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# Modification of a high performance epoxy matrix with poly(arylene ether-*co*-imidazole)s

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In an effort to improve toughness *N,N,N′,N′*-tetraglycidyl-4,4′diaminodiphenyl methane (TGMDA) was modified with poly(arylene ether-*co*-imidazole)s (PAE-*co*-Is). The PAE-*co*-Is contain imidazole units distributed randomly along the backbone which react with the epoxies upon curing. A system modified with 10% w/w high molecular weight polymer exhibited increases in fracture toughness of 1.7 times that of the unmodified system; however, controlled molecular weight PAE-*co*-Is were required to retain processablility. Modification also resulted in significant decreases in the tetrahydrofuran sensitivity. Scanning electron photomicrographs of the fractured surface showed stress whitening with no clear phase separation whereas poly(arylene ether)s without imidazole groups exhibited gross phase separation. © 1997 Published by Elsevier Science Ltd.

**(Keywords: epoxy; poly(arylene ether); poly(arylene ether imidazole); toughening)**

## INTRODUCTION

The use of epoxies as structural materials requires rigidity, resistance to creep, high glass transition temperature ($T_g$) and high impact strength. But damage tolerance and high impact strength are qualities of rubbery materials or thermoplastics rather than thermosets. This is currently the major problem in designing commercially viable high-performance epoxy resins for structural applications. Thermosets have a reputation of being very brittle, intractable, highly cross-linked materials, and many methods of maximizing and improving their toughness have been investigated. Blends of thermosets and rubbers[1], glassy thermoplastics[2] or reactive thermoplastics[3] are potential toughening matrices, wherein specific attributes of several polymers are combined into a single material.

Thermoplastic modifiers offer the advantage of high modulus and higher $T_g$ over liquid rubber modifiers, while improving mechanical properties. In comparison to thermosets, many thermoplastics can tolerate higher strains prior to failure and exhibit higher fracture toughness and better fatigue endurance[4]. These features have been incorporated into epoxies by mixing thermoplastic oligomers of varying molecular weight which have been end-capped with a reactive group (i.e hydroxy, epoxy or amino) into the unreacted epoxy. The system is then cured, and the thermoplastic is incorporated chemically via this reactive end group. The majority of these systems have a multi-phase morphology after cure and the potential to undergo undesired morphological changes at elevated temperatures under stress[5].

The goals of this study were to examine the physical and mechanical properties of random poly(arylene ether-*co*-imidazole)s (PAE-*co*-I) in order to identify promising candidates suitable for toughening epoxies. Ideally these systems should possess advantages over commercial resins of increased fracture toughness and the possibility of combining the high rigidity and ease of processing of the epoxy with the toughness of the PAE-*co*-I. The highly aromatic and polar structure of the poly(arylene ether imidazole) (PAEI) leads to inherently high glass transition temperature, thermal stability, and mechanical properties. The arylene ether unit should impart toughness of the modified system while the reactivity of the imidazole moiety with the oxirane ring allows for control of the distance between cross-links in the cured modified system. Therefore, it is postulated that if the poly(arylene ether) (PAE) and PAEI could be combined properly, the new material could serve as an epoxy resin toughening agent that would impart toughness and improved mechanical properties to the thermoset without substantially decreasing $T_g$ or thermal stability.

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## EXPERIMENTAL

### *PAEs and PAE*-co-*Is*

PAEs[6–9] and novel PAE-*co*-Is were prepared as reported[10–12] utilizing aromatic nucleophilic displacement of 2-phenyl-4,5,-bis(4-hydroxyphenyl) imidazole and/or various aromatic bisphenols by activated aromatic difluorides with exact and offset stoichiometric ratios. The polymerizations were performed in *N,N*-dimethylacetamide (DMAc) using potassium carbonate at elevated temperatures under nitrogen. In the PAE-*co*-Is the imidazole unit is distributed randomly along the polymer backbone. Unless otherwise stated, the imidazole concentration for the copolymers was generally held at 10 mol% of the total bisphenol concentration. This concentration was arrived at by screening a variety of copolymers which contained a range of imidazole concentrations[13].

### *Epoxy blends*

Modified epoxy resins were prepared by combining the epoxy resin and thermoplastic modifier with heating to 120°C for 4–8 h until a homogeneous yellow solution was obtained. The temperature was decreased to 100°C, and a stoichiometric amount of 4,4′-diaminodiphenyl sulfone (DDS) was added. The system was degassed and stirred until a homogeneous hot melt solution was obtained. The hot melt resin was poured into silicon rubber moulds of the dimensions needed to prepare various mechanical test specimens. The epoxies were cured for 1 h at 80°C, 1 h at 100°C, 4 h at 150°C, and 8 h at 200°C.

### *Moulded specimens*

Powdered PAE and PAE-*co*-I samples were compression moulded by heating to 275°C under 2 MPa for 1.5 h. Miniature compact tension specimens (1.57 × 1.57 ×0.64 cm thick) were machined from the mouldings and subsequently tested to determine fracture toughness $K_{\mathrm{Ic}}$ (critical stress intensity factor) according to ASTM E399 using a minimum of four specimens per test. Flexure three-point bend specimens with dimensions within a 16 : 1 length-to-depth ratio were machined from mouldings and subsequently tested according to ASTM D790 to determine flexural modulus using a minimum of four specimens per test.

### *Characterization*

Glass transition temperatures were determined from a Shimadzu DSC-50 differential scanning calorimeter. $T_g$s were determined at the half-point of the slope change from the baseline of the change in energy ($\Delta m$W) versus temperature curve, after heating of 20°C $\mathrm{min}^{-1}$ to 400°C and quenching.

Thermogravimetric analyses were conducted on a Seiko Tg/DTA 200/220 at a heating rate of 50°C $\mathrm{min}^{-1}$ from room temperature to 100°C, held for 30 min and then ramped at 2.5°C $\mathrm{min}^{-1}$ to 650°C in air at a flow rate of 15 $\mathrm{cm}^3\,\mathrm{min}^{-1}$. Thermal degradation was designated as the temperature of 5% weight loss. Inherent viscosity ($\eta_{\mathrm{inh}}$) measurements were obtained on 0.5% solutions at 25 or 35°C.

Dynamic mechanical thermal analysis of the polymers, oligomers and the blended materials was conducted on a duPont Model 982 analyser. Samples (3.3 × 1.4 cm) were cut from compression-moulded specimens or obtained from hot melt moulding in a silicon rubber mould. Tests were performed at a frequency of 1 Hz and a heating rate of 5°C $\mathrm{min}^{-1}$, between −150 and 500°C. Storage modulus ($E'$) and $\tan\delta$ were recorded.

Swelling experiments were performed on cured modified epoxy resins. A sample was dried for 72 h at 150°C, weighted, immersed in tetrahydrofuran (THF) and placed in a tightly sealed sample bottle. The mass of the sample was checked periodically and recorded to ±0.1 mg. The percentage of swelling was determined by

$$\text{swelling}(\%) = \frac{\text{swollen mass} - \text{initial mass}}{\text{initial mass}} \times 100$$

## RESULTS AND DISCUSSION

### *Arylene ether*-co-*imidazole polymers as epoxy modifiers*

The high molecular weight PAE-*co*-I (PAE-*co*-I-5) containing the fluorene ring system shown in *Figure 1* resulted in the most compatible mixture, which yielded cured void-free samples with the epoxy resin matrix *N,N,N′,N′*-tetraglycidyl-4,4′-diaminodiphenylmethane (TGMDA; Ciba-Geigy Araldite-722). This thermoset was chosen based on its low viscosity and ease in processing.

*Table 1* summarizes the effect of increasing polymer content on fracture toughness. The PAE-*co*-I-5 exhibited a fracture toughness of 1.83 MPa $\mathrm{m}^{1/2}$. The simple rule of mixture predicts the fracture toughness of the 10% w/w modified resin should be 0.53 MPa $\mathrm{m}^{1/2}$. The fracture toughness value for this modified resin was 24% greater than expected at 0.66 MPa $\mathrm{m}^{1/2}$, which is 1.7 times that of the unmodified epoxy. Further improvements in epoxy resin fracture toughness might be realized if higher PAE-*co*-I weight loadings were possible; however, samples containing higher loadings could not be prepared with this polymer/resin combination due to the high viscosity of the precured mixtures.

### *Arylene ether and arylene ether*-co-*imidazole oligomers as epoxy modifiers*

High molecular weight PAE-*co*-Is have limited solubility in the epoxy resin. As a result, controlled molecular weight PAE-*co*-I oligomers were investigated as tougheners. Stoichiometric imbalance of the monomers was employed to properly control molecular weight according to the Carothers equation by varying the molar ratio of bisphenol to dihalide. Since no end-capping agent was employed, stoichiometric imbalance resulted in polymer chains terminated with either hydroxy or fluorine groups. End-group functionality and molecular weight play a major role in the mechanical and thermal properties of a polymer. To assess the effects of stoichiometric offsetting and possible interaction of the end-group with the epoxy resin, polymer systems were prepared offsetting in favour of both the dihalide and bisphenol, holding the imidazole concentration distributed randomly along the polymer backbone constant at 10 mol%. All polymers in *Figure 2* designated as Olig-1 and Co-Olig-1 possess phenol end-groups, and Olig-2 and Co-Olig-2 possess fluoro end-groups.

The capability of PAEs without the imidazole moiety to serve as toughness modifiers for epoxy resins[14,15] was investigated. PAE homopolymers and oligomers were blended with the TGMDA 722 epoxy resin, and the

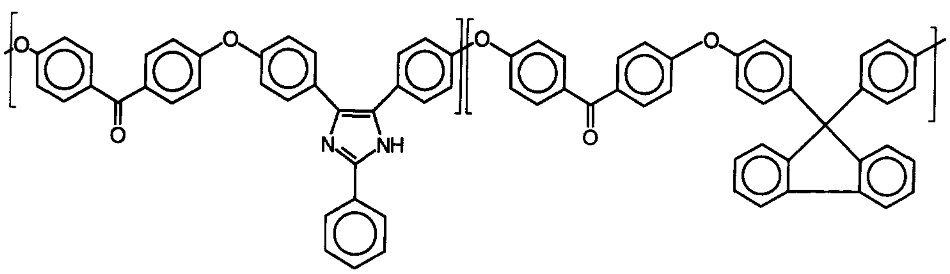


**Figure 1** Poly(arylene ether) PAE-*co*-I-5

**Table 1** Fracture toughness of TGMDA resins modified with PAE-*co*-I-5

| Polymer (wt%) | $K_{\mathrm{Ic}}$ (MPa m$^{1/2}$) |
|---|---|
| 0 | 0.39 ± 0.02 |
| 5 | 0.53 ± 0.03 |
| 7 | 0.57 ± 0.03 |
| 10 | 0.66 ± 0.05 |

solubility and toughness characteristics of the systems were determined.

The influence of the imidazole moiety on the solubility and incorporation of the polymer into the cured epoxy resin network is demonstrated in *Figure 3*. Upon initial mixing, both systems appeared to be miscible with the uncured epoxy resin, giving clear yellow solutions. However, the non-reactive homopolymer (7% w/w) was not compatible in the cured state, and was excluded as an opaque mass from the cured epoxy network (*Figure 3a*). The reactive copolymer (20% w/w) remained transparent when incorporated into the cured epoxy network (*Figure 3b*).

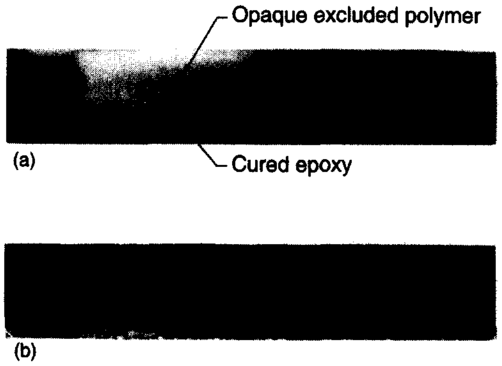


**Figure 3** (a) 7% w/w non-reactive homopolymer; (b) 20% w/w reactive copolymer

The solubility of the polymer/oligomer systems in the epoxy is influenced by the percentage of imidazole contained in the polymer and the composition of the oligomer end-groups. The oligomers with bisphenol end-groups required longer mixing times (10–18 h) than the fluoro-terminated oligomers (7–10 h) to obtain

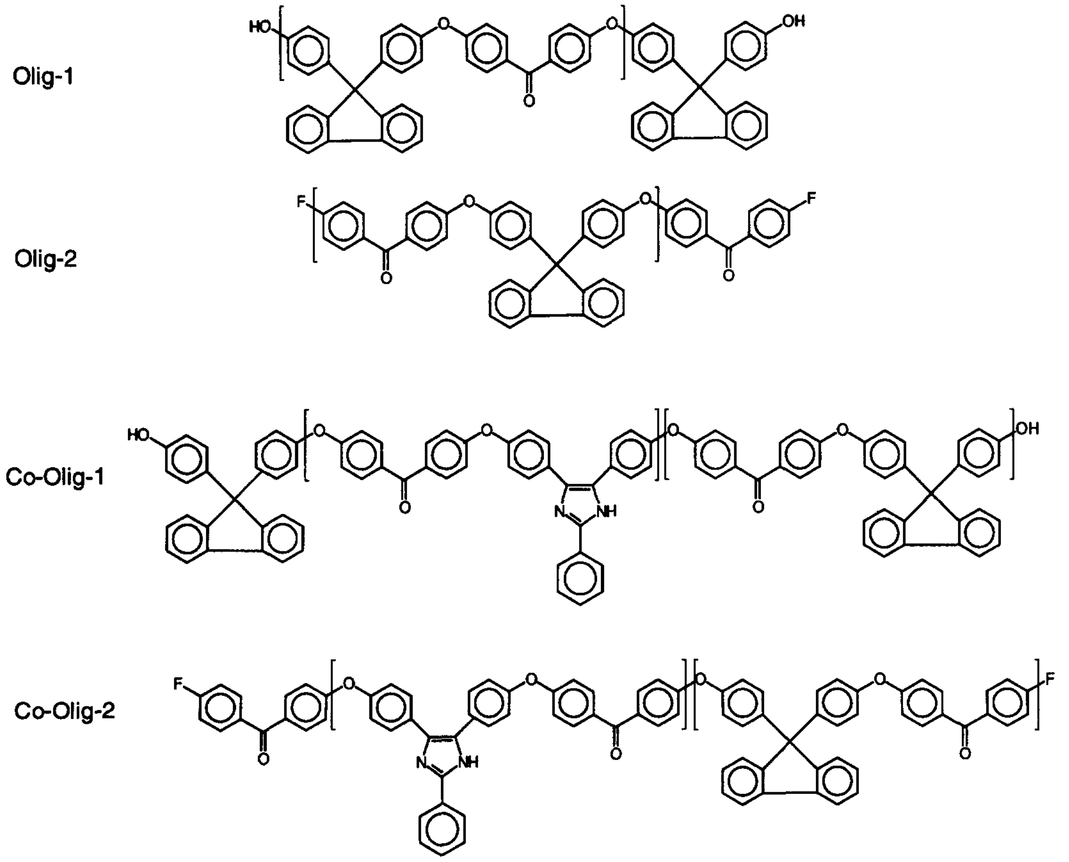


**Figure 2** Arylene ether oligomers

homogeneous mixtures. The PAE oligomers without the imidazole moiety required extended mixing times (+24 h) at elevated temperatures to become homogeneous. The 5% offset Olig-1 was insoluble even at elevated temperatures.

*Table 2* presents the mechanical properties of the neat homopolymers and copolymers along with the mechanical properties of the modified epoxy resins. Because of their low molecular weights, some oligomeric systems were too brittle to prepare moulded compact tension specimens, such as the 10% offset homo- and copolymers. The 5% offset Olig-2 homopolymer was capable of being moulded, but fractured when machined into the test specimen configuration. Although neat polymer properties could not be determined for these systems, they were blended and evaluated as possible epoxy resin tougheners.

Flexural modulus, strength and fracture toughness values for the neat polymers follow the expected trend of decreasing mechanical properties with decreasing molecular weight. The fracture toughness value of the 5% offset Co-Olig-2 is low at 0.52 MPa $m^{1/2}$; however, the modulus and strength values for this oligomer are in line with the other oligomers in this study. These modulus and strength values compare well with thin film properties of PAEIs previously reported[16]. Because of the limited miscibility of the epoxy with PAE-1 and 5% Olig-1, the mechanical properties of these systems could not be determined. The greatest improvement in fracture toughness was realized for the high molecular weight PAE-*co*-I-5 resin, which also had the highest fracture toughness in the neat polymer state. The second highest modified system in terms of fracture toughness was the 10% offset Co-Olig-2, with a 25% increase in fracture toughness over the unmodified resin. Both of these systems exhibited toughening greater than that predicted by a rule of mixtures relationship.

A second consideration in modifying high-performance epoxy resins for improved fracture toughness is the effects of the modifier on the thermal properties of the resin. $T_g$s and 5% weight loss data of the neat polymers, oligomers and modified systems are given in *Table 3*.

The thermal oxidative stability of the epoxy is less than that of the modifiers, and dominates the blends since it comprises 93% w/w of the modified system. The 5% weight-loss point for the modified resins is approximately equal to that of the unmodified resin. There is an overall decrease in $T_g$ with polymer modification. A decrease in $T_g$ of over 80°C was realized by incorporating 5% offset Co-Olig-2, while only a 20°C drop in $T_g$ resulted from the incorporation of PAE-*co*-I-5. A net lowering in $T_g$ is expected with modification of thermoset networks with thermoplastics due to the lowering of cross-link density.

Optimum increases in fracture toughness are realized through incorporation of the high molecular weight copolymer PAE-*co*-I-5 for the systems examined in this study. However, the high viscosity and difficulties in processing limit the application of this system. In order to prepare modified resins containing higher weight per cent thermoplastic, an oligomeric system of greater solubility and lower precure viscosity was chosen. Based on the solubility of the oligomer, fracture toughness, $T_g$ and 5% weight loss properties of the system, 10% offset Co-Olig-2 was chosen as a system likely to yield good modified epoxy resin specimens of higher polymer concentrations. Samples containing varying weight per cent of polymer were prepared and tested in terms of fracture toughness, flexural modulus and flexural strength. A summary of the data is presented in *Table 4*.

As expected, higher thermoplastic concentrations did not affect the point of 5% weight loss for the epoxy, and an overall decrease in $T_g$ resulted with the modified resins. Although the modified resins exhibit improvement in fracture toughness, increases in thermoplastic modifier concentrations as high as 20% w/w did not result in an additional increase in fracture toughness for the modified resin system.

**Table 2** Mechanical properties of polymer and TGMDA resins modified with 7% w/w polymer

| | $M_n$ ($g\,mol^{-1}$) theory | Neat polymer flexural modulus (MPa) | Neat polymer flexural strength (MPa) | Neat polymer $K_{Ic}$ ($MPa\,m^{1/2}$) | Modified epoxy flexural modulus (MPa) | Modified epoxy flexural strength (MPa) | Modified epoxy $K_{Ic}$ ($MPa\,m^{1/2}$) |
|---|---|---|---|---|---|---|---|
| Neat TGMDA | | | | | 3357 ± 214 | 75.8 ± 35.2 | 0.39 ± 0.02 |
| Homopolymers | | | | | | | |
| PAE-1 | | 4302 ± 41 | 133 ± 6.9 | 2.06 ± 0.19 | [b] | [b] | [b] |
| 10% offset Olig-1 | 10 400 | 3826 ± 21 | 33.8 ± 2.8 | [a] | 3833 ± 248 | 35.2 ± 4.8 | 0.36 ± 0.02 |
| 10% offset Olig-2 | 10 300 | 3398 ± 21 | 15.2 ± 2.1 | [a] | 2737 ± 620 | 9.0 ± 2.8 | [b] |
| 5% offset Olig-1 | 21 000 | 4364 ± 41 | 128 ± 6.9 | 1.64 ± 0.14 | [b] | [b] | [b] |
| 5% offset Olig-2 | 21 000 | 4026 ± 152 | 31.0 ± 0.7 | [a] | 3771 ± 317 | 17.9 ± 5.5 | 0.41 ± 0.01 |
| 10% imidazole copolymer PAE-*co*-I-5 | | 4123 ± 76 | 127 ± 13.8 | 1.83 ± 0.11 | 4688 ± 152 | 97.9 ± 3.5 | 0.57 ± 0.03 |
| 10% offset Co-Olig-1 | | 4074 ± 110 | 23.4 ± 3.5 | [a] | 3550 ± 159 | 65.5 ± 2.1 | 0.43 ± 0.04 |
| 10% offset Co-Olig-2 | | [a] | [a] | [a] | 3481 ± 276 | 54.5 ± 24.1 | 0.49 ± 0.06 |
| 5% offset Co-Olig-1 | | 2640 ± 55 | 9.70 ± 0.7 | 1.29 ± 0.08 | 2806 ± 200 | 38.6 ± 4.8 | 0.46 ± 0.05 |
| 5% offset Co-Olig-2 | | 4047 ± 138 | 30.3 ± 6.9 | 0.52 ± 0.18 | 3516 ± 441 | 53.1 ± 0.7 | 0.45 ± 0.04 |

[a] System too brittle to characterize

[b] Not tested due to high void content

**Table 3** Thermal properties of polymers and TGMDA resins modified with 7% w/w polymer

| Description | Polymer $T_g$ (°C, DSC) | Polymer 5% weight loss in air (°C, TGA) | Modified epoxy $T_g$ (°C, DSC) | Modified epoxy 5% weight loss in air (°C, TGA) |
|---|---|---|---|---|
| Neat TGMDA | | | 243 | 322 |
| Homopolymers | | | | |
| PAE-1 | 252 | 446 | $^b$ | $^b$ |
| 10% offset Olig-1 | 233 | 490 | 213 | 311 |
| 10% offset Olig-2 | 214 | 506 | $^a$ | 322 |
| 5% offset Olig-1 | 242 | 492 | $^b$ | $^b$ |
| 5% offset Olig-2 | 221 | 487 | $^a$ | 294 |
| 10% imidazole copolymers | | | | |
| PAE-*co*-I-5 | 243 | 458 | 224 | 330 |
| 10% offset Co-Olig-1 | 223 | 431 | 171 | 320 |
| 10% offset Co-Olig-2 | 205 | 461 | 188 | 323 |
| 5% offset Co-Olig-1 | 251 | 431 | 196 | 316 |
| 5% offset Co-Olig-2 | 226 | 492 | 164 | 323 |

$^a$ System too brittle to characterize
$^b$ Nonviable modified system

**Table 4** Properties of TGMDA resins modified with Co-Olig-2

| Polymer (wt%) | $T_g$ (°C, TGA) | 5% weight loss in air (°C, TGA) | Flexural modulus (MPa) | Flexural strength (MPa) | $K_{Ic}$ (MPa m$^{1/2}$) |
|---|---|---|---|---|---|
| 0 | 243 | 322 | 3557 ± 214 | 75.8 ± 34.5 | 0.39 ± 0.02 |
| 7 | 188 | 323 | 3481 ± 276 | 54.5 ± 24.1 | 0.49 ± 0.06 |
| 10 | 189 | 321 | 3371 ± 110 | 66.9 ± 34.5 | 0.49 ± 0.05 |
| 15 | 183 | 326 | 3722 ± 193 | 86.2 ± 20.6 | 0.48 ± 0.03 |
| 20 | 173 | 327 | 2172 ± 75.8 | 44.1 ± 13.8 | 0.51 ± 0.02 |

### *PAE-*co*-Is of varying imidazole concentrations as epoxy modifiers*

The imidazole concentration of the copolymer systems discussed so far was held constant at 10 mol% of the overall bisphenol concentrations. Increasing the amount of imidazole distributed along the polymer backbone decreases the molecular weight between cross-linking sites, and changes the mechanical properties of the modified system. High molecular weight PAE-*co*-I systems prepared using the same monomers as PAE-*co*-I-5 but containing 30 and 50 mol% imidazole were prepared and characterized. The data for both neat polymer and TGMDA 5% w/w polymer modified resins are summarized in *Tables 5* and *6*, respectively.

Increases in the imidazole concentration along the polymer backbone have only minimal effects on the glass transition temperature and 5% weight loss. It should be noted that the thermal stability by TGA of the 50 : 50 PAE : PAEI copolymer is slightly higher than that of the other variations, as previously observed for other 50 : 50 PAE : PAEI random copolymers of different chemical composition[17]. The 10% imidazole polymer exhibited $K_{Ic}$ values twice as high as the other polymers, and the flexural modulus value of the 30% imidazole was lowest. The 10% imidazole system also had far better flexural strength properties than the other two polymers at 127 MPa in comparison to 28 and 35 MPa for concentrations of 30 and 50% imidazole, respectively.

Increasing the concentration of imidazole from 10 to 30% resulted in a 30°C drop in $T_g$ for the 5% w/w modified resin, but increasing it to 50% yielded a resin with a $T_g$ only 10°C below the 10% system. Increasing the imidazole concentration increased the flexural modulus from 3357 MPa for the 10% imiadazole system to 3909 MPa for the 50% imidazole system. An increase in imidazole concentration increases the number of reaction sites between the thermoplastic modifier and the epoxy resin, which results in an overall increase in cross-link density.

### *Solvent swelling of modified resins*

Postmortem three-point bend samples were evaluated for solvent swelling at room temperature. The uncured epoxy, PAE-*co*-Is and PAEs are all soluble in THF. The sensitivity of the unmodified epoxy resin to THF was so severe that the sample fragmented after approximately 10 h of immersion. The highly cross-linked, three-dimensional network of the unmodified resin allows little flexibility for the polymer chains to accommodate infiltration of solvent molecules. The internal stresses applied by solvent absorption presumably caused a breakdown of the network. The non-reactive PAE oligomer dominated by hydroxyl end-groups can participate in epoxy curing reactions and therefore become chemically incorporated into the network. The resin modified with this oligomer remained intact for approximately 24 h but subsequently fragmented due to severe solvent stresses. Dihalide functional groups do not participate in epoxy curing reactions; the resin modified with the non-reactive PAE oligomer dominated by fluoro

**Table 5** Properties of neat polymers containing varying mole per cent of imidazole

| Description | $T_g$ (°C, DSC) | 5% weight loss in air (°C, TGA) | Flexural modulus (MPa) | Flexural strength (MPa) | $K_{Ic}$ (MPa m$^{1/2}$) |
|---|---|---|---|---|---|
| 10% imidazole | 243 | 458 | 4123 ± 75.8 | 126.8 ± 17.2 | 1.83 ± 0.11 |
| 30% imidazole | 239 | 419 | 3702 ± 303 | 27.6 ± 2.1 | 0.85 ± 0.05 |
| 50% imidazole | 232 | 468 | 4047 ± 44.8 | 35.3 ± 2.8 | 0.71 ± 0.09 |

**Table 6** Properties of TGMDA resins modified with 5% w/w polymer containing varying mole per cent of imidazole

| Description | $T_g$ (°C, DMA ) | 5% wt loss in air (°C, TGA) | Flexural modulus (MPa) | Flexural strength (MPa) | $K_{Ic}$ (MPa m$^{1/2}$) |
|---|---|---|---|---|---|
| Neat TGMDA | 243 | 322 | 3557 ± 214 | 75.8 ± 34.5 | 0.39 ± 0.02 |
| 10% imidazole | 207 | 320 | 3357 ± 303 | 93.1 ± 22.8 | 0.57 ± 0.03 |
| 30% imidazole | 179 | 329 | 3764 ± 214 | 80.0 ± 19.3 | 0.48 ± 0.05 |
| 50% imidazole | 197 | 333 | 3909 ± 66.9 | 91.0 ± 17.2 | 0.44 ± 0.02 |

end-groups resulted in immediate weight loss so severe the samples become non-viable for weighing after 7 h. This combination apparently forms a blended material which is not chemically incorporated into the epoxy matrix. Consequently, solvent immersion of such a system resulted in polymer extraction followed by fracture due to the severe solvent swelling of the resin.

All PAE-*co*-I-modified resins exhibited lower THF sensitivity than the neat epoxy or PAE modified resins. The 5% offset Co-Olig-1 modified resin had swollen to 2.68% at 24 h before sampling was discontinued due to solvent-induced fracture. The 10% offset Co-Olig-1-modified resin exhibited maximum solvent swelling of 1.61% at 82 h before solvent-induced sample fracture.

Of the PAE-*co*-I-5-modified resins studied (5, 10 and 20% w/w), the 10% w/w resin was the most solvent-sensitive. However, only 1.6% solvent swelling resulted for the 10% w/w sample after 105 h of immersion.

Increasing amounts of Co-Olig-2 modifier in the resin increased the amount of solvent absorption, as summarized in *Table 7*. The higher the amounts of reactive thermoplastic incorporated in the resin the greater the network flexibility. This flexibility allows the three-dimensional network to accommodate more solvent molecules. This is demonstrated by the increase of less than 1% solvent swelling for the 7% w/w modified resin to 10.2% solvent swelling for the 20% w/w modified resin after 105 h. The 20% w/w sample maintained its integrity without fracture and returned to within 0.2% of its pre-immersed weight upon drying, leading to the conclusion that the competing mechanisms of polymer extraction accompanied by solvent incorporation are not taking place.

### *Fracture surfaces and SEM*

Fracture toughness for the modified resins in this study was determined by the three-point bend test. When testing in this configuration the load rises linearly with strain, and a stress-whitened zone develops. This process zone is directly related to the energy-absorbing mechanism since it accounts for the total energy absorption prior to fast fracture[18]. The load then drops rapidly as the crack propagates. Matrix modifications lead to changes in the deformation behaviour of a system. Changes that increase toughness often increase the stress whitening of the process zone. In order to assess the fracture characteristics of the modified resin, scanning electron micrographs of fracture surfaces were examined.

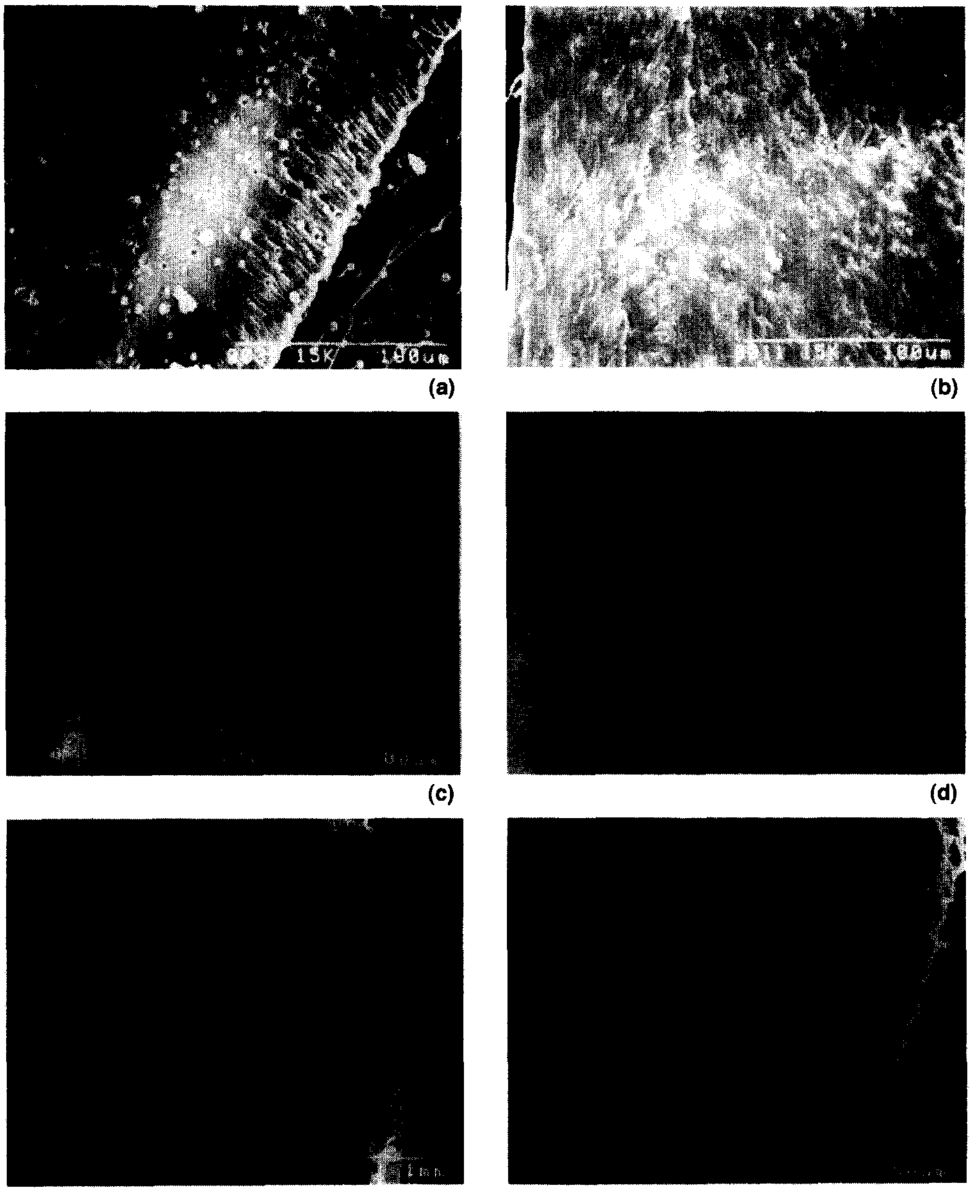
Scanning electron micrographs of the fracture surface of the unmodified epoxy resin are basically featureless, with very little evidence of striations, stress whitening or yielding at the boundary between the precrack and the process zone. This type of surface is representative of the brittle material with low fracture toughness values.

Scanning electron micrographs of TGMDA resins modified with non-reactive polymers show fracture surfaces indicative of complete phase separation with evidence of discrete particle pull out and very low interfacial adhesion (*Figure 4a*). The 5% offset Olig-2 modifier is dominated by the non-reactive dihalide end-groups; therefore, there is no chemical interaction between the epoxy and thermoplastic. The Olig-1 modifier exhibits some particle tearing along the fracture surface along with stress whitening, indicating more ductile fracture (*Figure 4b*). The reactivity of the hydroxyl end-groups allows Olig-1 to become incorporated into the epoxy network, thereby allowing for some interfacial interaction rather than complete phase separation. However, the brittleness of the neat PAE due to its low molecular weight did not afford any increase in fracture toughness for the modified system.

PAE-*co*-I-modified resins (7% w/w) did not show evidence of phase separation (*Figure 4c*). However, there appeared to be more ductile fracture along the process zone, as illustrated by an increase in stress whitening, which corresponds to an increase in fracture toughness.

Increasing the concentration of Co-Olig-2 from 7% w/w (*Figure 4d*) to 20% w/w (*Figure 4e*) did not lead to an increase in fracture toughness. Examination of the fracture surfaces for these modified resins, however, indicated an increase in stress whitening. Increased thermoplastic content led to more ductile failure in the process zone, and close examination of the fracture surface of the 20% w/w modified resin (*Figure 4f*) shows the beginnings of a phase-separated system.

A high degree of interface interaction results in a high degree of toughening when there is an energy-absorbing mechanism such as crazing or interfacial interactions.



(a) (b) (c) (d) (e) (f)

**Figure 4** Scanning electron micrographs of modified epoxy fractured surfaces

**Table 7** Percentage THF swelling of TGMDA resins modified with varying weight per cent of Co-Olig-2

| Hours | TGMDA | 7% w/w | 10% w/w | 15% w/w | 20% w/w |
|---|---|---|---|---|---|
| 4 | 8.34 | 0.02 | 0.06 | 0.01 | 0.11 |
| 7 | 22.85 | 0.02 | 0.12 | 0.02 | 0.13 |
| 24 | [a] | 0.02 | 0.13 | 1.50 | 1.60 |
| 33 | [a] | 0.02 | 0.22 | 2.30 | 2.20 |
| 57 | [a] | 0.03 | 0.53 | 5.00 | 2.20 |
| 82 | [a] | 0.09 | 0.54 | 5.00 | 6.80 |
| 105 | [a] | 0.80 | 0.99 | 5.20 | 10.20 |

[a] Non-viable system

However, the absence of a detectable phase separation does not eliminate the possibility of enhanced fracture toughness through thermoplastic modification. The presence of a bi-continuous network where two networks exist separately with attachments at the cross-link points or of a semi-interpenetrating network may also lead to increases in fracture toughness. The existence and toughening mode in operation for these types of systems are an area of debate. The absence of phase separation accompanied by an increase in fracture toughness for the PAE-*co*-I-modified epoxy resin provides evidence that non-traditional morphologies may lead to increased fracture toughness, although the mode of toughening is not fully understood.

## *Summary*

A series of PAEs and novel PAE-*co*-Is were prepared via aromatic nucleophilic displacement using 2-phenyl-4,5-bis(4-hydroxyphenyl) imidazole, various aromatic bisphenols and activated aromatic difluorides. The polymers were prepared using both exact and offset stoichiometric ratios, resulting in high molecular weight polymers and controlled molecular weight oligomers with either phenol or fluoro end-groups.

Modified TGMDA epoxies were prepared using stoichiometric quantities of DDS and various amounts of polymer or oligomer. The mixtures were stirred at elevated temperature until they became homogeneous, degassed, thermally cured and subsequently tested for flexural and toughness properties.

One modified system with 10% w/w high molecular weight PAE-*co*-I-5 exhibited improved fracture toughness ($K_{Ic}$) of 1.7 times that of the unmodified epoxy. Scanning electron micrographs of the fractured surface showed stress whitening and no clear phase separation. Oligomeric arylene ether-*co*-imidazoles resulted in only a 30% increase in fracture toughness at 20% w/w modifier concentrations and did not result in a phase-separated morphology although an increase in stress whitening was observed.

The unmodified TGMDA was highly sensitive to THF exposure, and resulted in greater than 20% solvent absorption after 7 h. High molecular weight PAEs and oligomers terminated with hydroxy and fluoro groups were extracted from the modified resin with THF. The difluoro-terminated oligomers were the most readily extracted. Incorporation of PAE-*co*-Is improved the THF sensitivity of epoxy resins. Solvent sensitivity results reinforce the notion that PAE-*co*-Is are chemically incorporated into epoxy matrices while PAEs without reactive end-groups are physical blends.

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