

# Electrochemical curing of epoxy resins

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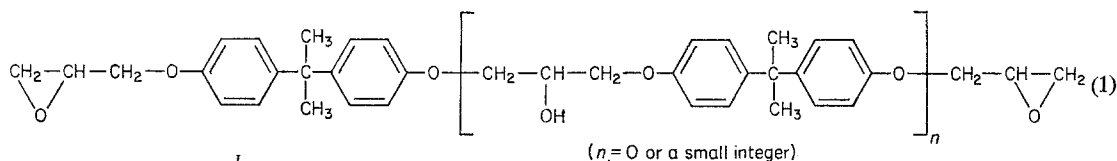
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An electrochemical method has been developed for bonding electrically-conductive adherends. The procedure is based on the electrochemical generation of a curing agent from an otherwise chemically-unreactive precursor mixed with an epoxy resin sandwiched between the bonding members. The one-part epoxy resin is storage stable and cured rapidly on passage of current.

## 1. Introduction

Conventional epoxy-resin formulations require the mixing of an epoxy resin and a curing agent or hardener [1]. A typical resin is the bisphenol A variety (I) within which epoxy groups are

an electrochemically-active precursor is converted to the curing agent. The precursor may be an amide, disulphide, metal-amine complex, carboxylate salt of an amine or other compounds. Carboxylate salts of amines normally effect very slow curing at room temperature but electro-



situated at the ends of the molecule. Curing agents react with the epoxy groups and harden the resin, some examples are amines (primary, secondary, tertiary), mercaptans, phenols, carboxylic acids, amides and alcohols.

One-part epoxy adhesives are composed of a mixture of the epoxy resin and a slowly-reacting curing agent. In both types the cure may be significantly hastened by heating, which is a necessity with some formulations.

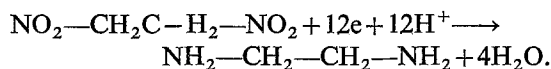
There is considerable incentive to develop one-part, storage-stable adhesives which will cure at ambient temperatures on activation. This paper reports initial experiments with electrochemical curing of epoxy resins in which

chemical activation leads to rapid curing. The precursor is mixed with a suitable epoxy resin and, normally, a quaternary ammonium salt to aid conductivity.

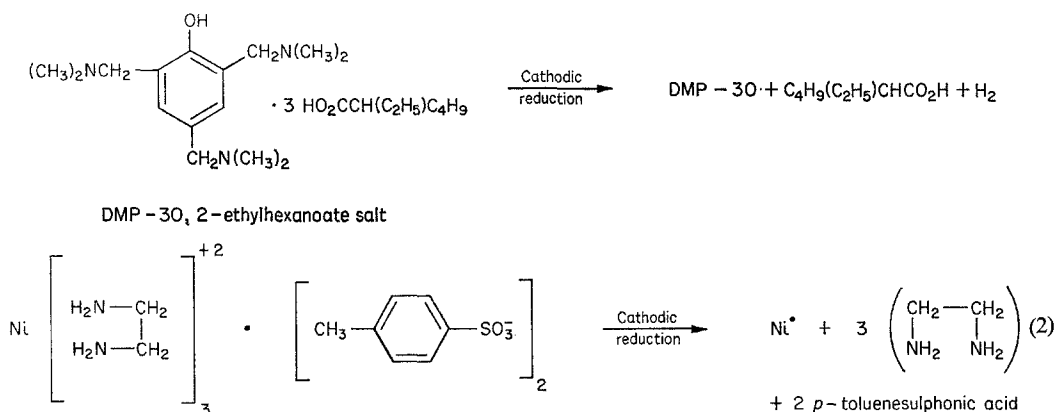
It is well known [2] that amines can be prepared electrochemically by reduction of a large variety of organic derivatives including carboxylic acid amides, imines, amine salts, diazonium salts, sulphonamides, nitro compounds, hydroxylamines, nitroso compounds, and azides. Organic disulphides are readily reduced to mercaptans. Some examples of these reactions are:

(a) amine formation from a carboxylic acid salt (Equation 1, see p. 228):

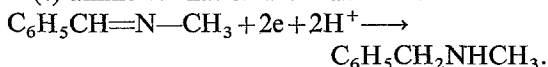
(b) amine formation from a nitro compound:



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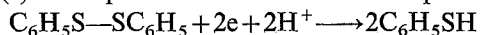


(c) amine formation from an imine:



(d) amine formation from metal complexes (Equation 2):

(e) mercaptan formation from a disulphide:



It is therefore apparent that electrochemical oxidation of certain 'precursor' compounds [3] can also lead to potential curing agents.

## 2. Experimental

The adhesive employed was a 55/45 mixture by weight of the following epoxy resins: DER 664 (Dow Chemical Company), a solid diglycidyl ether of bisphenol A (formula I), having an epoxy equivalent of about 875-975 and a Durran's m.p. of 95-105° and an Araldite RD-2 (Ciba-Geigy Corporation), a diglycidyl-ether of 1,4 butanediol having an epoxy equivalent of

Table 1. Adhesive mixtures studied with aluminium cups

Example no.	Curing agent precursor Compound	Wt %	Supporting electrolyte Compound	Wt %	Electrochemical cure		
					Charge passed Coulombs	Time (h)	% Cure
1	2-methylimidazole benzoate	10	—	—	28.2	16*	20
2	dimethylamine succinate	10	—	—	18.8	0.3	5
3	DMP-30 2-ethylhexanoate	3	$\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_3\text{N}^+\text{BF}_4^-$ in $n\text{-BuOH} + \text{NO}_2\text{CH}_3$	5 ~15		0.25	64
4	DMP-30 2-ethylhexanoate	3	$\text{Et}_4\text{N}^+ p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$ in $n\text{-BuOH} + \text{NO}_2\text{CH}_3$	2 ~15	37.2	16*	25.5
5	DMP-30 2-ethylhexanoate	3	$\text{MeBu}_3\text{N}^+\text{BF}_4^-$ in $n\text{-BuOH} + \text{NO}_2\text{CH}_3$	3 15	35	16*	54
6	Cyclohexanone Oxime	5	$\text{MeBu}_3\text{N}^+\text{BF}_4^-$	3	20.7	0.3	18
7	Benzalaniline	5	$\text{Et}_4\text{N}^+ p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$	3	16.0	0.3	22
8	Benzylidisedulphide	5	$\text{Et}_4\text{N}^+ p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$	6	16.8	0.3	51.2
9	Azobenzene	5	$\text{Et}_4\text{N}^+ p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$	5	16.1	0.3	21.3
10	Diphenyldisulphide	10	$\text{Et}_4\text{N}^+ p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$	5	17	0.3	51
11	Naphthalene 1,8-disulphide	5	$\text{Et}_4\text{N}^+ p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$	5	20.3	0.3	35
12	Diphenyldisulphide	5	$\text{C}_6\text{H}_5(\text{CH}_3)_3\text{N}^+\text{Br}^-$	5	17.3	0.3	15
13	Diphenyldisulphide	5	$(\text{C}_2\text{H}_5)_4\text{N}^+\text{C}^-$	5	22.3	0.3	35.7
14	Diphenyldisulphide	10	$(\text{C}_2\text{H}_5)_4\text{N}^+\text{Cl}^-$	5	26.7	0.3	47.2
15	Diphenyldisulphide	10	$\text{Na}^+(\text{C}_6\text{H}_5)_4\text{B}^-$	5	7.3	0.3	32.7
16	Diphenyldisulphide	10	$(\text{C}_4\text{H}_9)_4\text{N}^+\text{C}_{10}\text{I}_4^-$	15	19.5	0.3	35
17	Diphenyldisulphide	10	$(\text{C}_4\text{H}_9)_4\text{N}^+\text{I}^-$	10	36	0.3	37.0
18	Diphenyldisulphide	10	$(\text{C}_4\text{H}_9)_4\text{N}^+\text{Br}^-$	10	23.5	0.3	38.0

\* Electrolyzed for approximately 15 min then allowed to stand at ambient temperatures for remainder of indicated time.

about 76 and a viscosity of about 20 centipoises at 25°.

The resin was combined with a curing agent precursor and usually a supporting electrolyte, by dissolving in a minimum of warm, anhydrous methylene chloride. The solvent was removed under vacuum and the mixture applied to the conductive pieces to be bonded. A coarse nylon mesh separator was inserted to prevent shorting. A constant-current d.c. power supply was used for the electrolysis.

### 3. Results

#### 3.1. Aluminium cups

Initial experiments were carried out with two aluminium cups set back-to-back (Fig. 1). The

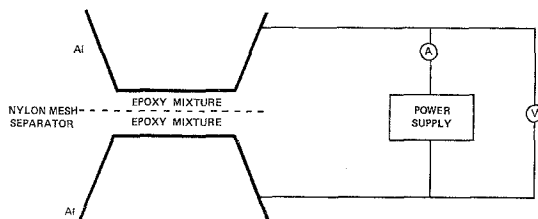


Fig. 1. Experimental set-up for bonding Al cups.

surface area of each face was 3 in<sup>2</sup>. The clamped structure was electrolyzed at an initial current of about 20 mA and a voltage of 50 V. The voltage rose to 350 V in 15 min when electrolysis was terminated. The polarity was reversed about once each minute so that curing agent was generated at both surfaces. The percentage cure was determined by infrared analysis of a thin film of the resin smeared on KBr plates. If the electrolyzed resin was left overnight at room temperature the degree of curing was usually raised a further 10 to 15%.

Table 1 lists experiments conducted under a variety of conditions with various curing-agent precursors and supporting electrolytes. In the absence of electrolysis, little or no curing is observed for many of these systems. In one experiment (No. 10) in which both the electrolyzed system and a non-electrolyzed blank were heated in an oven at 100° for 17 h, the blank showed only a 10% cure, while the electrolyzed sample was firmly bonded (>85% cure). Post heat-treatment of cured epoxy resins is necessary to achieve a high degree of cross-linking.

The charge passed corresponded well with that required to convert the precursor to the curing agent.

#### 3.2. Aluminium sheets

Two aluminium sheets measuring 12 in by 4 in by  $\frac{1}{8}$  in as shown in Fig. 2 were cleaned in chromic

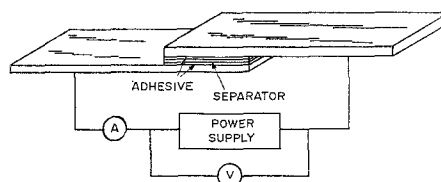


Fig. 2. Electrochemical curing of Al sheets.

acid-sulphuric acid mixture and coated with epoxy resin mixture. A fine nylon mesh separator was placed between the  $\frac{1}{2}$  in lap and the assembly clamped together. Electrolysis was at 200 mA with current reversal every 30 s. Within 10 min, the voltage rose from an initial value of 30 V to 350 V, and the electrolysis was terminated.

Lap shear-tests were made directly or after the indicated period of post-cure treatment. The lap-shear strength determinations were made on 1.0 in strips using ASTM Method D 1002-64. Results are given in Table 2. As before, blank runs showed very little or no cure compared to electrolyzed samples.

Significantly, many formulations listed in Tables 1 and 2 exhibited no noticeable curing by i.r. analysis on sitting at room temperature for periods up to 3 months.

### 4. Discussion

The success of electro-initiated curing of epoxy resins depends upon the conversion of suitable inactive precursors to active curing agents. Although no attempt has been made to ascertain the nature of the actual curing agents generated, the reactions operative are as shown in Equations (a) to (d). Significantly, gaseous evolution was noted in most of the examples and where lower disulphides have been utilized, the characteristic odour of electro-generated mercaptan is evident. Electrochemically-produced anionic species such as azobenzene anion-radical, benzyl mercaptide,

Table 2. Adhesive mixtures studied with aluminium sheets

Example no.	Curing agent precursor		Supporting electrolyte		Current mA	Electrochemical cure		Maximum lapshear (psi)
	Compound	Wt %	Compound	Wt %		Charge passed Coulombs	Post cure treatment	
19	N-Benzylidene-methylamine	15	Et <sub>4</sub> N <sup>⊕</sup> <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> <sup>⊖</sup>	2.5	5	4.7	—	2320
20	C <sub>6</sub> H <sub>5</sub> -N=N-C <sub>6</sub> H <sub>5</sub>	5	Et <sub>4</sub> N <sup>⊕</sup> <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> <sup>⊖</sup>	5	20	5.5	5 days at 100°C	1880
21	C <sub>6</sub> H <sub>5</sub> -N=N-C <sub>6</sub> H <sub>5</sub>	5	Et <sub>4</sub> N <sup>⊕</sup> <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> <sup>⊖</sup>	5	0	0	5 days at 100°C	1480
22	Imidazole nickel nitrate	3	Et <sub>4</sub> N <sup>⊕</sup> <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> <sup>⊖</sup>	5	50	40	16 h at 80°C	361
23	C <sub>6</sub> H <sub>5</sub> -N=N-C <sub>6</sub> H <sub>5</sub>	2.5	Et <sub>4</sub> N <sup>⊕</sup> <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> <sup>⊖</sup>	5	200	60	16 h at 100°C	809
24	+ C <sub>6</sub> H <sub>5</sub> -S-S-C <sub>6</sub> H <sub>5</sub>	2.5	Et <sub>4</sub> N <sup>⊕</sup> <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> <sup>⊖</sup>	5	no current passed		16 h at 100°C	< 50
	+ C <sub>6</sub> H <sub>5</sub> -S-S-C <sub>6</sub> H <sub>5</sub>	2.5						

and DMP-30 alkoxide, may be involved to some extent as curing agents.

Among the advantages of electrochemical curing are the following. A one-part adhesive which has long-term storage stability at room temperature is used. Curing is relatively rapid and is initiated only on the passage of current which allows ease of manipulation during fabrication. Completion of electrolysis of the precursor at constant current is indicated by a sharp increase in voltage. The number of coulombs passed during bonding corresponds approximately with that required to convert the precursor to the curing agent. The curing process is carried out at room temperature and adequate bond-strengths are obtained. Further development of this technique should lead to increased bond strengths. The cost of energy to effect bonding is low, in the range of 0.03–0.2¢/ft<sup>2</sup> depending upon operating voltage and assuming a power cost of 1.0¢/kWh. The scope of the technique is limited by the need for conductive members; however, it may be possible wherein non-conductive adherends are involved, to use metal-coated materials, or Exmet graphite cloth

layers (Exmet Corporation) in the resin sandwich.

Evolution of gases, probably H<sub>2</sub>, O<sub>2</sub> or CO<sub>2</sub>, has been observed in most of the experiments. The results suggest that electrochemical curing is not limited to a thin film at the electrode resin interface where the curing agent is generated. Gas evolution and ohmic heating probably contribute to the development of a uniformly cured bond.

This technique of bonding is the subject of a U.S. patent [4].

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## References

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