Morphologies and Properties of Cured Epoxy / Brominated-phenoxy Blends

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Abstract

The 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% with a weight, a co-continuous phase structure between cured epoxy and brominated-phenoxy was found. In dynamic mechanical analysis (DMA) of the cured blends, every loss tangent (tanδ) curve as a function of temperature showed 2 peaks at 128 ℃ and 155 ℃ respectively. Since 128 ℃ and 155 ℃ could be attributed to neat brominated-phenoxy and neat cured epoxy respectively, it was found that the cured epoxy phases and the brominated-phenoxy phases were incompatible together and the Tg of cured epoxy phases did not decrease. When brominated-phenoxy content was 40% with a weight, although brominated-phenoxy was continuous phases, it was found that the rubbery plateau on storage modulus (E’) still existed. Furthermore, tensile strength and tensile elongation of the cured blends were increased together. The T-peel adhesion strength and the lap-shear adhesion strength were also increased together. These phenomena could be due to the co-continuous structures consisted by the rigid cured epoxy phases of thermosets and ductile the brominated-phenoxy phases of thermoplastics.

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, the poor toughness and the low T-peel adhesion strength have been pointed out for disadvantages. The addition of rubbers to epoxy resins has been investigated in order to enhance the above disadvantages.\(^8\)\(^-\)\(^{16}\) While, rubber-added epoxy resins usually result in lowering Tg 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 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 disadvantages of having lower Tg, 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, Tg and heat deflection temperature.\(^23\)

We have also been investigated the morphologies and the properties of epoxy/brominated-phenoxy blends in order to apply them to adhesives for “Flexible Printed Circuits (FPCs)”\(^2\). Brominated-phenoxy was used for incombustibility. The morphologies were analyzed by scanning transmission electron microscopy (STEM), energy dispersive X-ray fluorescence spectroscopy (EDX). For thermal properties, dynamic mechanical analysis (DMA) was measured. Storage modulus (E\(^\prime\)) 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 been demanded high tensile strength and high T-peel adhesion strength without significantly decreasing elongation, lap-shear adhesion strength and Tg in order to maintain the reliability of FPCs. But, since a lot of previous adhesives for FPCs have been composed of epoxy/rubber blends, the rubber domains invariably resulted in significant reduction in the tensile strength, the modulus and the Tg’s.\(^24\)\(^-\)\(^{27}\) Then the reliability has not been sufficient.

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

EXPERIMENTAL
Materials

Epoxy

For epoxy, phenol, 4,4’-(1-methylethyldiene) bis-, polymer with chloromethyl oxirane (Diglycidyletherbisphenol A), “Epotohto YD-128” produced by Tohto Kasei Co., Ltd. Japan, was used. The epoxide equivalent weight (EEW) is 185g/mol and the molecular structure is presented in Figure1.

Brominated-phenoxy

For brominated-phenoxy, oxirane, 2,2’-[(1-methylethyldiene) bis(2,6-dibromo-4,1-phenylene) oxymethylene]bis-, homopolymer, “Phenotohto YPB-40” produced by Tohto Kasei Co., Ltd. Japan, was used. The \( M_w \) determined by gel permeation chromatography with polystyrene standards is 50,000 and the bromine content is 25% with a weight. The molecular structure is also presented in Figure1.

Curing Agent

For a curing agent, novolac type phenol-formaldehyde resin “Shownol BRG-557” produced by Showa Highpolymer Co., Ltd. Japan, was used. The hydroxyl equivalent weight is 105g/mol and the molecular structure is also presented in Figure1.

Curing Promoter

For a curing promoter, 2-ethyl-4-methylimidazol “Curezole 2E4MZ” produced by Shikoku Co., Ltd. Japan, was used. The molecular structure is also presented in Figure1.
【Figure1】 Molecular structures of materials.

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 (Mw=35,000, Br content; 25% with a weight)

Figure1 Molecular structure of materials.
Formulations

Formulations for this study are presented in Table1. Everyone was prepared to be a 50wt% varnish. For a solvent, methylethylketone (MEK) was used. An equivalent weight ratio between epoxy and novolac phenolic resin (curing agent) is 1:1.

<table>
<thead>
<tr>
<th>Components and items of properties</th>
<th>Run-0</th>
<th>Run-1</th>
<th>Run-2</th>
<th>Run-3</th>
<th>Run-4</th>
<th>Run-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy resin</td>
<td>63.6</td>
<td>59.3</td>
<td>54.8</td>
<td>49.9</td>
<td>44.6</td>
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<td>Curing agent</td>
<td>35.8</td>
<td>33.5</td>
<td>30.9</td>
<td>28.2</td>
<td>25.2</td>
<td>21.9</td>
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<td>Curing promoter</td>
<td>0.6</td>
<td>0.6</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.4</td>
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<tr>
<td>Modifier</td>
<td>0</td>
<td>6.6</td>
<td>13.8</td>
<td>21.4</td>
<td>29.7</td>
<td>38.8</td>
</tr>
<tr>
<td>Component ratio with a weight</td>
<td>100:0</td>
<td>90:10</td>
<td>80:20</td>
<td>70:30</td>
<td>60:40</td>
<td>50:50</td>
</tr>
<tr>
<td>Strage modulus $E'$ at 23 $^\circ$C ($\times 10^9$MPa)</td>
<td>2.90</td>
<td>3.32</td>
<td>2.51</td>
<td>2.49</td>
<td>2.60</td>
<td>2.32</td>
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<tr>
<td>at 190 $^\circ$C ($\times 10^7$MPa)</td>
<td>2.60</td>
<td>2.52</td>
<td>2.26</td>
<td>1.91</td>
<td>1.41</td>
<td>0.88</td>
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<td>Glass transition temperature: Tg ($^\circ$C)</td>
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<td>156</td>
<td>152</td>
<td>152</td>
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<td>Coefficient of thermal expansion at $&lt; T_g$: $\alpha_1$ (ppm)</td>
<td>55</td>
<td>56</td>
<td>48</td>
<td>50</td>
<td>84</td>
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<tr>
<td>at $&gt; T_g$: $\alpha_2$ (ppm)</td>
<td>172</td>
<td>186</td>
<td>170</td>
<td>188</td>
<td>182</td>
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<tr>
<td>Tensile strength (MPa)</td>
<td>33.3</td>
<td>56.6</td>
<td>37.8</td>
<td>61.0</td>
<td>61.7</td>
<td>63.8</td>
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<td>Elongation (%)</td>
<td>2.1</td>
<td>3.9</td>
<td>2.7</td>
<td>4.0</td>
<td>5.3</td>
<td>6.9</td>
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<tr>
<td>T-peel adhesion strength (N/25mm)</td>
<td>3.4</td>
<td>3.7</td>
<td>3.8</td>
<td>4.0</td>
<td>5.3</td>
<td>7.5</td>
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<tr>
<td>Lap-shear adhesion strength (MPa)</td>
<td>7.0</td>
<td>6.2</td>
<td>8.7</td>
<td>7.6</td>
<td>10.4</td>
<td>9.1</td>
</tr>
</tbody>
</table>

Measurements

Scanning Transmission Electron Microscopy (STEM)

A method for morphological analyses of the cured epoxy/phenoxy blends was performed by STEM. S-4700 produced by Hitachi Co., Ltd. Japan was used for a STEM instrument. The accelerated voltage was 27KV. Specimens were prepared as follows. First, the varnish formulations presented in Table1 were coated on two Teflon sheets with a size of 45mm × 150mm and a thickness of 1mm. 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 10mm × 30mm and a thickness of 0.1mm. They were pressed at 0.98MPa and 170°C for 2 h in vacuo as a pre-curing. The pre-cured epoxy/brominated-phenoxy blends were revealed from the Teflons. Finally, the revealed pre-cured epoxy/brominated-phenoxy blends sheets were heated at 190°C for 1 h in an oven to be post-cured. The post-cured 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 post-cured 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 (EDX)**

Another morphological analysis was performed by EDX. EDX is the 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 Co., Ltd. Japan was used. The distribution of bromine in brominated-phenoxy was mapped with EDX. The accelerated voltage was also 20KV. Specimens were used the same of STEM.

**Dynamic Mechanical Analysis (DMA)**

For a DMA test machine, DMS 6100 produced by SEIKO Instrument Co., Ltd. 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 10Hz and a constant heating rate of 2°C/min. $E'$ at rubbery plateau regions gives the information of cross-linking densities of the cured epoxy/brominated-phenoxy blends and $\tan \delta$ gives the information of $T_g$. For specimens, the above post-cured epoxy/brominated-phenoxy blends sheets which were described in STEM were used. The size was 5mm × 30mm and the thickness was 0.1mm.

**Thermal Mechanical Analyses (TMA)**

TMA was performed in order to determine coefficients of thermal expansion ($\alpha_1$ and $\alpha_2$) of the cured epoxy/brominated-phenoxy at a constant heating rate of 2°C/min. $\alpha_1$ is a coefficient of thermal expansion at temperature below $T_g$. $\alpha_2$ 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 Co., Ltd. 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 Co., Ltd., Japan), and tensile tests were performed in accordance with JIS K 7161 (equal to ISO 527-1) at 23 ℃-65RH% and at a crosshead speed of 1mm/min.

Lap-shear Adhesion Strength

Copper plates (C1100P), having a size of 25mm × 100mm and a thickness of 5mm, sanded with #200 sandpapers, were used for adherents. Specimens were prepared as follows. First, the varnish formulations presented in Table1 were coated on the two adherents with an area of 25mm × 12.5mm respectively. Next, the coated adherents were heated in an oven at 135 ℃ for 5min to dry MEK of a solvent. Then, the dried coated adherents were stuck together with a thickness of 0.1mm and they were pressed and pre-cured at 0.98MPa and 170 ℃ for 2h. Finally, they were post-cured at 190 ℃ for 1h 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 2mm/min in a controlled environment of 23 ℃-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 25mm × 150mm and a thickness of 0.25mm, sanded with #200 sandpapers were used for adherents. Specimens were prepared as follows. First, the varnish formulations presented in Table1 were coated on the two adherents with an area of 25mm × 100mm respectively. Next, the coated adherents were heated in an oven at 135 ℃ for 5min to dry MEK of a solvent. Then, the dried coated adherents were stuck together through 3 stainless wires of 0.1mm diameter for spacers and they were pressed and pre-cured at 0.98MPa and 170 ℃ for 2h in an oven. Finally, they were post-cured at 190 ℃ for 1h 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 100mm/min in a controlled environment of 23℃-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 Co., Ltd. Japan was used and the accelerated voltage was 27KV.

**RESULTS AND DISCUSSION**

**Morphologies of Cured Epoxy/Brominated-phenoxy Blends**

**STEM**

STEM micrographs of cured epoxy/brominated-phenoxy blends are presented in Figure2. 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 less than 14% with a weight (Run2), cured epoxy forms continuous phases. While, when a content of brominated-phenoxy is 30% with a weight (Run4), cured epoxy and brominated-phenoxy form co-continuous phases. When a content of brominated-phenoxy is 40% with a weight (Run5), brominated-phenoxy forms a continuous phases, i.e., phase transportation could take place when a content of brominated-phenoxy is in 30~40% with a weight. Siddhamalli and Kyu\textsuperscript{23} reported that, at higher phenoxy content of 30% with a weight, a co-continuous morphology was observed on SEM micrographs of fracture surfaces of diamino diphenyl sulfone(DDS)-cured epoxy(diglycidyletherbisphenol A\textsuperscript{2} Epon-828 supplied by Shell Chemical Co. U.S., EEW=185-192 g) / phenoxy( PKHM-30 supplied by Phenoy Associatees) blend compositions and the cured epoxy phases are segregated into spherical domains. Furthermore, Yamanaka and Inoue\textsuperscript{28} 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 above previous studied are very close to our results, the spherical domains observed in our cured epoxy in Run-5 would be also interconnected SD.
Figure 2  STEM micrographs of cured epoxy/brominated-phenoxy blends.

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.
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, i.e., 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 dynamic mechanical analysis (DMA) and SEM respectively. Homogeneous and inhomogeneous epoxy/phenoxy blends can be also prepared by kinetic control of the curing rate, i.e., in the mixture of epoxy/phenoxy/1-cyanoethyl-4-methylimidazole (CEMI) as an accelerator, when the mixture contains 0.3 or 0.5phr CEMI, the final cured product is transparent and morphologically homogeneous, while when the mixture contains 0.15phr or less CEMI, the resultant product is translucent to opaque. It was explained by kinetic and thermodynamics, i.e., 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 owning to the epoxy molecular weight increase still allows the phenoxy to diffuse and coalesce to form a separate phase.

In our study, since cured epoxy and brominated-phenoxy did not dissolved together, brominated-phenoxy molecules could not be locked within the cured epoxy networks and phase separation could proceed. It would be also due to that, since the curing rate is relatively low and the compatibility between cured epoxy phases and brominated-phenoxy phases is not stable thermodynamically, the phase separation could be favored.
Bromine mapping in cured epoxy/brominated-phenoxy blends by EDX. Brighter places correspond to bromine.

Figure 3

Run-1

Run-2

Run-3

Run-4

Figure 3 Bromine mappings in cured epoxy/brominated-phenoxy blend by EDX. Brighter places correspond to bromine.
Thermal Properties

DMA

Storage Modulus (E’)

E’ data as a function of temperature are presented in Figure4 and E’ data at 23 ℃ and 190 ℃ are presented in Table1. Once E’ at 23 ℃ increased as shown in Run-1, thereafter they decreased. The phenomena of the increase would be described afterward in terms of “antiplastization” and the decrease of E’ would be due to a plasticizing effect of brominated-phenoxy. E’ at 190 ℃ was shown as E’ on rubbery plateaus. Generally, it is known that the cross-linking density (ρ) of cured resins is proportion to E’ on rubbery plateau as shown in equation 1.

\[ \rho = \frac{E’}{3\phi RT} \]  

(1)

where, \( \phi \) is Front Coefficient, usually that is near equal to 1. R is Gas Constant. T is absolute temperature. As shown in Figure4 and Table1, E’ on the rubbery plateau regions (at 190 ℃) decreased with increasing amount of brominated-phenoxy. These phenomena should be due to unreacted brominated-phenoxy, which diluted the cross-linking densities of cured epoxies. But, even at a cured blend containing brominated-phenoxy of 40wt% (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 Figure2.
**Figure 4**  Effect of brominated-phenoxy content on storage modulus ($E'$) as a function of temperature. (●); Run-0, (○); Run-2, (□); Run-4, (□); Run-5, -; Average

![Graph showing effect of brominated-phenoxy content on storage modulus ($E'$) as a function of temperature.](image)

**Figure 4**  Effect of brominated-phenoxy content on storage modulus ($E'$) as a function of temperature.

**Loss Tangent (tanδ)**

Tanδ data as a function of temperature are presented in Figure 5. The temperature corresponding to the maximum for α relaxation in tanδ is described as the glass transition temperature ($T_g$) in Table 1. 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. 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 which reduce the free volume available for molecular motion in stiff-chain of thermosets such as cross-linked epoxies and thermoplastics such as polycarbonates.

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 equation 2.

\[ f = V_1 f_1 + V_2 f_2 + KV_1 V_2 \]  \hspace{1cm} (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. The free volume is then 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 moles phenol (DGEBA-P), a reaction product of 1,2-epoxy-3-phenoxyp propane and 4-hydroxyacetanilide (EPPHAA) and a reaction product of vinylcyclohexene dioxide and 4-hydroxyacetanilide (VCDHAA) have been investigated previously.\textsuperscript{32-39}

【Figure5】 Effect of brominated-phenoxy content on loss tangent (tan$\delta$) as a function of temperature. (□);Run-0, ( △ );Run-1, ( ○ );Run-2, ( ▪ );Run-4, ( □ );Run-5, - ;Average

Figure5 Effect of Br-phenoxy content on relationships between tan$\delta$ and temperature of cured epoxy/brominated-phenoxy blends.
TMA

TMA data of cured epoxy/brominated-phenoxy blends are presented in Figure 6, and coefficients of thermal expansion, which are calculated from the sloops on TMA curves. Coefficients of thermal expansion below Tg ($\alpha_1$) and those over Tg ($\alpha_2$) are presented in Table 1. $\alpha_1$ 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 $\alpha_2$.

【Figure6】Effect of brominated-phenoxy content on TMA. (●);Run-0, (○);Run-2, (■);Run-4, (□);Run-5, -;Average

Figure6  Effect of brominated-phenoxy content on TMA.
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 1. 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 values are described in Table 1. 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 Kyu had been 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 with a weight showed a co-continuous 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 Tg was the same as the results of ours. The impact properties of the cured blend were measured by Instrumented Falling Weight Impact test (IFWI). 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 20wt%, and for a phenoxy content of 20wt%, 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 co-continuous 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 co-continuous morphologies should facilitate a more uniform stress distribution in the material under load and thereby avoid premature failure due to localized stress concentration.43

**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 1. A remarkable increase in T-peel adhesion 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.

![Figure9](image)

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

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

【Figure 10】 SEM micrographs of T-peel fractured surfaces.

<table>
<thead>
<tr>
<th>Run</th>
<th>Br-Phenoxy (Epoxy:Br-Phenoxy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run-1</td>
<td>6.6% (90:10)</td>
</tr>
<tr>
<td>Run-2</td>
<td>13.8% (80:20)</td>
</tr>
<tr>
<td>Run-4</td>
<td>29.7% (60:40)</td>
</tr>
<tr>
<td>Run-5</td>
<td>38.8% (50:50)</td>
</tr>
</tbody>
</table>

Figure 10 SEM micrographs of T-peel fractured surfaces.

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 1. 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, Tomita and Mizumachi had been investigated into viscoelastic
properties of epoxy resin which was 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% with a weight, cured epoxy forms a continuous phase. On the other hand, when it was 30% with a weight, cured epoxy and brominated-phenoxy formed co-continuous phases together. When it was 40% with a weight, brominated-phenoxy formed continuous phases, i.e., it was found that phase transportation took place at the brominated-phenoxy content of 30~40% with a weight.

(2) **Thermal Properties;** Two distinct Tg’s were found in all cured
epoxy/brominated-phenoxy blends. Since higher Tg was shown in 150 °C, it would be attributed to cured epoxy phases, i.e., it was found that Tg of cured epoxy was not decreased. On the other hand, since lower Tg was shown in 128 °C, it would be attributed to brominated-phenoxy phases. Furthermore, when brominated-phenoxy content was 7% with a weight, suppression of β-relaxation was found in the tanδ curve as a function of temperature. The phenomena could be explained in terms of the “antiplasticization”, i.e., brominated-phenoxy for stiff polar additives reduce the free volume of cross-linked epoxies for thermosets.

(3) Mechanical and Adhesive Properties; Although brominated-phenoxy formed continuous phases when brominated-phenoxy content was in 30～40% with a weight, the E’ values in the cured blends still have rubbery plateaus, i.e., 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 Tg.

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