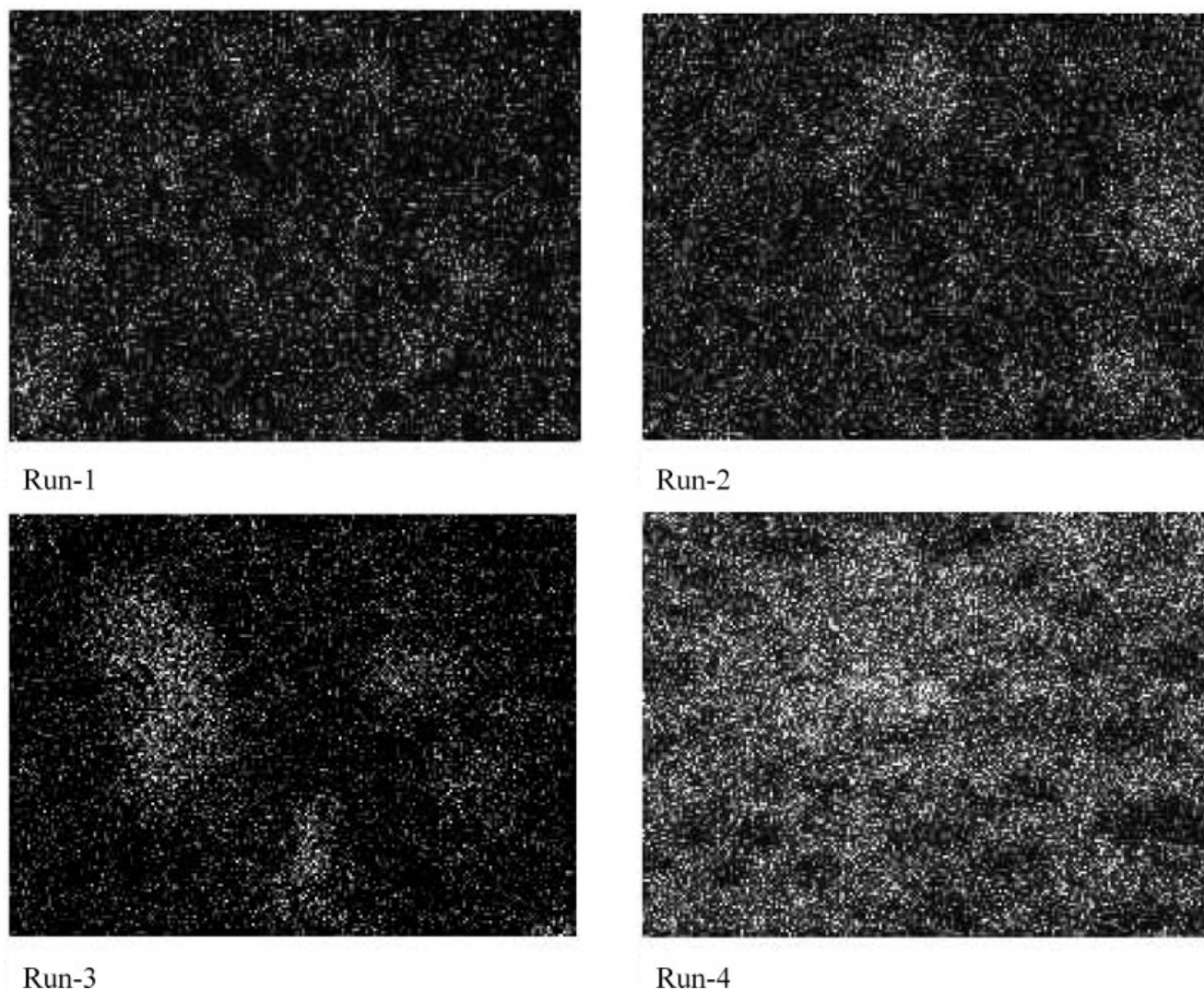


Figure 3 Bromine mapping in cured epoxy/brominated-phenoxy blends by EDX; brighter places correspond to bromine.

zation^{29–36} and the decrease of E' would be due to a plasticizing effect of brominated-phenoxy. E' at 190°C was shown as E' on rubbery plateaus. Generally, it is known that the crosslinking density (ρ) of cured resins is proportional to E' on rubbery plateau as shown in eq. (1).³⁷

$$\rho = E'/3\phi RT \quad (1)$$

where, ϕ is front coefficient; usually it is near equal to 1. R is gas constant. T is absolute temperature. As shown in Figure 4 and Table I, E' on rubbery plateau regions (at 190°C) decreased with increasing amount of brominated-phenoxy. These phenomena should be due to unreacted brominated-phenoxy, which diluted the crosslinking densities of cured epoxies. But, even at a cured blend containing brominated-phenoxy of 40 wt % (Run5), the rubbery plateau E' still exists. So, it was found that a cured blend of Run-5 still maintains the properties due to cross-

linked matrix structures even though morphologically the continuous phases have changed to brominated-phenoxy of a thermoplastic as shown in Figure 2.

Loss tangent ($\tan \delta$). $\tan \delta$ data as a function of temperature are presented in Figure 5. The temperature corresponding to the maximum for α relaxation in $\tan \delta$ is described as the glass transition temperature (T_g) in Table I. Two distinct T_g s are found in the cured epoxy/brominated-phenoxy blends. Since every higher T_g is found at 155°C, it would be attributed to cured epoxy-rich phases; while, since every lower T_g is found at 128°C, it would be attributed to brominated-phenoxy-rich phases respectively.²³ Furthermore, as shown in Run-0 and Run-1 in Figure 5, once the β -relaxation is suppressed, thereafter it is converted into increase. The suppression of β -relaxation in Run-1 could be explained in terms of the concept of “antiplasticization” or “fortifying” by brominated-phenoxy. The concept of “antiplasticizers” or “fortifiers” being stiff polar additives

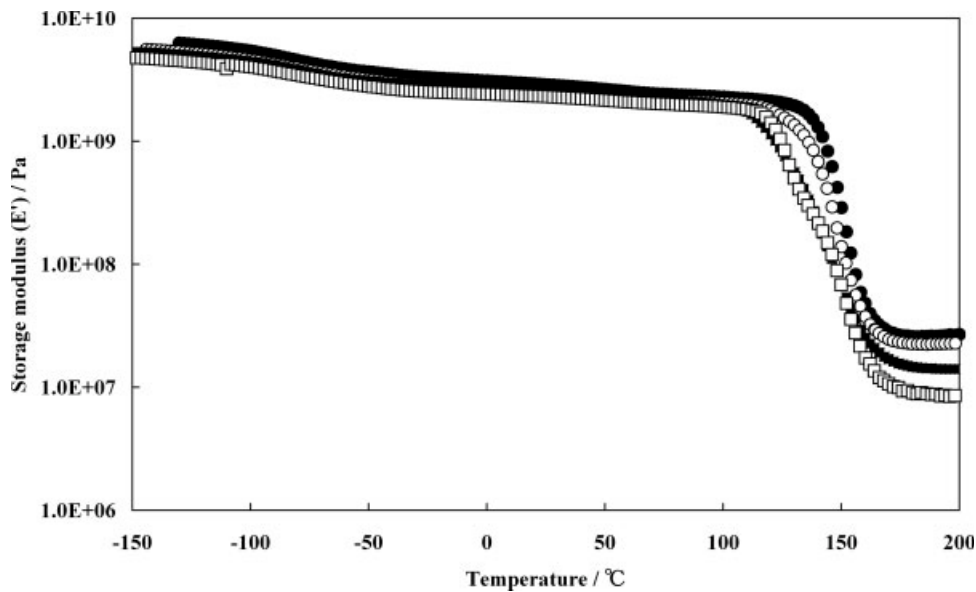


Figure 4 Effects of brominated-phenoxy content on storage modulus (E') as a function of temperature. (●), Run-0; (○), Run-2; (■), Run-4; (□), Run-5.

which reduce the free volume available for molecular motion in stiff-chain of thermosets such as crosslinked epoxies and thermoplastics such as polycarbonates.^{29–36} In terms of the free volume concept, when an additive (volume fraction V_1 , fractional free volume f_1) is added to a polymer (volume fraction V_2 , fractional free volume f_2) the free volume of the mixture (f) is given by eq. (2).³⁸

$$f = V_1f_1 + V_2f_2 + KV_1V_2 \quad (2)$$

where, K is an interaction parameter. The principle of “antiplastization” is that the interaction parameter between a polymer and an additive is negative and large. Then the free volume is decreased by the additive. For “antiplasticizers” in cured epoxies, polychlorinated biphenyls (PCB's), dibutyl phthalate (DBP), an adduct of a mole diglycidylether of bisphenol A with 2 mol phenol (DGEBA-P), a reaction product of 1,2-epoxy-3-phenoxypropane and 4-hydroxyacetanilide (EPPHAA) and a reaction prod-

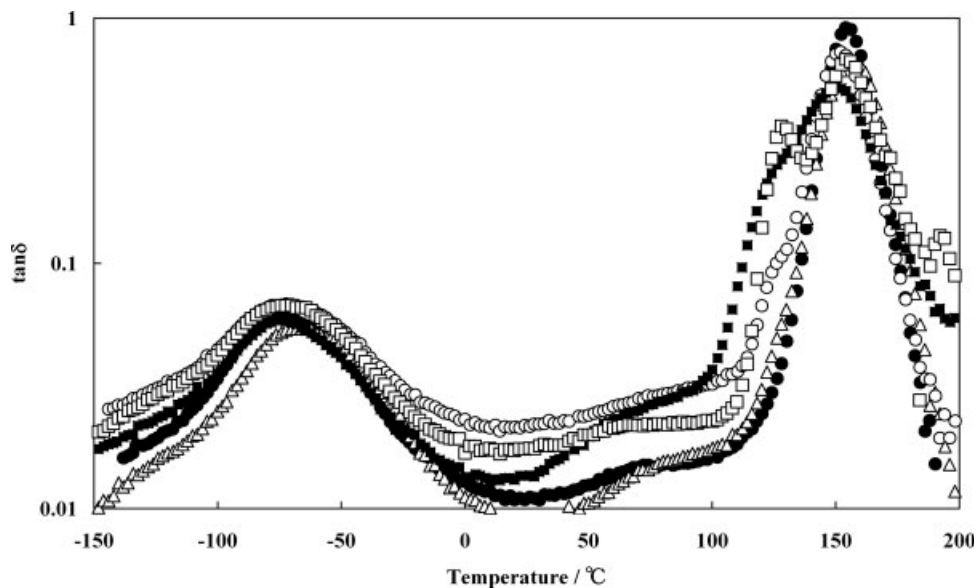


Figure 5 Effects of brominated-phenoxy content on loss tangent ($\tan \delta$) as a function of temperature. (●), Run-0; (△), Run-1; (○), Run-2; (■), Run-4; (□), Run-5.

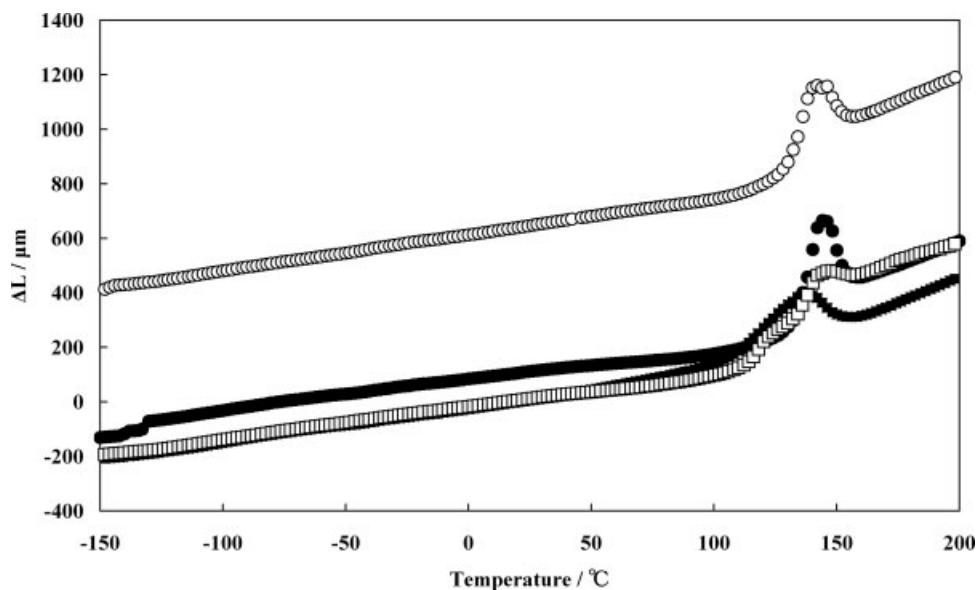


Figure 6 Effects of brominated-phenoxy content on TMA. (●), Run-0; (○), Run-2; (■), Run-4; (□), Run-5.

uct of vinylcyclohexene dioxide and 4-hydroxyacetanilide (VCDHAA) have been investigated previously.^{29–36}

TMA

TMA data of cured epoxy/brominated-phenoxy blends are presented in Figure 6, and coefficients of thermal expansion, which are calculated from the slopes on TMA curves. Coefficients of thermal expansion below T_g (α_1) and those over T_g (α_2) are presented in Table I. α_1 in Run-4 and Run-5 is a little higher than that in Run-0–Run-3 respectively. The phenomena would be related with that i.e., a continuous phase in these cured blends have converted to brominated-phenoxy from cured epoxy as shown in

Run-4 and Run-5. On the other hand, there does not seem to be a big difference on every α_2 .

Mechanical properties

Tensile strength and elongation

Tensile strength data of cured epoxy/brominated-phenoxy blends as a function of brominated-phenoxy content are presented in Figure 7 and the average values are described in Table I. Cured epoxy/brominated-phenoxy blends (Run-1–Run-5) show higher tensile strength than control (Run-0).

Tensile elongation data of cured epoxy/brominated-phenoxy blends as a function of brominated-phenoxy content are presented in Figure 8 and the average

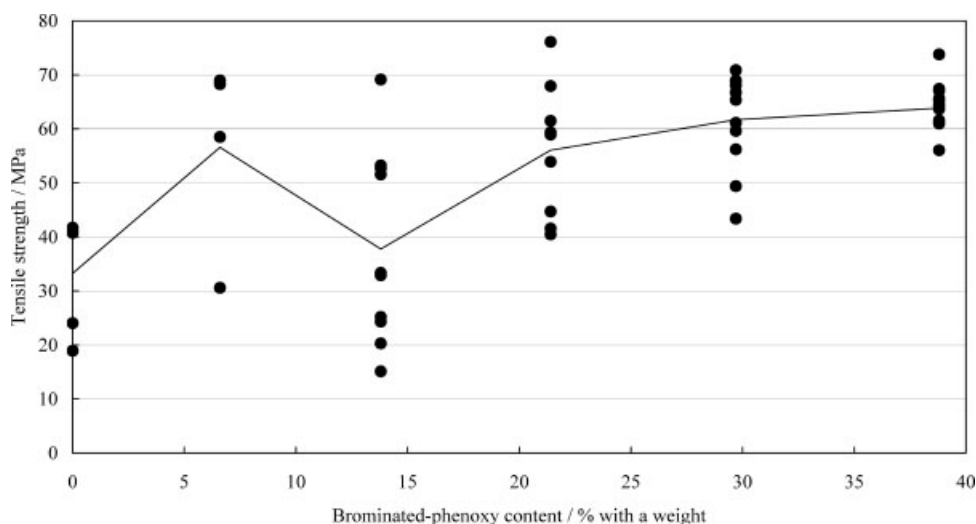


Figure 7 Tensile strength of cured epoxy/brominated-phenoxy as a function of brominated-phenoxy content.

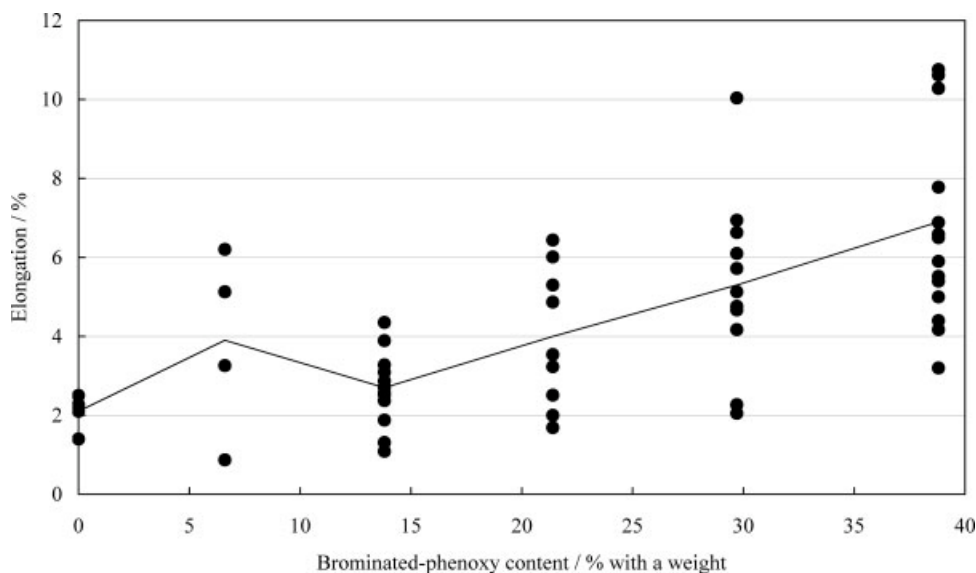


Figure 8 Elongation of cured epoxy/brominated-phenoxy as a function of brominated-phenoxy content.

values are described in Table I. The data in cured blends of Run-1–Run-5 are also higher than that of control (Run-0). Especially, the elongation of Run-4 and Run-5 shows a remarkable high value respectively.

In Run-5, brominated-phenoxy domain, which is a thermoplastic, forms continuous phases as shown in Figure 2. But they still have rubbery plateaus of E' as shown in Figure 4, i.e., they still maintain the properties of thermosets. So, the tensile elongation would be increased by ductility due to the thermoplastic properties and the tensile strength would be increased by rigidity due to the thermoset properties.

Shiddhamalli and Kyu²³ investigated the relationships among tensile strength, elongation, impact properties and morphologies of cured epoxy/phenoxy blends. They reported that the morphology obtained for an epoxy/phenoxy blend of 80/20 by weight showed a cocontinuous structure like that of our cured blend of Run-4. For the properties of the cured blend of 80/20, they also reported that tensile strength, elongation and toughness were increased at little or no expense of flexural modulus, glass transition or heat deflection temperature. The increase of tensile strength and elongation without the decrease of T_g was the same as the results of ours. The impact

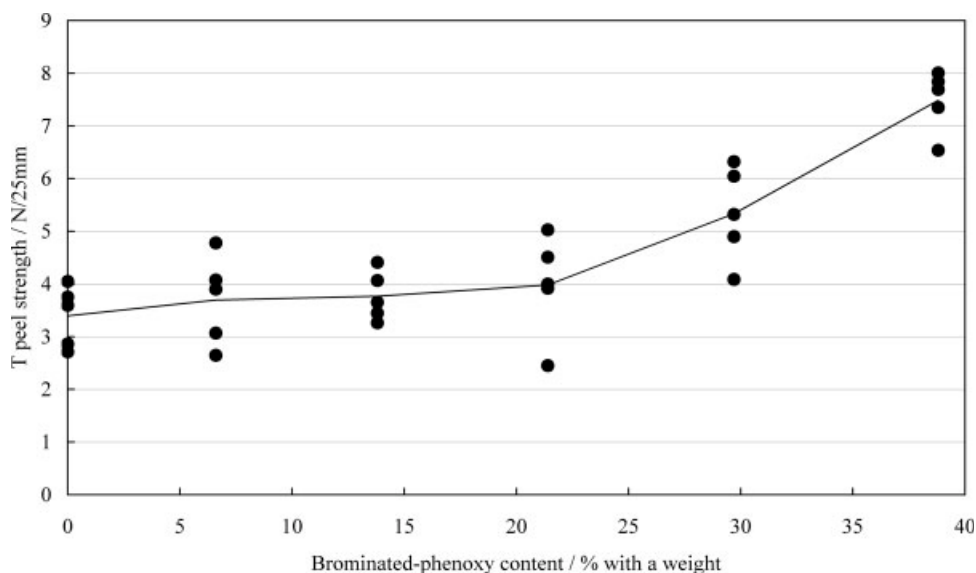


Figure 9 T-peel adhesion strength of cured epoxy/brominated-phenoxy as a function of brominated-phenoxy content.

properties of the cured blend were measured by Instrumented Falling Weight Impact test (IFWI).³⁹ In the IFWI method, two impact properties were reported. First is the maximum force necessary for penetration of the test specimens. The second value is the total energy absorbed during the impact events. The first and the second value increased together with increasing content of phenoxy up to 20 wt %, and for a phenoxy content of 20 wt %, the second value increased 2.5–3.0 times with respect to the neat cured epoxy matrix.

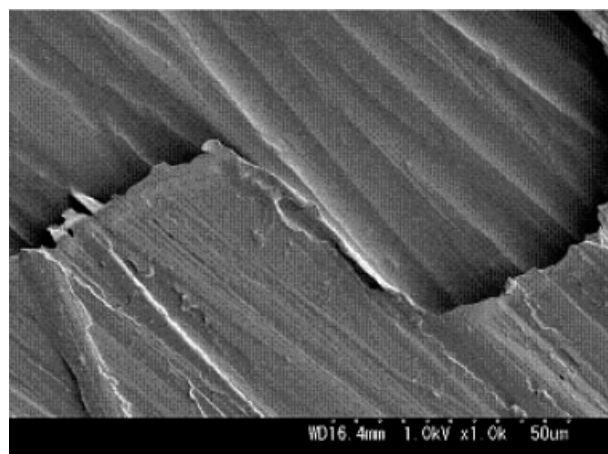
These previous studies are much similar to the results of ours, i.e., since the cured epoxy/brominated-phenoxy blends of Run-4 showed a cocontinuous morphology, the cured blends could also show better impact properties than that of the neat cured system. It should be due to that, the strong interaction among the phases in cocontinuous morphologies should facilitate a more uniform stress

distribution in the material under load and thereby avoid premature failure due to localized stress concentration.⁴⁰

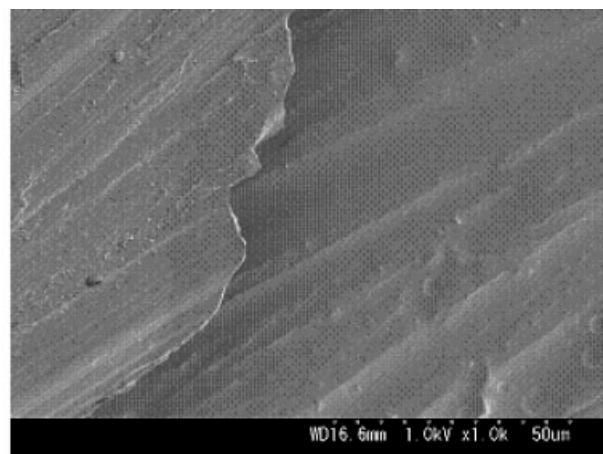
T-peel and lap-share adhesion strength

T-peel adhesion strength data of cured epoxy/brominated-phenoxy blends as a function of brominated-phenoxy content are presented in Figure 9 and the average values are described in Table I. A remarkable increase in T-peel adhesion strength is found in Run-4 and Run-5 respectively. The fracture mode of Run-0–Run-3 was interfacial and that of Run-4–Run-5 was cohesive respectively. Nakaya et al.^{24,25} also found that peel adhesion strength of cured epoxy/phenoxy blends increased more as the phenoxy content increased more.

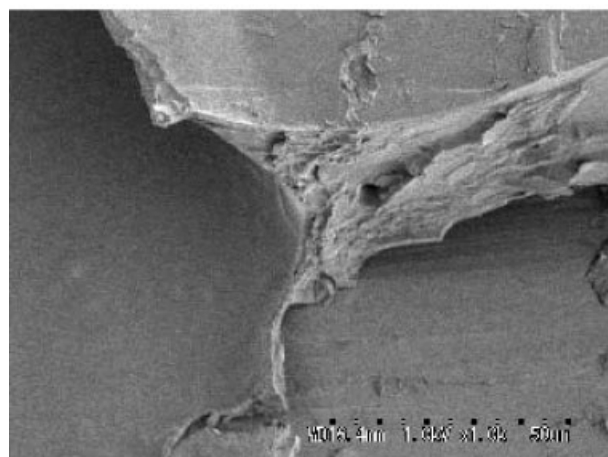
SEM micrographs for fractured surfaces of T-peel adhesion strength specimens are presented in Figure 10.



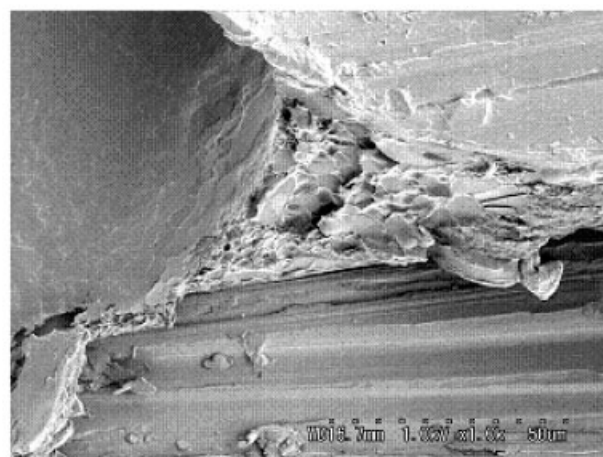
Run-1 Br-Phenoxy 6.6%
(Epoxy:Br-Phenoxy=90 : 10)



Run-2 Br-Phenoxy 13.8%
(Epoxy:Br-Phenoxy=80 : 20)



Run-4 Br-Phenoxy 29.7%
(Epoxy:Br-Phenoxy=60 : 40)



Run-5 Br-Phenoxy 38.8%
(Epoxy:Br-Phenoxy=50 : 50)

Figure 10 SEM micrographs of T-peel fractured surfaces.

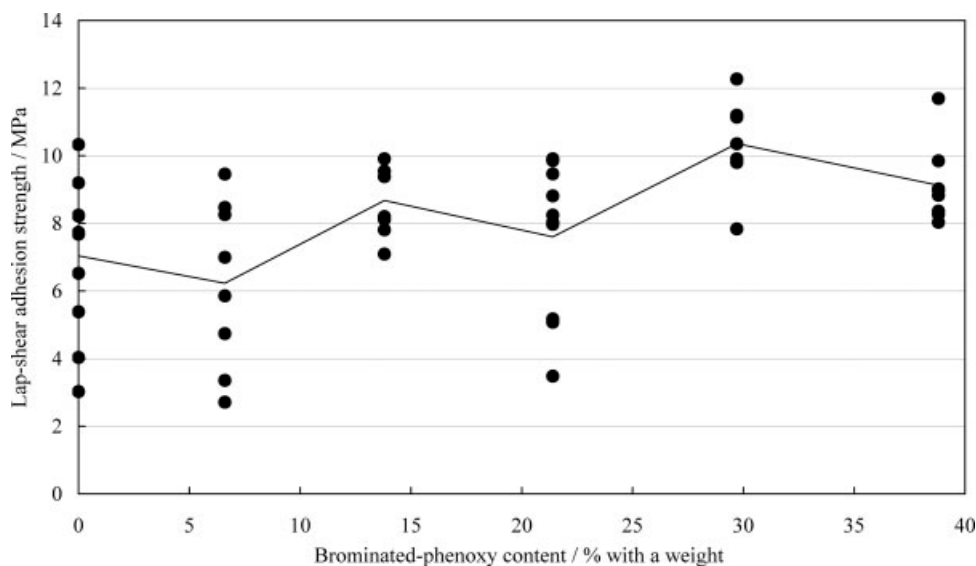


Figure 11 Lap-shear adhesion strength of cured epoxy/brominated-phenoxy as a function of brominated-phenoxy content.

In Run-1 and Run-2, the fracture mode was interfacial respectively, and the surface appearances seem to be smooth. On the other hand, in Run-4 and Run-5, the fracture mode was cohesive respectively, and the surface appearances seem to be rough and be torn up. The fracture surfaces of Run-4 and Run-5 in Figure 10 also show some evidence of a localized plastic deformation or a torn up appearance mentioned above.

Lap-shear adhesion strength data of cured epoxy/brominated-phenoxy blends as a function of brominated-phenoxy content are presented in Figure 11 and the average values are described in Table I. In Run-4 and Run-5, it was found that not only T-peel adhesion strength but also lap-shear adhesion strength increases. As mentioned above, in Run-4 and Run-5, it would be due to that both properties of ductility derived from thermoplastics and rigidity derived from thermosets exist together.

Hatano et al.⁴¹ and Mizumachi et al.⁴² investigated the viscoelastic properties of epoxy resin, which consisted by diethylenetriamine-cured epoxy. They reported that when the cured epoxies are too ductile, high values of adhesive strength are not obtained because the molecular cohesion of the cured epoxies becomes very low in this state. On the other hand, when cured epoxies are too rigid, high values of adhesive strength are also not obtained because interfacial fracture occurs. Maximum adhesive strength could be obtained when cured epoxies are not too ductile and not too rigid. T-peel adhesion strength and lap-shear adhesion strength in our study could be also increased together. It would be due to a good balance of the ductility and rigidity.

CONCLUSIONS

1. Morphologies: When a content of brominated-phenoxy was less than 14 wt %, cured epoxy forms a continuous phase. On the other hand, when it was 30 wt %, cured epoxy and brominated-phenoxy formed cocontinuous phases together. When it was 40 wt %, brominated-phenoxy formed continuous phases, that is, it was found that phase transportation took place at the brominated-phenoxy content of 30–40 wt %.
2. Thermal properties: Two distinct T_g s were found in all cured epoxy/brominated-phenoxy blends. Since higher T_g was shown at 155°C, it would be attributed to cured epoxy phases, that is, it was found that T_g of cured epoxy was not decreased. On the other hand, since lower T_g was shown at 128°C, it would be attributed to brominated-phenoxy phases. Furthermore, when brominated-phenoxy content was 7 wt %, suppression of β -relaxation was found in the $\tan \delta$ curve as a function of temperature. The phenomena could be explained in terms of the “anti-plasticization,” that is, brominated-phenoxy for stiff polar additives reduce the free volume of crosslinked epoxies for thermosets.
3. Mechanical and adhesive properties: Although brominated-phenoxy formed continuous phases when brominated-phenoxy content was in 30–40 wt %, the E' values in the cured blends still have rubbery plateaus, that is, the cured blends would not have only thermoplastic properties but also thermoset properties. As the results, the tensile elongation and the tensile strength

could be increased together, furthermore, the T-peel adhesion strength could be increased without decreasing the lap-shear adhesion strength and the T_g .

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