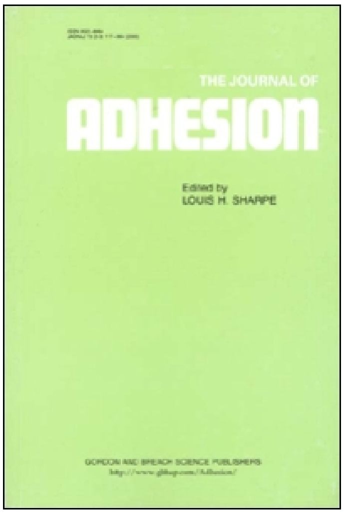

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Adhesive and Mechanical Properties of Reactive Polysulfone Modified Epoxy Resins*

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The diglycidyl ether of bisphenol-A epoxy resin (EPON 828®) was cured with 4,4′-diaminodiphenylsulfone (DDS) and, optionally, an animophenyl functional reactive polyethersulfone (R-PES, $<M_n>$ = 10k) as a co-curing agent. Commercial polysulfone, Udel® P-1700, was also utilized to afford epoxy-Udel® blends (or semi-IPNs). Cured epoxy polymers were subjected to T_g determinations, plane strain fracture toughness (K_{IC}) tests, adhesive bond strength measurements, tensile tests and chemical resistance studies. The morphologies of the fractured samples were studied by SEM and correlated to the property changes. Only the reactive polysulfone modification improved both fracture toughness and adhesive properties without detracting from the good mechanical properties and chemical resistance.

KEY WORDS epoxy; reactive PES; adhesion; fracture toughness; tensile; chemical resistance.

1 INTRODUCTION

Epoxy resins have received much attention in high performance composites and structural adhesive applications because of some exceptional properties. During the past decades, many scientists and engineers have conducted a large research effort to develop impact-resistant epoxy polymers with high glass transition temperatures. A number of papers have indicated that fracture toughness of epoxy resins could be enhanced by functionalised rubber corporation[1–7] or by high performance thermoplastic polymer blending.[8–15] However, it was widely recognized that the improved fracture toughness by rubber modification was at the expense of lowered thermal and mechanical properties. Commercial thermoplastic polymer blendings have also been known to be effective in improving the adhesive properties[16,17] and the fracture toughness of epoxy resins without a major reduction in mechanical properties.[11–14] However, it is assumed that due to the absence

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of chemical bonds between thermoplastic phases and epoxy phases, thermoplastic blends may not provide as good chemical resistance and mechanical properties as the unmodified epoxy resins. On the other hand, utilization of functionalised (thus reactive) thermoplastic modifiers has been a major thrust in our laboratory and has proven to be outstanding in affording tough, chemically-inert epoxy networks.[18–21] Recently, it has been reported[22,23] that reactive thermoplastic poly (arylene ether)s can also be utilized for bismalimide systems.

Although non-reactive commercial polymers such as Udel® P-1700 polyethersulfone and Ultem® 1000 polyetherimide are very effective in achieving high fracture toughness,[9,11,13,14] it appears that the significance of the reactive end-groups in thermoplastic modifiers is not appreciated, despite the early demonstrations of the effectiveness of functionalised rubber toughening agents. Therefore, it was of interest to demonstrate the superior properties of the reactive thermoplastic-modified epoxy resins over the non-reactive polymer blends, by utilizing aminophenyl-terminated polyethersulfone. Plane strain fracture toughness, adhesive and mechanical properties and chemical resistance were measured and correlated to the end-groups on the thermoplastic modifiers along with phase separation behaviors.

2 EXPERIMENTAL

2.1 Materials

The digylcidyl ether oligomers based on bisphenol-A epoxy resin (EPON 828®, EEW = 189) was provided by Shell Chemical Company and the curing agent, 4,4′-diaminodiphenylsulfone (DDS, Aldrich), was used as received. Aminophenyl-functional reactive polyethersulfone (R-PES, $\langle M_n \rangle$ = 10,460 g/mole) oligomers, prepared in our laboratory, were utilized as a co-curing agent. The detailed synthesis of reactive polyethersulfone is provided elsewhere.[20] Commercial polysulfone, Udel® P-1700, supplied by Amoco, was utilized to afford Udel®-epoxy blends.

2.2 Resin Preparation

The degassed DGBEA epoxy resin system was mixed with the curing agent, DDS, and stirred at approximately 140°C until a clear mixture was obtained. The mixture was degassed again in a vacuum oven until most of the bubbles were removed. If the thermoplastic modifier, either aminophenyl-terminated polyethersulfone (R-PES) or Udel® P-1700, was utilized, the epoxy resin was mixed with the thermoplastic modifier and then with the curing agent. In all resin mixtures, the molar ratio of epoxy resin to amine curing agent was maintained at 2:1 to allow for a complete network formation. However, since Udel® P-1700 is non-functional, it does not affect the stoichiometric balance. The degassed clear resin mixture was poured into a preheated silicone rubber mold at 130°C and cured in an air convection oven with a pre-optimized cure cycle; 4 hours at 130°C and additional 2 hours at 220°C, followed by slow cooling in the oven. The loadings of R-PES and Udel® P-1700 were extended to 30 and 20 wt.%, respectively, which were perhaps maximum loadings without utilizing solvent.

2.3 Property Measurements

The thermal behavior of epoxy networks, such as T_g values, were determined by a Perkin Elmer Dynamic Mechanical Analyzer (DMA-7) in a 3-point bending mode at a heating rate of 10°C/minute. The specimen dimensions for DMA were 20 × 6 × 1.5mm. The chemical resistance of reactive polysulfone modified and Udel® blended samples were evaluated by immersing the samples (3 × 6 × 20mm) in chloroform, and monitoring color and shape change at room temperature. The morphology of modified or unmodified samples was analyzed with scanning electron microscopy (SEM), using a ISI-SX-40 at 20kV. All samples were coated with Au-Pd to avoid charging problems. The phase separation behavior was investigated with the samples from all tests; fracture toughness, tensile, adhesion and chemical resistance tests.

The fracture toughness (K_{IC}) was measured with Single-Edge-Notched Bending (SENB) specimens, following ASTM Standard D-5045-91. The molded samples were ground with an emery paper to afford a rectangular shape. The specimens, 3 × 6 × 40mm, were sawed to generate a notch and then a crack was initiated by tapping with a liquid-nitrogen-chilled, fresh razor blade. The samples were tested in 3-point bending mode at a test rate of 0.5 inch (12.7mm)/minute. Approximately 10 samples were tested and fracture toughness values were calculated by the formula provided in ASTM D-5045-91, where the samples had a pre-crack length of 0.45 to 0.55 of hight.

The mechanical properties of modified or unmodified epoxy resins were measured *via* tensile tests on an Instron 1123 employing a strain gauge extensometer, Instron 2630-013. The dog-bone shape samples (ASTM D-638 #5) were prepared in a silicone rubber mold and cured as described previously. If needed, the samples were sanded with an emery paper to provide the proper shape. The samples were tested at room temperature and at a cross head speed of 0.5 inch (12.7mm)/minute, following ASTM Standard D-638. Approximately 10 samples were tested and the results were averaged.

Adhesive properties were measured with single lap shear samples prepared from Ti-6Al-4V alloys, following ASTM Standard D-1002. The Ti-6Al-4V alloy adherends (5 × 1) inch (127 × 25.4mm) were sand blasted and Pasa-Jell 107® treated. The surface-treated adherends were coated with the epoxy resin mixture to provide a coating thickness of approximately 10 mils (0.25mm). Single lap shear samples with 1 × 0.5 inch (25.4mm) overlap were prepared in an air convection oven without an applied pressure. The same cure cycle as described earlier was utilized. Adhesive bond strengths were measured at room temperature, 100°C and 150°C at a cross head speed of 0.05 inch (12.7mm)/minute on an Instron 1123. Four or more samples were tested and the results were averaged. The environmental chamber, an Instron-3116, was utilized for the elevated temperature tests and at least 10 minutes were allowed for temperature equilibration before the measurements were conducted.

3 RESULTS AND DISCUSSION

3.1 Thermal Behavior

All modified and unmodified samples were, in general, transparent and light amber in color. The modified epoxy resins appear to have only a single T_g at 5 wt.% loading of the modifier, but two T_gs at higher loadings, as shown in Table I. The T_g values did not vary with the loading of modifier, indicating no or little phase mixing. The upper T_gs are from the epoxy phase, while the lower T_gs are from the polysulfone thermoplastic modifier.

TABLE I
Glass transition temperatures of reactive polysulfone modified, and Udel® P-1700 blended epoxy resins

wt.%	Reactive PES	Udel® P-1700
0%	199	—
5%	203	202
10%	180, 205	180, 202
15%	180, 203	182, 201
20%	179, 203	181, 201
25%	180, 203	—

*Measured by DMA in 3-point bending mode at 10°C/min.

3.2 Fracture Toughness

As expected, K_{IC} fracture toughness increased with R-PES as well as with the Udel® P-1700 as indicated in Figure 1. A K_{IC} value of 1.80 MPa-m$^{0.5}$ was obtained with 30 wt.% R-PES, which is nearly triple that of the control (0.65 MPa-m$^{0.5}$) and approximately 75% of the fracture toughness of thermoplastic Udel® P-1700

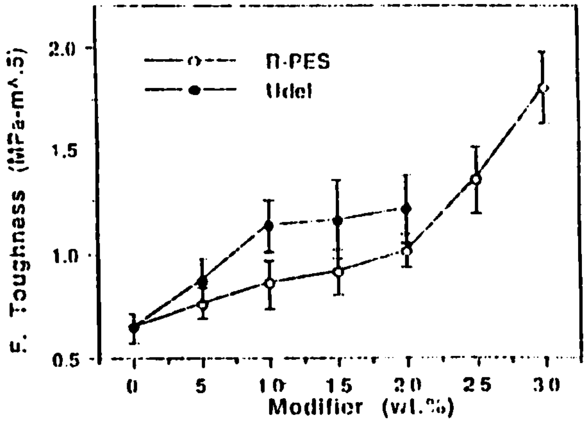

FIGURE 1 Improved fracture toughness of epoxy resins with reactive polysulfone (R-PES) modification and Udel® P-1700 blending.

itself.[20] An inflection of fracture toughness at 20 wt.% R-PES was observed, which may be explained by phase inversion from dispersions of the thermoplastic to a co-continuous or continuous thermoplastic phase. Fracture toughness of Udel® P-1700 blended epoxy resins increased sharply with 5 and 10 wt.% loadings, then approximately leveled off at 15 and 20 wt.%. The fracture toughness improvement by the R-PES modification is thus much greater than that provided by Udel® blending, which is attributed to the reactive end groups in R-PES. The chemical bonds between R-PES and epoxy chains provided strong adhesion between R-PES and the epoxy phases, which is evidenced by SEM analysis, tensile and adhesive properties and chemical resistance tests.

The single edge notched bending (SENB) specimens of the epoxy control showed a featureless, shiny fracture surface, while phase separation was observed

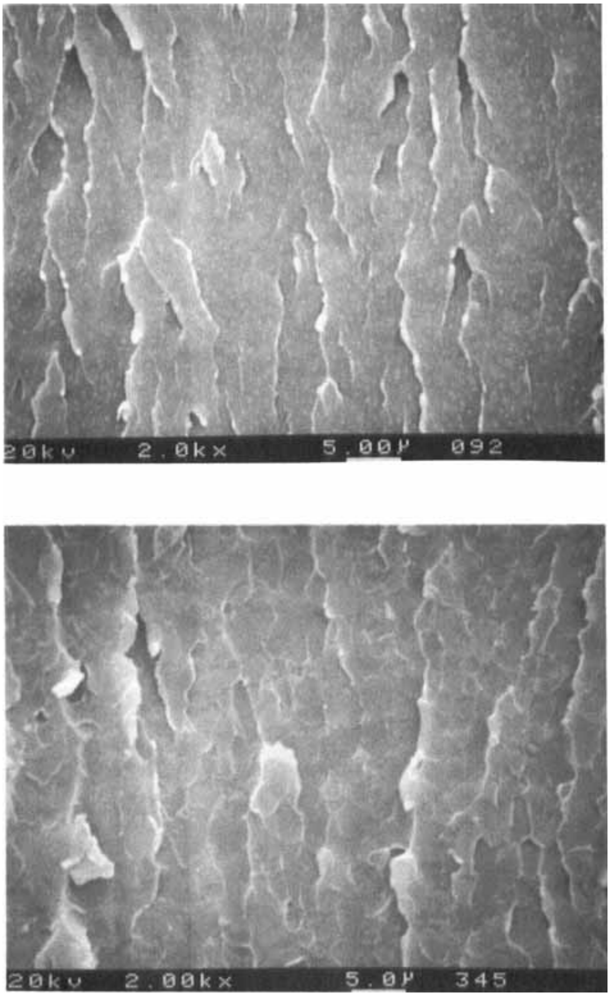

FIGURE 2 SEM micrographs of 10 wt.% R-PES (a) and 25 wt.% R-PES (b).

in the R-PES modified epoxy resins as well as in Udel® blended samples. The epoxy continuous phase with the polysulfone spheres of about 0.5m in diameter was developed at the R-PES loadings of 5, 10 and 15 wt.% (referred to as Type 1 morphology) as shown in Figure 2. However, the polysulfone continuous phase with deformed honeycomb-like epoxy spheres was observed at 20 wt.% or higher loading (Figure 2), which is often called the phase-inverted morphology (Type 2 morphology). Incomplete phase inversion was observed at the 20 wt.% loading of R-PES, which might be considered to be in the transition range. The inflection of fracture toughness at 20 wt.% R-PES may be explained by the phase inversion;

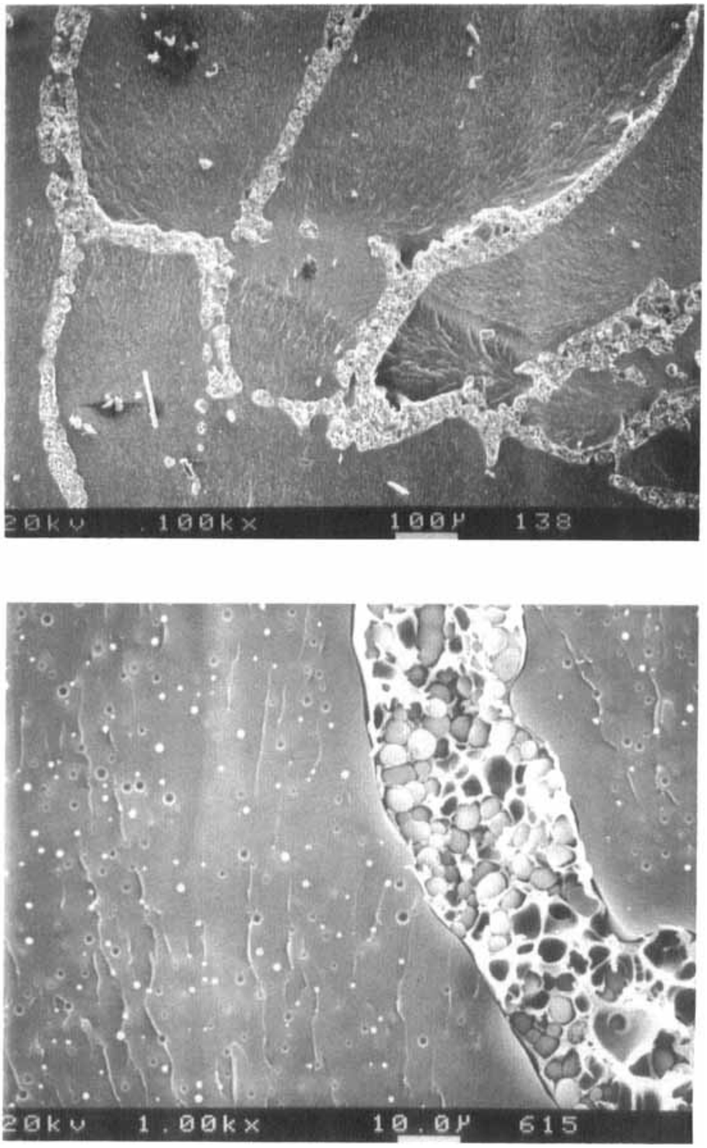

FIGURE 3 SEM micrographs of 10 wt.% Udel® blended epoxy resins at 100x (a) and 1000x (b).

e.g., epoxy continuous phases transforming to a R-PES continuous morphology. The SEM micrographs also revealed that the fracture occurred through the R-PES spheres (or epoxy spheres), leaving a mirror image morphology. It was also noticed that R-PES modification increased the surface roughness by producing a wrinkle-like surface in Type 1 or a peak-valley type in Type 2 morphology. The improved fracture toughness by R-PES modification is mainly attributed to the functional reactive aminophenyl groups in R-PES, which can form a chemical bond with epoxy groups and thus provide strong adhesion between the two phases. The tough, ductile character of R-PES and surface roughness may also have made some contribution.

The Udel® blended samples showed, to a first approximation, a similar morphology as the R-PES modified epoxy resins. The Udel® blending provided either Type 1 morphology at 5 wt.% loading, with about 1μm Udel® spheres, or Type 1 morphology surrounded by Type 2 morphology at 10 wt.% Udel® as shown in Figure 3. As the loading of Udel® increased, the area of Type 2 morphology increased at the expense of Type 1 morphology, and Type 2 morphology dominated at 20 wt.% loading of Udel®. However, unlike in the R-PES modification, fracture must have occurred at the interface of epoxy and Udel® phases due to weak adhesion between them. This is evidenced by clean Udel® spheres in Type 1 morphology and clean, smooth surfaces of epoxy spheres and Udel® phases in Type 2 morphology. This observation was expected from the non-functional character of Udel®. However, the ductile failure of Udel® continuous phase was observed, possibly due to the high molecular weight of Udel® (25k), compared with R-PES (10k). The improved fracture toughness by Udel® blending might be attributed to two factors; surface roughening and ductile fracture of Udel® phases, but the contribution by the latter may be small due to the lack of adhesion between Udel® and epoxy phases.

3.3 Mechanical Properties

In general, the R-PES modification only provided minor changes in the tensile properties of the epoxy networks, relative to those produced by Udel® blending. The low strain rate tensile properties of control samples were: tensile strength of 85 MPa, strain of 5% and modulus of 2.9 GPa. These values did not change with 20 wt.% or lower loadings of R-PES (Figure 4). However, a 20 wt.% loading of R-PES provided slightly increased strain (6.3%) and decreased modulus (2.4GPa), without a noticeable tensile strength change. The inflection of tensile properties at 20 wt.% R-PES is well correlated to the fracture toughness data and thus may be attributed to the R-PES continuous morphology. On the other hand, as shown in Figure 5, Udel® blending dramatically decreased tensile properties, even at 5 wt.% loading. A number of investigators reported that Udel® blending improved the fracture toughness of epoxy resins without detracting from good mechanical properties.[11-14] However, the properties in the literature were measured by a flexural test in 3-point bending, which has the same testing mode, Mode 1, as the fracture toughness test. Therefore, a flexural test may not be an appropriate test to detect tensile mechanical property changes.

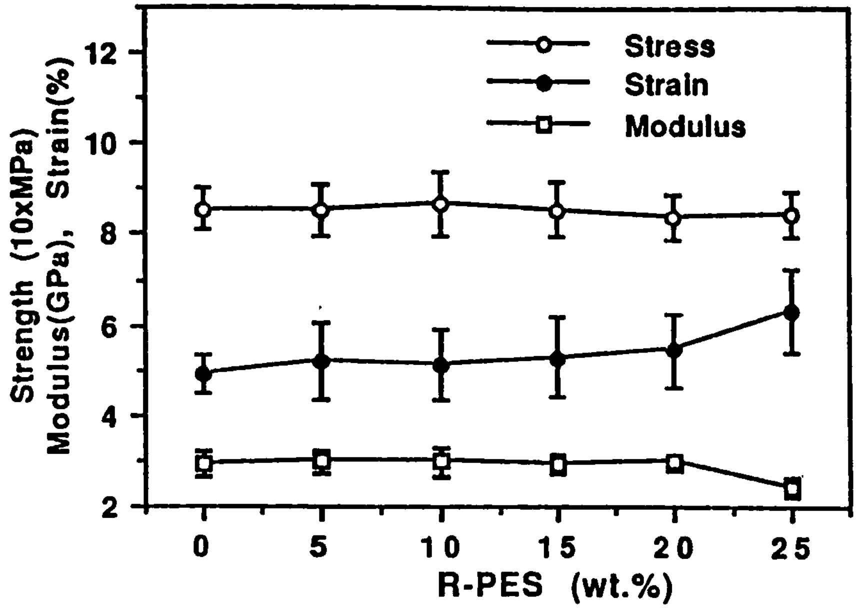

FIGURE 4 Tensile properties of reactive polysulfone modified epoxy resins.

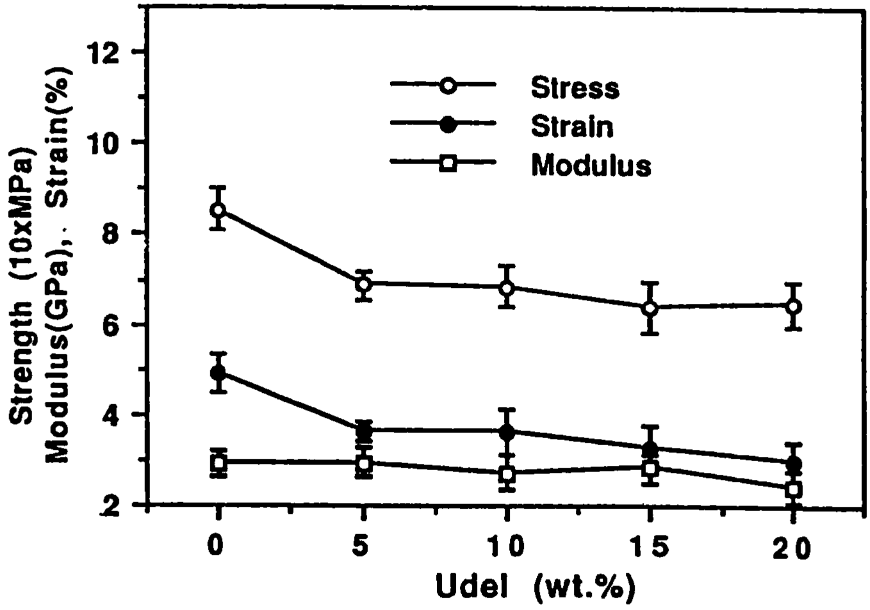

FIGURE 5 Tensile properties of Udel® P-1700 blended epoxy resins.

The tensile samples, which are much smaller than SENB specimens, exhibited somewhat different phase separation behavior from the SENB samples. Tensile samples with 5, 10 and 15 wt.% R-PES did not show phase separation but those with 20 and 25 wt.% loading exhibited a phase-inverted morphology. This might be due to the sample size (3 × 6 × 40mm *vs.* 3 × 1.5 × 50mm), which controls the heat conduction. However, the Udel® blended tensile samples showed a clear phase separation as observed in the Udel® blended SENB specimens. The reduced tensile properties of Udel® blended epoxy resins could be explained by the non-functional character of Udel® and thus the weak adhesion between the epoxy and Udel® phases. It is interesting that tensile strength and modulus of Udel® blended epoxy resins are very similar to those reported for Udel® P-1700: tensile strength of 70 MPa and modulus of 2.5 GPa.[24]

3.4 Adhesive Properties

Adhesive properties of the modified epoxy networks were determined with single lap shear samples prepared from Ti-6Al-4V alloys. Single lap shear strength increased with the R-PES modification; from 3500 psi with the control, to 6400 psi at a 25 wt.% loading (Figure 6-A). As the loading of reactive thermoplastic modifier increased, the epoxy polymers become more tough, resulting in improved adhesive bond strength. On the other hand, Udel® blended systems exhibited a maximum adhesive bond strength (4800 psi) (33.1MPa) with a 10 wt.% blending, compared with 6500 psi (44.8MPa) with Udel® P-1700 itself. At lower loadings of Udel®, enhanced fracture toughness improved adhesive bond strength, but at higher loadings weak adhesion between Udel® and epoxy phases resulted in low adhesive bond strength.

In the 100 and 150°C tests, the adhesive bond strengths increased with R-PES modification of 20 wt.% or lower loadings and then decreased (Figure 6-B). However, Udel® blending decreased the adhesive bond strength at 100 and 150°C tests, in general, as indicated in Figure 6-B. The adhesive bond strength variation of R-PES modified epoxy resins with temperature could be explained by the brittle-ductile behavior of the epoxy resins, as previously published.[25] The unmodified epoxy networks are relatively brittle at room temperature and display relatively low adhesive bond strength. As temperature increased, the epoxy polymers become more ductile, resulting in improved adhesive bond strength.

The R-PES modified adhesive samples did not show any obvious phase separation even with a 30 wt.% loading, but rather only sheared, cracked, rough surfaces (Figure 7). This may be attributed to sample size; the bondline thickness of approximately 3 mils (0.25mm), which affects heat conduction and thus the reaction rate. Udel® blended samples showed two distinct morphologies depending on the loading. The samples with 5 wt.% Udel® showed sheared, cracked, rough surfaces, as observed in the R-PES modified samples. However, the 10 wt.% or higher Udel® blending developed mostly Type 2 morphology. It is interesting to note that adhesive bond strengths increased with R-PES modification, and the inflection of adhesive bond strength at 20 wt.% R-PES is well correlated to fracture toughness and tensile properties, despite lack of a significant phase separation in the adhesive samples.

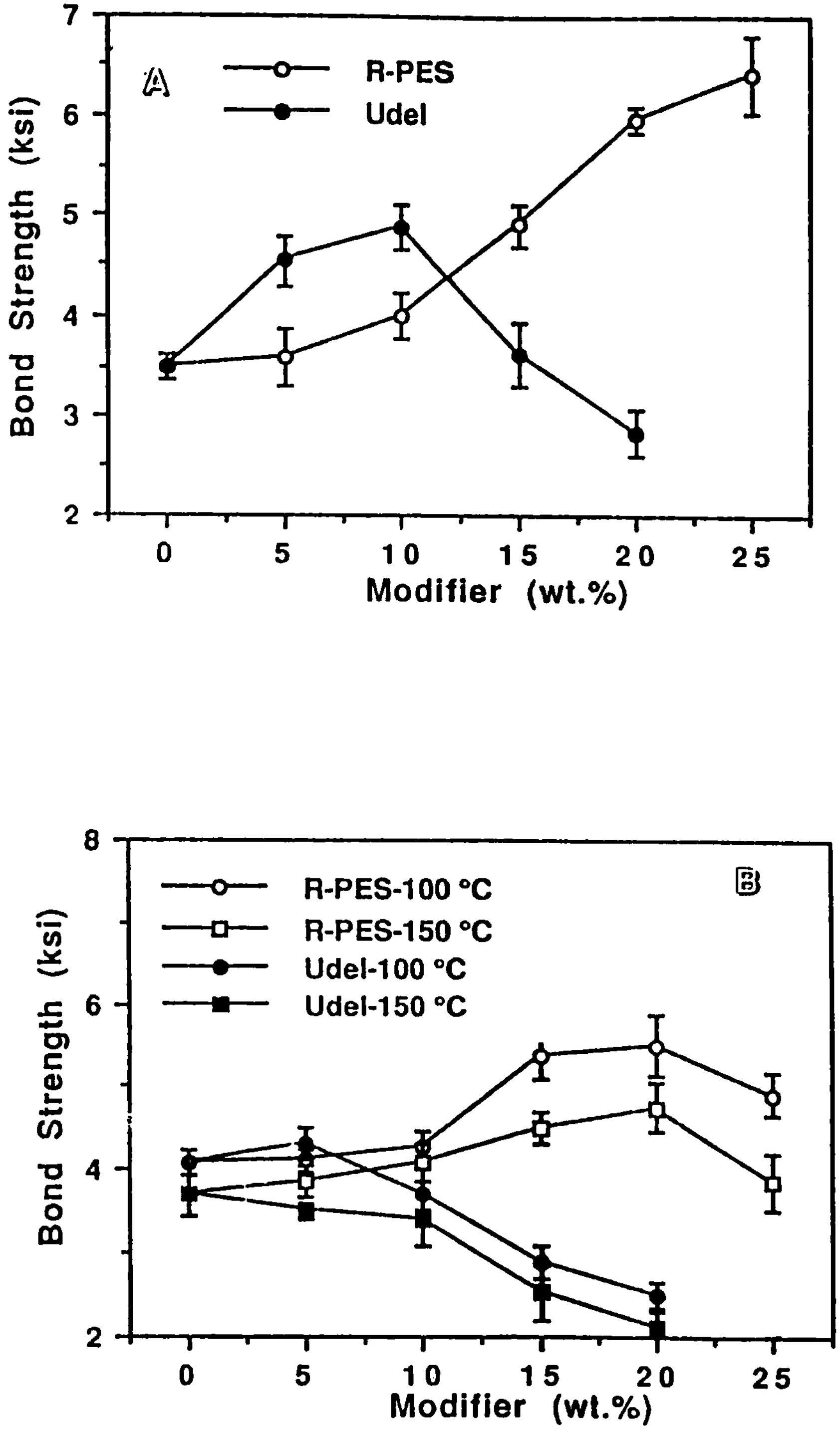

FIGURE 6 Adhesive properties of reactive polysulfone modified and Udel® blended epoxy resins

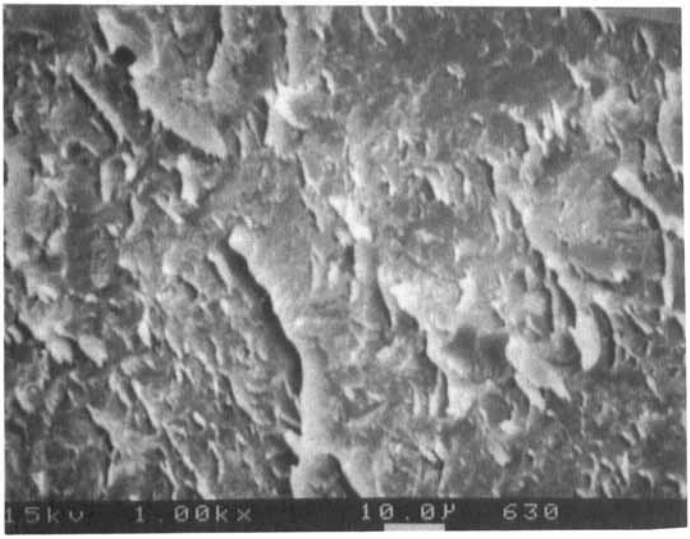

FIGURE 7 Fractured surface of Ti-6Al-4V alloy with 10 wt.% R-PES modified epoxy resins.

FIGURE 8 SEM micrographs of chloroform-extracted 10 wt.% Udel® blended samples after immersing for 10 minutes.

3.5 Chemical Resistance

The R-PES modified epoxy resins exhibited excellent chemical resistance in chloroform; no color or shape changes were observed after 72 hours. Since, unlike Udel®, R-PES formed chemical linkages with epoxy groups, the R-PES modification apparently did not alter the chemical resistance of the epoxy networks. Although no changes were observed in the 5 wt.% Udel® blended samples, the samples with 10 wt.% or higher loadings of Udel® showed a change from light brown and transparent to white and opaque. Because 5 wt.% Udel® blending developed Type 1 morphology, the Udel® spheres were protected by the continuous epoxy domain, providing good chemical resistance. However, at higher loadings of Udel®, the continuous Udel® phases in Type 2 morphology were attacked by chloroform as soon as the samples were immersed. Eventually, the samples were swelled and turned to milky-shake like solution. The SEM micrographs indicated that Udel® phases, either spheres or continuous, were removed by chloroform extraction as shown in Figure 8.

4 SUMMARY AND CONCLUSIONS

Although Udel® P-1700 is known to be a good thermoplastic modifier in the toughening of epoxy resins, this investigation clearly demonstrates the superiority of the R-PES modification. In general Udel® blending improved the fracture toughness and adhesive properties of epoxy resins, at least to some extent, but decreased mechanical properties and chemical resistance. The morphology studies by SEM revealed that the property changes are mainly attributable to the absence of chemical linkages between the Udel® and epoxy phases, leading to better phase separation and very low levels of adhesion. The improved properties by Udel® blending may be attributed to the ductile character of Udel®.

However, the aminophenyl-functional polysulfone modification remarkably improved the fracture toughness and adhesive bond strengths without detracting from good mechanical properties and chemical resistance. In contrast to Udel® blending, the improved properties of R-PES modification are mainly attributable to the reactive end groups of R-PES, which provided the chemical bonds between R-PES and epoxy groups and thus good adhesion between them. The morphology studies indicated that a rather complete phase-inverted morphology developed with 25 wt.% of R-PES, at which point inflections were observed in fracture toughness, tensile properties, and adhesive properties. It is interesting that the samples of tensile, fracture toughness and adhesion tests provided different phase separation behaviors, but similar trends in properties.

Acknowledgements

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