

## Evaluation of Poly(2,6-dimethyl)-1,4-phenylene Oxides and Related Copolymers for High Temperature Adhesive Application\*

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### Synopsis

Poly-(2,6-dimethyl)-1,4-phenylene oxides and related copolymers have been evaluated for high temperature adhesive applications. Because of the high-melting character of these polymers, proper wetting was found to be difficult to achieve. Where such conditions can be obtained, good tensile strength values have been reached up to 600°F. The introduction of allyl group and epoxy group into such polymers provides sites for thermosetting. The fast setting rate of these groups, however, introduces difficulty in bonding procedure. Problems and ways to improve the initial bonding of specimens are discussed.

### INTRODUCTION

Polymeric adhesives have been reviewed recently by Powers<sup>1</sup> and their applications in structural materials discussed in a recent symposium.<sup>2</sup> In general, several factors should be considered in the development of a high temperature adhesive. They are: (1) proper wetting and coverage of the adhesive material must be initially present; (2) the curing process should preferably be one that is free of volatile by-products; (3) there should be some active anchoring groups on the adhesive polymer; (4) after curing a thermoset structure should be better than that of a thermoplastic one; (5) in a formulation, curing must occur at a temperature lower than that withstood by the least stable component.

In searching for suitable systems, a large number of high temperature stable polymers were synthesized.<sup>3</sup> Among them were triazine epoxies, triazine condensed-ring polymer (Melon), benzoguanamine polymers, polyphenylenes, and polyphenylene ethers. All these polymers have high temperature stability. By thermogravimetric analysis, polyxylenol (poly-2,6-dimethyl-1,4-phenylene oxide) showed a decomposition temperature of 400°C., and Melon showed a decomposition temperature of around 660°C.

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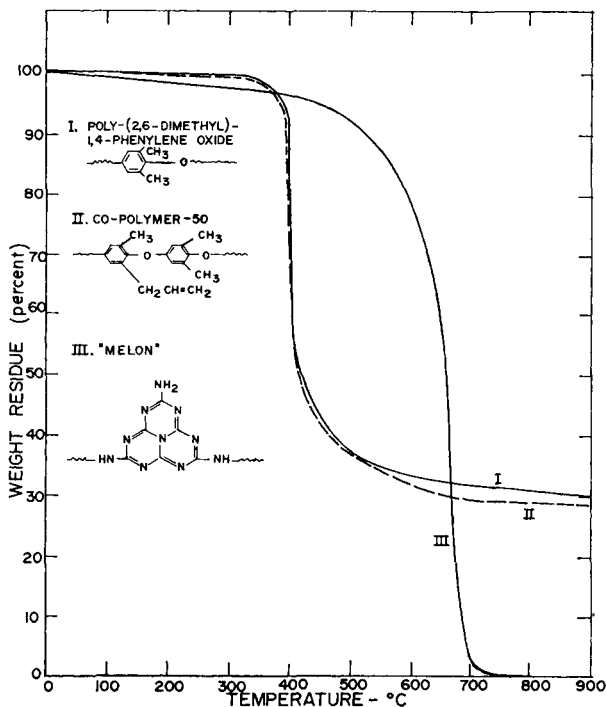


Fig. 1. Thermogravimetric analysis (150°C./hr. under N<sub>2</sub>).

(Fig. 1). However, as an adhesive Melon could not be used because it failed to melt up to its decomposition. Part of our work was therefore to improve such physical deficiency by chemical modification of these polymers without too much alteration of the backbone structure so as not to impair the thermal stability.

## EXPERIMENTAL MATERIALS AND METHODS

Poly-(2,6-dimethyl)-1,4-phenylene oxide was prepared according to Price polymerization.<sup>4</sup>

Copolymers of 2,6-dimethyl-4-bromophenol and 2-methyl-6-allyl-4-bromophenol were made by a similar method.<sup>6</sup> Most of the work was carried out with a 50:50 copolymer.

Samples of the copolymer were epoxidized by the peracetic acid method, as reported elsewhere.<sup>7</sup> Because of the possibility of degradation of the phenylene oxide linkage by peracetic acid, only theoretical amounts or below of peracetic acid should be used in the epoxidation procedure.

The remainder of the work was in extensive testing and evaluation of selected promising candidates for high temperature adhesives.

Our decision to concentrate our work on the polyphenylene oxide system was based on the following considerations: (1) the chemistry of the polymer is better understood;<sup>4,5</sup> (2) relatively high molecular weight polymers

can be made; (3) thermoplasticity of the parent system allows better wetting possibilities; (4) demonstrated good adhesion at room temperature to stainless steel; (5) thermal stability as shown by TGA and about 30% residue up to 900°C; (6) comparatively simple preparation and good reproducibility; (7) sites on the backbone available for modification to improve adhesion; (8) the polymerization process lends itself readily to copolymer preparation.

Accordingly, the methyl side chains of the polymer were converted in part to reactive groups to permit crosslinking of the adhesive during the bonding process. Modification to useful reactive polymers by this attack proved somewhat more difficult than anticipated, crosslinking occurring in some cases during preparation, leading to intractable polymers. Emphasis was accordingly shifted to the principle of using a monomeric phenol already containing a reactive group. For this purpose 2-methyl-6-allyl-4-bromophenol was selected as the primary candidate.

This monomer was used as base material in arriving at a typical adhesive of the polyphenylene oxide system. Upon curing, the polymer thermosets to a crosslinked form that has good heat resistance. By copolymerization with 2,6-dimethyl-4-bromophenol, a spectrum of copolymers was prepared.<sup>6</sup> Selected polymers were further modified by epoxidation of the pendant allyl group.<sup>7</sup>

This paper reports our preliminary work in the evaluation of these new copolymers for possible high temperature adhesive application.

### Adhesive Evaluation of the Polymer

The test specimens were sheared from flat 0.062 in. stainless 302 steel, 2 B finish, 4 × 1 in. strips from Whithead Metals of Philadelphia, Pa. These strips were not ideally flat as a slight curvature due to shear was visible under the microscope. Some smooth machined samples were obtained from the Picatinny Arsenal and they were so indicated wherever they were used. However, the results obtained on the two types of strips were comparable.

#### A. Pretreatment of Test Strips

The strips were prepared by soaking in perchloroethylene for several weeks, scouring thoroughly with scouring powder, then etching essentially according to MIL A834 (U.S.A.F.) which involves soaking for 2 min. at 180–200°F. in a mixture of 35% hydrochloric acid (841 ml.), 85% orthophosphoric acid (89 ml.), and 60% hydrofluoric acid (43 ml.), followed by a thorough rinsing with distilled water and oven drying for 10–15 min. at 180–200°F. The strips were used on the same day of preparation, as rust occurred with storage for more than a day.

After the polymeric adhesives were prepared, which will be discussed in detail later, the lap shear specimens were pressed in an electrically heated CXL Carver press, with temperature control by a thermostwitch. Two types of sample holders (jig) were used to secure the specimens at 1/2 in.

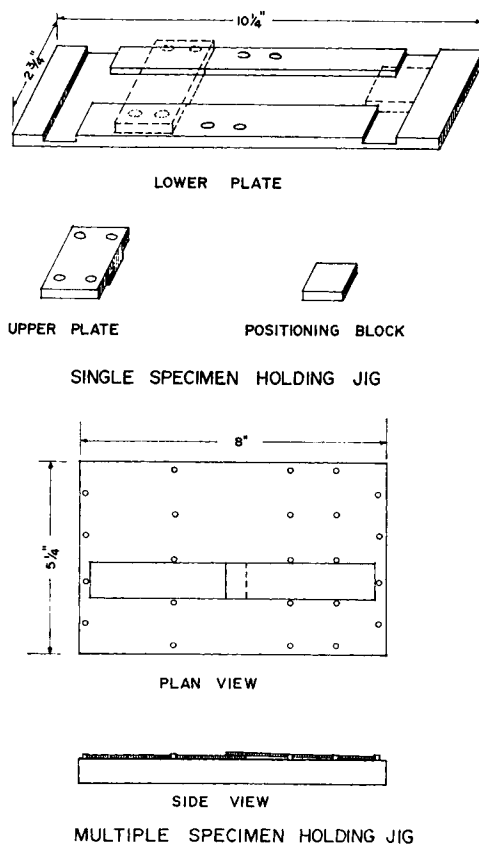


Fig. 2. Specimen holders.

overlap. A single specimen holder (Fig. 2) consisted of  $\frac{3}{8}$  in. thick,  $10 \times 2\frac{7}{8}$  in. aluminum plate with a  $1\frac{1}{2}$  in. longitudinal groove to accommodate the test strips. A removable block in the groove positioned to the strips at  $\frac{1}{2}$  in. overlap. Pressure from the press was applied on a block over the lap shear specimen. Temperature was measured by a thermocouple placed in a well in the block just over the overlap. (In earlier work the upper plate was loosely secured to the lower plate in the groove by Allen bolts. This practice was found to be undesirable as the press was then landing on the bolts.)

The advantage of pressing a single specimen was that it eliminated the possibility of uneven distribution of pressure when more than one specimen is pressed at a time. The disadvantage was time consumed in preparation which was not desirable in screening a large number of samples in order to ascertain a large number of physical variables which is inherent in any physical testing program of this type. Time saving can be achieved when preheated plates are used in 10 min. press time, and the specimens removed hot, thus eliminating both heat-up and cooling times in the press. This

greatly accelerated output of the tests while still permitting post-curing of any number of specimens at a time in an oven.

A four-specimen holder designed by Picatinny Arsenal was used in some of our work. This holder secures the specimens at the proper overlap by several brass pegs inserted in an aluminum block alongside the lap shear specimens. The height of the overlap just exceeded that of the pegs, so that pressure on the press impinged directly on the overlaps. Specimens prepared in the holder showed no greater variability than that found in the single specimen jug.

### *B. Adhesive Preparation*

In applying the adhesives a number of experimental systems were employed.

**Glass Cloth Laminate Technique.** The etched faces of specimens were coated with chloroform solutions of a polymer by brushing. Three coats were used with intermittent drying. A Volan-A-treated glass cloth (Berton Plastics H 112) was impregnated with the same solution either by brushing or by dipping and stretched out in a frame during drying. The painted strips and laminates were air-dried one week before use to insure slow complete drying. (Periods shorter than this gave some plasticizing effect due to retained solvent.) The laminates were then cut to  $1 \times \frac{1}{2}$  in., inserted between the coated strips and bonded under the above-mentioned conditions.

**"Dough" Films.** The polymers were treated in the proportion of 10 parts of acetone per 1 part of polymer. This gave a dough of polymer softened by the acetone and supernatant acetone solution containing only a small proportion of lower molecular weight polymer. The doughs were pressed out between polished plates into sheets of about 0.01 in. thickness. After partial drying the sheets were cut into 1 in. wide strips and permitted to air-dry before use as laminates between polymer coated strips. (Here again prolonged drying over at least a one week period was required to remove final trace of solvent.)

**Prime Coating.** In this system one of the above described laminates was pressed between strips which were prime-coated with a material which improves the wetting of the polymeric adhesive. Among these were the amino-silicon A-1100 and diphenyl oxide. Preliminary results were encouraging but not sufficient time was available to complete this phase.

## RESULTS AND DISCUSSION

Initially, we were encouraged by the fact that the poly(2,6-dimethyl)-1,4-phenylene oxide resulted in a good adhesive bond for stainless 302 steel. As this polymer is essentially a new adhesive system, conventional methods of application are not adequate. The high melting characteristic of the polymer makes adequate flow and proper wetting of the stainless steel surface difficult. Three methods of application have therefore been investi-

gated. (1) The polymer was applied as a powder or a paste. This method was abandoned because unless the polymer can be obtained in very fine form, it was not possible to get any uniform glue line. (2) The metal surface was precoated with solution of the polymer. To insure a good glue line a thin film of the polymer on a piece of glass cloth impregnated with the polymer is inserted between the slabs. (3) Primer or plasticizer was used in the polymer or on the metal strips. While the volatility of additives introduces undesirable effects, this method did promote flow and adhesion. (In general, attempts were made to bond at the lowest possible temperature to minimize thermosetting, then increase the temperature to complete the thermoset process.) Most of the high temperature evaluations were carried out at 500°F. and 600°F. over periods from 30 min. to one week. Thus far, all our specimens show thermal decomposition at 750°F. to give a hard solid residue. Thus, this temperature must be accepted as the upper limit for the uncompounded adhesive. Based on the experience with novolac epoxy and silicones, the compounded adhesive could well exceed the uncompounded material. Our early experience indicated that this copolymer had better tensile strength than the conventional novolac epoxy. The copolymer 50 gave a maximum value of 724 psi lap-shear strength after 1/2 hr. at 600°F.; an epoxy 538 psi; a copolymer 70 gave 1372 psi after 17 hr. at 500°F. and 242 psi after one week at 500°F. A homopolymer of 2-methyl-6-allyl-4-bromophenol reached 990 psi after 4 hr. at 500°F. and fell only to 840 psi after 17 hr. In all cases the failure was adhesive with contributory failure from oxidation being noted in the case of the longer exposure times. Oxidation failure, according to investigators of other high

TABLE I  
Lap Shear Tensiles of Poly-2,6-Disubstituted-1,4-Phenylene oxides on Stainless Steel

Adhesive no.	De- scription <sup>a</sup>	Bond <sup>b</sup>	Cure		Tensile, psi <sup>c</sup>					
					°F.	Min.	500°F.			600°F., 0.5 hr.
							72°F.	0.5 hr.	4 hr.	
56-C	PX	P	550	3	1240	81				
	PX	F	550	3	1530	49				
	PX	G.L.	550	3	3150	129				
56	Copol. 50	G.L.	500	5	1270	703	545	317	577	
		P	400	5	2540			515		
12	Copol. 50	G.L.	500	5	2135	655				
29	Copol. 50	F	390	30	138				938	
53	Copol. 70	F	500	30	223				1132	
56	PMAP	G.L.	360	30	1930	245	965		750	
31	PMAP	F	375	30	2567	153			500	

<sup>a</sup> PX = Polyxylenol; Poly(2,6-dimethyl) phenylene oxide; Copol. 50 = from 50 mole-% 2-methyl-6-allyl-4-bromophenol; Copol. 70 = from 70 mole-% 2-methyl-6-allyl-4-bromophenol; PMAP = homopolymer of 2-methyl-6-allyl-4-bromophenol.

<sup>b</sup> P = applied as powder; F = applied as film from chloroform solution in the case of PX, from acetone "dough" film in the case of the other polymers.

<sup>c</sup> Average of 2 to 6 tests.

TABLE II  
Lap Shear Tensiles of Epoxidized Poly-2,6-Disubstituted 1,4-Phenylene Oxides on Stainless Steel

Adhesive <sup>a</sup>	Description			Cure			Shear tensile, psi <sup>c</sup>			
	[ $\eta$ ]	Allyl, meq./g.	Epoxy, meq./g.	Bond <sup>b</sup>	Temp., °F.	Time, min.	500°F.			
							0.5 hr.	4 hr.	17 hr.	
1	0.135	1.31	1.19	GL	500	5	1450	695		
1	0.135	1.31	1.19	P	500	5			Did not bond	
2	0.258	2.10	0.90	GL	500	5	870	550		
2	0.228	2.10	0.90	P	500	5			Did not bond	
3	0.112	1.68	1.32	GL	500	30	1080	825		538
3	0.112	1.68	1.32	GL	500	30	980	792	250	646
3	0.112	1.68	1.32	GL	400	5	1050	1030		360
3	0.112	1.68	1.32	GL	400	5	830	724	840	120
4	0.228	1.84	1.15	GL	400	5	386	264		
4	0.228	1.84	1.16	GL	500	30		412		
5	0.263	2.36	0.65	GL	500	5	590	650	715	715
6 <sup>d</sup>	0.341	4.94	0.78	F	400	30	590	650	715	715
Epoxy novolac (commercial)					500	10	2150	200		

<sup>a</sup> Unless otherwise noted, all adhesives are epoxy derivatives of copolymer 50.

<sup>b</sup> GL = film deposited on surface of strips from CHCl<sub>3</sub> solution of polymer and dried, a glass cloth laminate impregnated with resin (dried) in between; F = film from acetone "dough" of polymer, dried; P = polymer applied as powder, particles sintered at end of cure, not fused.

<sup>c</sup> Average of 2 to 6 tests.

<sup>d</sup> An epoxy derivative of poly-2-methyl-6-allyl-1,4-phenylene oxide.

temperature adhesives, occurs below the thermal decomposition temperature and one would expect this would apply also to the polyphenylene oxides unless a fortuitous reaction was promoted which would supply new covalent bonds. It seems likely that if our conditions of bonding could be improved to give a firm continuous glue line with minimum exposure to air, the strength should be substantially improved.

Based on the physical testing procedures in the Experimental Section, the testing results are summarized in Tables I and II.

The thermogravimetric analysis on two of the poly-(2,6-disubstituted)-1,4-phenylene oxides are compared in Figure 1. It can be seen that the partial replacement of methyl groups in the dimethyl prototype by allyl groups in copolymer 50 did not significantly affect the thermal stability.

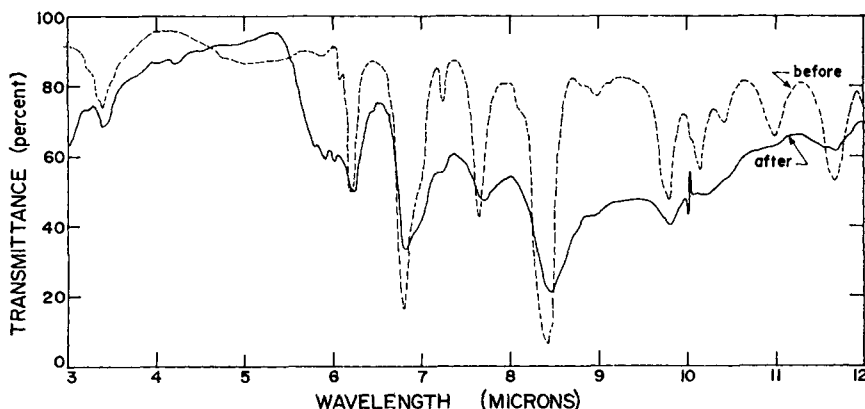


Fig. 3. Spectra of copolymer 50 before and after cure.

The extensive changes occurring in the copolymer 50 upon curing can be seen in its infrared spectra in Figure 3. Here spectra of an adhesive film of the copolymer are compared before and after cure (500°F., 30 minutes). The allyl band at 11  $\mu$  disappeared after cure, indicating the cross linking reaction of the allyl groups may have been complete.

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### Résumé

Les poly-(2,6-diméthyl)-1,4-phénylène oxydes et les copolymères correspondants ont été étudiés en vue d'applications comme adhésif pour températures élevées. Une adhésion convenable est difficile à obtenir à cause du point de fusion élevé de ces polymères. Quand de telles conditions peuvent être atteintes, de bonnes valeurs sont obtenues à 600°F pour la résistance à la tension. L'introduction d'un groupe allylique et d'un groupe époxy dans de tels polymères fournit des emplacements propices au thermodurcissement. La rapide vitesse de fixation de ces groupes, cependant, introduit des difficultés dans le processus de liaison. On discute des problèmes et des façons d'améliorer la liaison initiale des échantillons.

### Zusammenfassung

Poly-(2,6-dimethyl)-1,4-phenylenoxyd und entsprechende Copolymere wurden hinsichtlich ihrer Eignung als Hochtemperaturklebstoffe untersucht. Wegen des hohen Schmelzpunktes dieses Polymeren war es schwierig, einwandfreie Benetzung zu erzielen. Wo dies trotzdem erreicht werden konnte, wurde gute Zugfestigkeit bis hinauf zu 600°F erhalten. Die Einführung von Allyl- und Epoxygruppen in solche Polymere ergibt Angriffspunkte für die Wärmehärtung. Die hohe Härtungsgeschwindigkeit dieser Gruppen führte jedoch zu Schwierigkeiten beim Bindevorgang. Probleme und Möglichkeiten bei der Verbesserung der anfänglichen Bindung der Proben werden diskutiert.

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