

Adhesive and Flame Resistance Behavior of Poly(arylene ether phosphine oxide) (PEPO) and PEPO-Modified Epoxy Resins

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ABSTRACT: Poly(arylene ether phosphine oxide) (PEPO) with controlled molecular weights and amine end-groups was synthesized, and used as an adhesive, a coating material for adherend or a modifier for diglycidyl ether of bisphenol A (DGEBA)-based epoxy resins. Closely related poly(arylene ether sulfone) and commercial polyethersulfone, Udel® P-1700, were also utilized for comparison purposes. Adhesive behavior was measured via single lap shear samples as a function of coated polymer type, test temperature (R.T. and 100°C), and aging condition in boiling distilled water or 5% salt water. Flame resistance of PEPO and PEPO-modified epoxy resin was evaluated by TGA and a flame test. PEPO exhibited better adhesive properties than PES or Udel® P-1700. PEPO coating on an Al adherend markedly improved adhesive property of PES and Udel® even at 100°C, and after aging study failure mode changed from adhesive to cohesive with the PEPO. Aminophenyl terminated PEPO-modified epoxy resins also exhibited highly improved adhesive behavior and flame resistance, compared to control samples. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1198–1205, 2001

Key words: poly(arylene ether phosphine oxide); adhesion; coating; flame resistance

INTRODUCTION

Structural adhesives have received much attention due to their many advantages over mechanical fastening, such as reduction in stress concentration, corrosion protection, design flexibility, and the ability to join thin or dissimilar materials.¹ A number of polymers such as the epoxy resins, polyimides, and poly(arylene ether)s have been introduced and utilized in structural applications. However, there are a number of drawbacks, for example, poor adhesion to metallic sub-

strates and inadequate thermal stability, especially for long-term durability.^{1–3}

It may be expected that the adhesive properties of structural adhesives could be enhanced by either changing the chemical structure of the adhesives or by modifying the surface of adherends. There has been a great deal of research carried out to synthesize new monomers for such purposes. Recently, phosphine oxide-containing monomers were introduced by McGrath and coworkers, and are known to increase adhesive properties⁴ and also flame resistance.^{5–8} It was also reported that the improved adhesion might be due to phosphine oxide moiety, which provides strong interaction to other polymers and metallic substrates.⁹

The importance of the interphase is well recognized by researchers because the interphase may

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be different chemically and physically from either the polymeric adhesive or the adherend, and has to be carefully designed to achieve good adhesion between the adherend and the adhesive.^{10,11} One of the critical issues in forming a strong interphase involves surface modification of adherends. In structural applications, especially for the aerospace industries, Ti-6-4 alloys and Al alloys have been widely utilized because of their light weight and good mechanical properties. Thus, it is not surprising that a considerable amount of research have been conducted to find ways to improve their adhesion.^{12–21}

Because the oxide layer on the surface of Al or Ti-6-4 substrate reduces adhesion, a number of surface modification techniques have been proposed, such as degreasing, solvent washing, acid etching and anodization.^{12–18} In addition, surface coating with silane coupling agents has also been widely utilized.^{19–21} Recently, plasma spraying and coating by plasma polymerization have been introduced and are gaining popularity. It was also reported that the adhesion to carbon fiber and thus composites properties were greatly enhanced by a thin polymer coating.^{22–23}

In this investigation, phosphine oxide containing poly(arylene ether), poly(arylene ether phosphine oxide) (PEPO), was synthesized and utilized as either an adhesive, a coating material for Al alloys, or a modifier for epoxy resins. Their adhesive properties and flame resistance were evaluated and compared to those of the analogous commercial poly(arylene ether sulfones), Udel® P-1700.

EXPERIMENTAL

Materials

PEPO (poly arylene ether phosphine oxide) and PES (poly arylene ether sulfone) with controlled

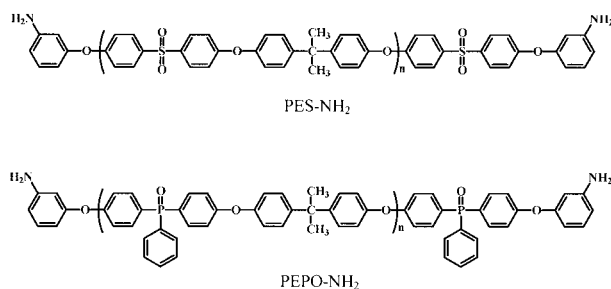


Figure 1 Chemical structure of PES and PEPO.

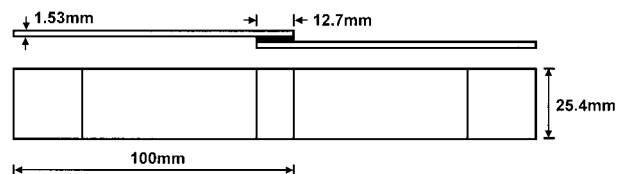


Figure 2 Schematic diagram of single lap shear specimen.

molecular weight (15,000 or 20,000 g/mol) and amine end-groups were prepared by methods described elsewhere.^{6,7} The chemical structure of PEPO and PES are shown in Figure 1. The diglycidyl ether of bisphenol A (DGEBA) epoxy resin (Epikot-828, EEW = 189) was provided by Kumho-Shell (Korea) and the curing agent, 4,4'-diamino-diphenylsulfone (DDS, Aldrich) was used as received. A commercial polyethersulfone, Udel® P-1700, was also utilized for comparison purposes.

Adhesive Property Measurement

Adhesive properties were measured via single lap shear specimens prepared from Al alloys (25.4 × 101.6 mm), following ASTM D-1002 (Fig. 2). Al coupons were treated in sulfuric acid (ASTM 2651-79) for 10 min and cleaned in an ultrasonic bath with distilled water, followed by drying and coating with polymer solution to preserve the cleaned surface. The coating was either the same polymer as the adhesive or PEPO, to investigate the effect of the surface coating. The coating solution was prepared by dissolving the polymer in CHCl₃ to afford 5 wt % solution.

Thermoplastic adhesives such as PEPO (20k), PES (20k) and Udel® P-1700 were compression molded at 260°C with a hot press to produce a film adhesive, then cut to a 30 × 15 mm size. Epoxy adhesives were prepared by mixing 15k PEPO or 15k PES in epoxy resin, and the homogenous mixture was applied directly to the surface of Al coupons to achieve a thickness of 1–2 mm, without separately preparing a film. Single lap shear samples with thermoplastic adhesives were prepared with a bonding jig by stacking the Al coupon, adhesive and Al coupon again. They were designed to have a bonded area of 12.5 × 25.4 mm. The bonding temperature was optimized by varying from 260 to 320°C under a fixed holding time of 30 min and pressure of 2 MPa. After heating to 200°C under contact pressure at a heating rate of 7°C/min, a pressure of 2 MPa was

Table I Characteristic of Poly(arylene ether)s

	Target (M_n) (g/mol)	End Group	Tit. (M_n) (g/mol)	$[\eta]$ (dL/g) ^a	T_g (°C) ^b
PES	15,000	NH ₂	16,770	0.25	181
	20,000	NH ₂	20,780	0.28	185
PEPO	15,000	NH ₂	16,290	0.33	187
	20,000	NH ₂	21,970	0.38	192

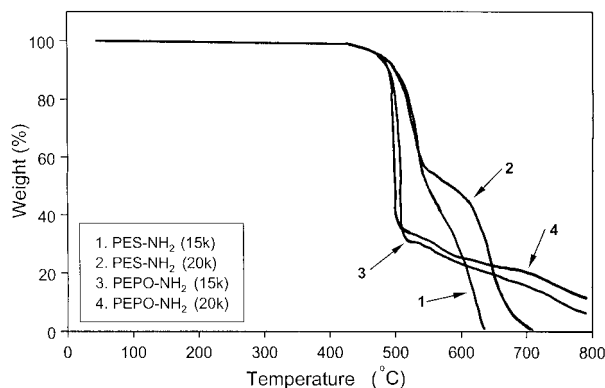
^a 25°C, chloroform.^b T_g by DSC, second heat in nitrogen.

applied and then the samples were further heated to 260, 280, 300, or 320°C at a heating rate of 7°C/min. After holding for 30 min, the samples were allowed to cool to R.T. under pressure. Single lap shear samples with epoxy adhesives were prepared by stacking two epoxy coated adherends, followed by curing at 130°C for 4 h and 220°C for 2 h.

Single lap shear strength was measured with an Instron 5567 at 1.25 mm/min at R.T. Some samples were tested at 100°C after being equilibrated for 10 min. Four or more samples were tested, and the data were averaged. Some samples were subjected to aging either in boiling distilled water for 2, 3, or 6 days or in 5 wt % salt water for 1 or 3 days. The failure mode of the samples was also evaluated by SEM (JEOL, JSE-5800) to elucidate the adhesion mechanism. All samples for SEM were coated with Au-Pd prior to analysis.

Flame Resistance of PEPO and PEPO-Modified Epoxy Resin

The samples for the flame resistance test were prepared by compression molding thermoplastic

**Figure 3** Thermal stability of PES and PEPO via TGA.

polymers and cutting them into sections, 7 × 30 mm in size. PEPO-modified epoxy samples were prepared from DGEBA-based epoxy resins, PEPO, and curing agent, 4,4' diaminodiphenylsulfone (DDS). Epoxy samples were cured in an air convection oven with the optimized cure cycle; 4 h at 130°C, following by additional 2 h at 220°C with the loading of modifier being varied from 5 to 30 wt %.

The flame resistance of PES, PEPO, and modified epoxy resins was evaluated via thermogravimetric analyzer (TGA, TA-2050) in air first, while selected samples were further subjected to a flame test with an alcohol lamp. As soon as the PES and PEPO films began to burn, they were removed carefully from the flame and the time for flame to extinguish in air was measured. Modified epoxy samples (7 × 30 × 3 mm) were also tested in the same manner. Three or more samples were tested, and the results were averaged.

RESULTS AND DISCUSSION

Characteristics of PEPO and PEPO-Modified Epoxy Resin

The glass transition temperature of PEPO measured by DSC was 190°C, which was slightly

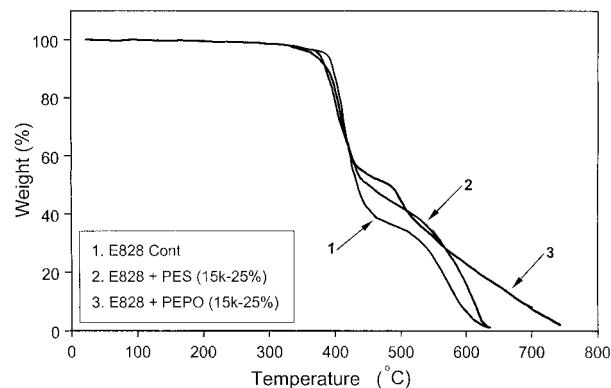
**Figure 4** Thermal properties of epoxy samples modified with PES and PEPO via TGA.

Table II Effect of Bonding Temperature on the Adhesive Properties of PEPO and Udel® P-1700

Bonding Temperature (°C)	PEPO-NH ₂ (20k)	Udel® P-1700
260	22.5 ± 2.6MPa	17.6 ± 2.1MPa
280	27.9 ± 2.4MPa	19.7 ± 1.5MPa
300	28.3 ± 1.4MPa	19.8 ± 1.6MPa
320	26.9 ± 2.8MPa	19.9 ± 1.4MPa

higher than that of PES (Table 1). The titrated molecular weights determined by acid titration of the aminophenol end groups were 16,290 and 21,970 g/mol (PEPO), and 16,670 and 20,780 g/mol (PES), respectively. The thermal stability of polymers measured by TGA in air at 10°C/min is shown in Figure 3. PES showed a two-step degradation process in air with no residue remained above 700°C, while PEPO exhibited a sharp drop at around 500°C, followed by very slow degradation. PEPO showed slightly poorer thermal stability in the 500–600°C range compared to PES, but much better stability in the 600–800°C range, showing more than 10% residue at 800°C. TGA demonstrated excellent thermal stability of phosphine oxide containing polymer, especially in the high temperature range.

The T_g value of epoxy samples cured with DDS was around 195°C. But the epoxy samples modified with 15 wt % PES showed two distinct T_g s (182, 192°C), indicating good phase separation. However, all samples modified with PEPO exhibited a single T_g , consistent with recent report that these systems are miscible.⁹ The control epoxy samples and the PES-modified epoxy samples showed two-step degradation in TGA analysis; a sharp decrease at approximately 400°C, and a slow decrease to 0 wt % in the 500–650°C range

(Fig. 4). On the other hand, PEPO-modified epoxy samples exhibited a sharp decrease at around 400°C but a very slow decrease from 450 to 760°C. At 650°C, PEPO-modified epoxy samples showed almost 20 wt % residue, while PES-modified epoxy samples did not show any, indicating excellent thermal stability of PEPO-modified epoxy resins (Fig. 4).

Adhesive Behavior of PEPO

Bonding Condition Optimization

As indicated,²⁴ bonding conditions such as time, temperature, and pressure are very important to achieve maximum adhesive bond strength. In this study bonding temperature was optimized with PEPO and Udel® P-1700 under fixed a pressure of 2 MPa and a holding time of 30 min (Table 2). As bonding temperature increased from 260 to 320°C, the adhesive bond strength increased dramatically in the beginning, then leveled off with further increase in bonding temperature. A similar trend was observed from Udel® P-1700. Therefore, 280°C was chosen as the optimum bonding temperature for this study.

Effect of Surface Coating

The adhesive properties of PEPO, PES, and Udel® P-1700 were measured first with Al alloys coated with the same polymer as the adhesives via single lap shear samples. The PEPO adhesive resulted in 27.9 ± 2.4 MPa, while 17.2 ± 1.2 MPa and 19.7 ± 1.5 MPa were obtained from PES and Udel® P-1700, respectively (Table 3). As expected, PEPO showed the highest single lap shear strength followed by PES and Udel. However, when Al alloys were coated with PEPO polymer regardless of the adhesive, Udel® P-1700, and PES exhibited 22.1 ± 2.3 MPa and 28.3 ± 2.0

Table III Effect of Surface Coating on the Adhesive Properties of Poly(arylene ether)s at RT

Adhesive	PEPO Coating		Same Polymer Coating	
	SLSS ^a	Failure Mode	SLSS	Failure Mode
Udel® P-1700	22.1 ± 2.3MPa	C ^b	19.7 ± 1.5MPa	A ^c
PES-NH ₂ (20k)	28.3 ± 2.0MPa	C	17.2 ± 1.2MPa	A
PEPO-NH ₂ (20k)	27.9 ± 2.4MPa	C	27.9 ± 2.4MPa	C

^a SLSS: Single lap shear strength.

^b C: Cohesive failure.

^c A: Adhesive failure.

Table IV Effect of Surface Coating on the Adhesive Properties of Poly(arylene ether)s at 100°C

Adhesive	PEPO Coating		Same Polymer Coating	
	SLSS ^a	Failure Mode	SLSS	Failure Mode
Udel® P-1700	20.1 ± 1.9MPa	C ^b	17.3 ± 1.2MPa	A ^c
PES-NH ₂ (20k)	24.7 ± 2.1MPa	C	14.8 ± 1.4MPa	A
PEPO-NH ₂ (20k)	26.4 ± 1.7MPa	C	26.4 ± 1.7MPa	C

^a SLSS: Single lap shear strength.

^b C: Cohesive failure.

^c A: Adhesive failure.

MPa, respectively, which can be compared with PEPO coating/PEPO adhesive combination (27.9 MPa).

This could be explained by the combined effect of high toughness of PES and Udel adhesive, and the bridging effect by PEPO coating, which provide strong adhesion at the interface. The failure mode was certainly changed from adhesive failure with the same polymer coating to cohesive failure with PEPO coating. It can be noted that changing the surface coating may have a tremendous effect on the adhesive properties, again indicating the importance of interphase.

At 100°C test conditions, PES and Udel® adhesive with PEPO coating also exhibited much higher adhesive bond strength than those with PES or Udel® coating (Table 4), although 100°C testing provided approximately 5–15% lower single lap shear strength than at R.T. The improved adhesive bond strength with PEPO coating can be explained by the strong interaction of phosphine

oxide moiety with the Al substrates as well as the PES or Udel® P-1700 adhesives.

Effect of Aging

Single lap shear strength measured after aging in boiling distilled water decreased rapidly in the first 3 days, but leveled off with 6 days of aging, as shown in Figure 5. As can be seen, the PES and Udel® P-1700 adhesives with PEPO coating showed similar adhesive bond strength as PEPO coating and PEPO adhesive after aging for 3 days. However, the adhesive bond strength of PES and Udel® P-1700 with PES or Udel® coating was much lower than PEPO-coated samples. PES and Udel® P-1700 also provided higher adhesive bond strength with PEPO coating than PES or Udel® coating even after aging in 5 wt % salt water (Fig. 6). It can be said that PEPO coating provided a strong bridging effect between Udel® or PES and Al alloys.

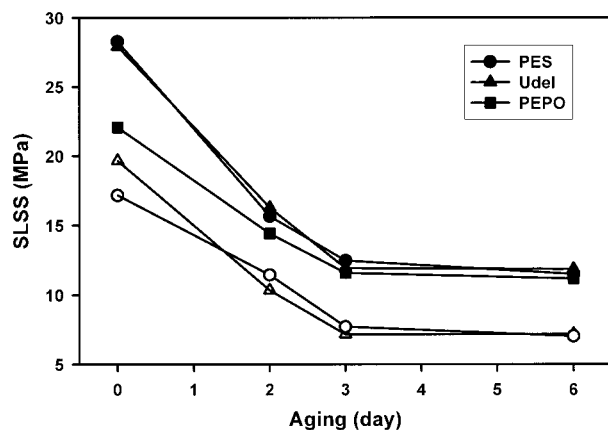


Figure 5 Effect of aging in boiling distilled water on the adhesive properties of poly(arylene ether)s (open symbol: same polymer coating; filled symbol: PEPO coating).

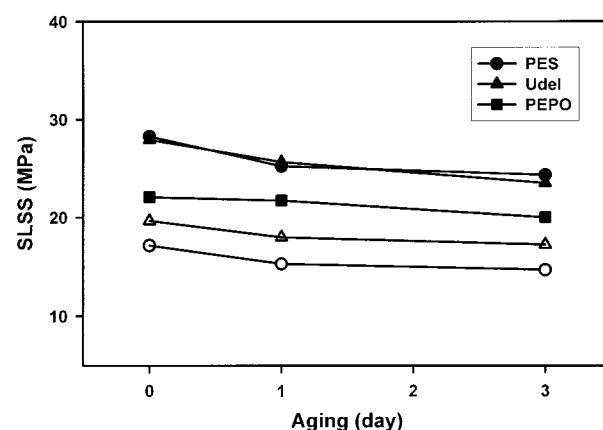


Figure 6 Effect of aging in 5% salt water on the adhesive properties of poly(arylene ether)s (open symbol: same polymer coating; filled symbol: PEPO coating).

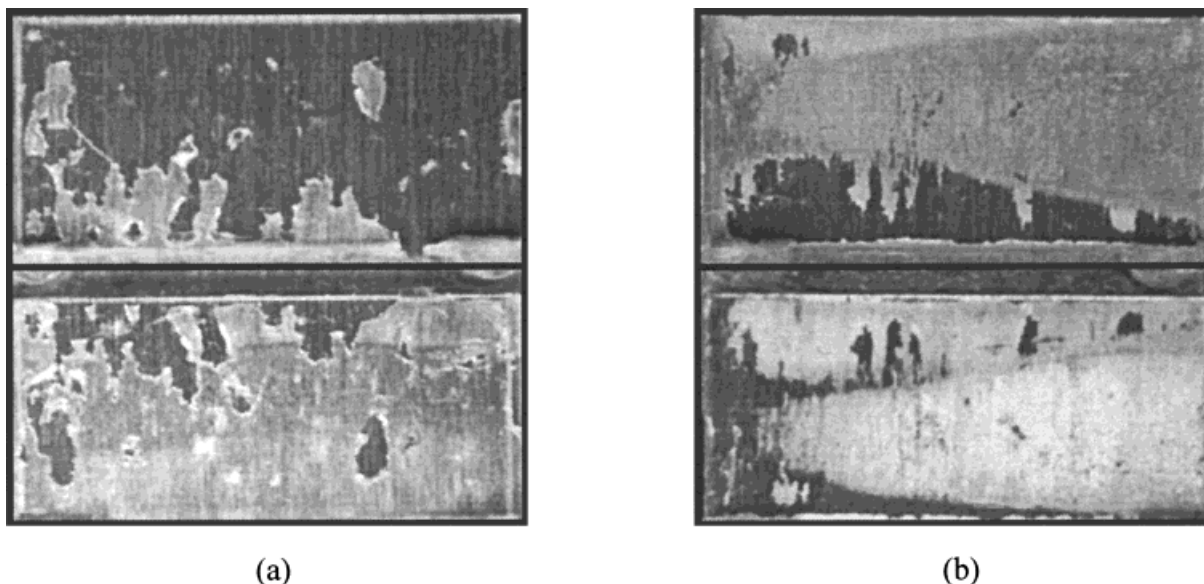


Figure 7 Failure surface of Al adherend with Udel® P-1700 adhesive, A: Udel® coated, B: PEPO coated.

Failure Mode Analysis

The samples prepared with Udel® P-1700 adhesive and Udel® P-1700 coating showed adhesive failure mode, judging from SEM analysis. However, cohesive failure was observed when the Al substrates were coated with PEPO instead of Udel® P-1700, indicating that PEPO coating can enhance adhesion at the interface. The single lap shear samples prepared with PES adhesive showed mixed failure, but cohesive failure area changed from 50 to 90% when PES coating was changed to PEPO coating (Fig. 7). It can be said that PEPO has strong interaction with the Al substrate as well as with other adhesives due to the high polarity of phosphine oxide in the main polymer chain, and thus increases interfacial adhesion between the adherend and the adhesives.

Adhesive Properties of PEPO-Modified Epoxy Resin

The epoxy resin showed SLSS value of 15.2 ± 0.8 MPa, while 10 wt % PES and PEPO modified epoxy resin exhibited 17.6 ± 0.6 MPa and 19.3 ± 0.7 MPa, respectively (Table 5). The 10 wt % PEPO-modified epoxy samples showed higher adhesive strength than 10 wt % PES-modified epoxy samples or epoxy control samples. Enhanced single lap shear strength may be attributed to PEPO, which provided strong intermolecular interaction between the epoxy resin and the Al substrate. However, at 20 wt % loading, PEPO-modified epoxy resin exhibited lower single lap shear strength (22.8 ± 1.4 MPa) than PES-modified resin (24.8 ± 1.3 MPa). This can also be explained by the strong intermolecular interaction between PEPO and

Table V Adhesive Properties of PES and PEPO-Toughened Epoxy Resins

Adhesives	10 wt % Loading		20 wt % Loading	
	SLSS ^a	Failure Mode	SLSS	Failure Mode
Epoxy control	15.2 ± 0.8 MPa	C ^b	—	—
Epoxy + PES (15k)	17.6 ± 0.6 MPa	C	24.8 ± 1.4 MPa	C
Epoxy + PEPO (15k)	19.3 ± 0.7 MPa	C	22.8 ± 1.2 MPa	C

^a SLSS: Single lap shear strength.

^b C: Cohesive failure.

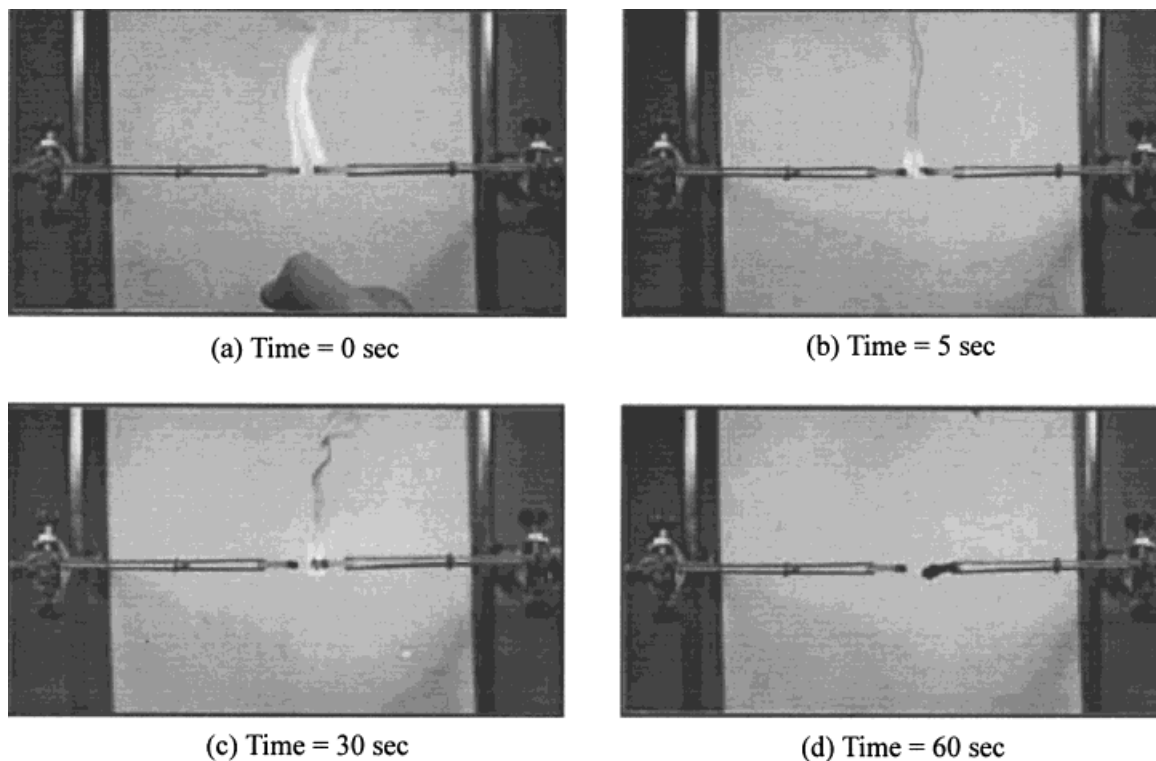


Figure 8 Flame resistance tests of epoxy control (right) and PEPO-modified epoxy (left) samples.

the epoxy resin, resulting in high viscosity and thus poor flow, as evidenced by the very large bond-line thickness. All samples resulted in cohesive failure based on visual inspection, indicating good adhesion.

Flame Resistance by a Burning Test

The PEPO and PES films were subjected to a burning test with an alcohol lamp to measure the flame resistance of polymers. It took approximately 30 s for the PES films to start burning when they were exposed to the flame. When the film was removed from the lamp, burning continued until the film was destroyed. However, PEPO films took approximately 60 s to ignite and burning lasted for only a few seconds after the films were removed from the flame. As expected from TGA results, PEPO films showed much better flame resistance (self-extinguishing) than PES films. The epoxy samples modified with 20 wt % PEPO showed a burning time of 20–30 s after removal from the flame (Fig. 8). However, the epoxy control samples as well as PES-modified samples burned up completely even after the removal of the flame. The flame tests clearly dem-

onstrated the improved flame resistance of PEPO and PEPO-modified epoxy samples.

CONCLUSIONS

The phosphine oxide containing poly(arylene ethers) were successfully prepared and utilized as modifier for epoxy resins. Major findings are as follows;

1. PEPO exhibited higher SLSS with Al adherend than PES or Udel® P-1700 at RT, as well as at 100°C even after aging in distilled water or salt water.
2. PEPO coating significantly improved the adhesive bond strength of PES and Udel® P-1700.
3. PEPO and PEPO-modified epoxy resins showed excellent thermal stability and good flame resistance.
4. Enhanced adhesion via PEPO coating may be due to phosphine oxide moiety, which provided strong interaction to the adherend as well as the adhesive.

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