

Properties of Epoxy Resins Cured with Ring-Alkylated *m*-Phenylene Diamine Blends

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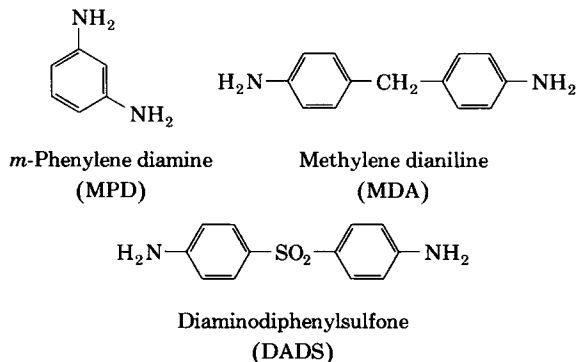
Synopsis

Diglycidyl ether of bisphenol-A was cured, individually, with diaminoisopropyl benzene (DAIPB), diaminoethyl benzene (DAEB), blends of DAIPB/DAEB (up to 40 wt % DAEB), and DAIPB modified with up to 5 wt % amine-terminated poly(butadiene-co-acrylonitrile) liquid rubber (ATBN). For each diamine system glass transition temperature (differential scanning calorimetry) and room temperature tensile properties (Instron) were determined. Blends of DAIPB/DAEB produced cured resins displaying greatly increased tensile strength (up to 50% higher) and slightly lower glass transition temperature compared with resins cured with either diamine alone. DAIPB modified with ATBN yielded moderately improved tensile properties over DAIPB alone. Blends of DAIPB/DAEB (from 10 to 40 wt % DAEB) were observed to be eutectic liquids at room temperature.

INTRODUCTION

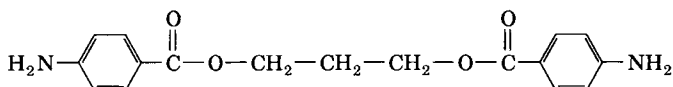
Aromatic diamines have been in use for many years as curing agents for epoxy resins. They were originally introduced to increase the glass transition temperature (T_g) of the cured resins, thereby imparting increased dimensional stability at elevated temperatures.¹ In addition, they were found to yield long pot lives favorable for B-stage fabricating operations, and they produced cured resins of good physical properties and good resistance to solvents and chemicals. Two of the most important industrial applications for these systems are in the area of electrical insulation, where they serve as adhesives, coatings, and encapsulants, and in the aerospace industry where they are used as curing agents for epoxy composite matrix resins.²⁻⁴

The most widely used aromatic diamines for curing of epoxy resins are shown below:



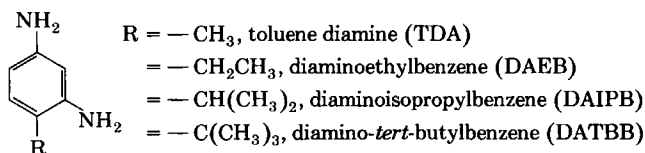
In the aerospace composite industry, DADS is the clear favorite due to the 30–40°C increase in heat distortion temperature it imparts over both MPD or MDA.⁴ For many other applications, MPD or MDA are preferred for their lower cost and because a less energetic cure schedule is required. In fact, since a liquid curing agent is desired, eutectic mixtures of MPD and MDA are readily available on the market.⁵ However, MDA, and to a lesser extent MPD, have come under increasing attack due to their high toxicity. In fact, MDA has been found to produce cancer in laboratory rats.⁶ Thus, there is a need for new aromatic diamines which can serve as replacements for MDA and/or MPD/MDA eutectic mixtures.

One approach toward lessening the toxicity of aromatic diamines is to introduce ring substituents which can be readily metabolized, to a carboxylic acid, for example. This is an obvious advantage of the commercial curing agent trimethylene glycol di-*p*-aminobenzoate,⁷ which upon ingestion is hydrolyzed to produce the nontoxic *p*-aminobenzoic acid (PABA). Such a drastic departure from the basic MDA or MPD structure, however, causes change in the performance properties of the cured resins.



Trimethylene glycol di-*p*-aminobenzoate

In a series of recent publications,^{8,9} we have reported the properties of epoxy resins cured with ring-alkylated MPDs. We anticipate that these compounds will prove less toxic than MDA or MPD because of the alkyl group, which can be readily oxidized in the body to produce the diamino benzoic acid.



An additional advantage imparted by the alkyl group is a significant lowering of the melting point relative to MPD. For example, DATBB is a liquid, and DAIPB is a soft solid at room temperature. Branched alkyl groups are preferred for Friedel-Crafts alkylation chemistry; they are more suitable and less likely to cause an internal plasticization effect in the cured resin. In fact, we have found that larger alkyl substituents, such as isopropyl or *tert*-butyl, actually increase the T_g of the cured resin.^{8,9} The one significant disadvantage observed with the use of ring-alkylated MPDs was a 30–35% loss in cured-resin tensile strength compared with MPD. It was shown that this effect was not due to incomplete curing, which could conceivably be caused by the steric bulk of the ring substituent, but rather seemed to be due to the physical presence of the large alkyl group within the crosslinked network.^{8,9}

Because of the several disadvantages associated with the ring-alkylated MPDs, we sought ways to increase the tensile strength of the cured resins.

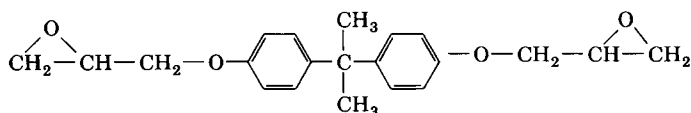
One approach, the results of which are reported herein, was to produce a rubber-toughened epoxy resin by incorporation of small amounts of a rubbery diamine, i.e., amine-terminated poly(butadiene-co-acrylonitrile) liquid rubber (ATBN). Related investigations of rubber-toughened epoxy resins have been recently reported.^{10,11} However, a second more successful approach presented itself in the course of our investigations. In an effort to achieve a stable room temperature-liquid diamine blend based principally on DAIPB, it was discovered that certain blends of ring-alkylated diamines combine synergistically to yield cured resin tensile strengths comparable to MPD and much higher than either ring-alkylated diamine when used alone. We report the physical properties of epoxy resins cured with one such system, i.e., various blend ratios of DAIPB and DAEB.

EXPERIMENTAL

Materials

The DAIPB and DAEB were experimental quantities supplied by Dr. Arthur Bayer of First Chemical Corp. ATBN (Hycar, B. F. Goodrich) was used without purification.

The epoxy resin, diglycidyl ether of bisphenol-A (DGEBA) (DER 332, Dow Chemical Co.), was used without purification. According to the manufacturer, it is pure DGEBA without appreciable amounts of higher molecular weight oligomers and has the following structure:



Diglycidyl ether of bisphenol-A
(DGEBA)

Procedures

The equivalent weight of DGEBA was determined to be 172.1, by titrating epoxide groups using the hydrogen bromide/acetic acid method.¹

The procedure for curing epoxy resins in glass molds was as follows: DGEBA was heated using a circulating air oven at 85°C. Meanwhile, excess amounts of the diamines were heated just to melting in a sealed container. Appropriate amounts of the liquified diamines were combined, and then a stoichiometric equivalent of the epoxy resin was added to the diamine mixture. The three components were mixed thoroughly and evacuated at 60°C for 15 min to remove air bubbles. The reaction mixture was poured into an 85°C glass mold which was prepared in advance by lightly spraying mold release agent (MR 515, Green Chem. Products Inc.) to the inner surfaces of the mold. It was determined that the prepared mold must be baked for at least 2 h in advance of curing to obtain proper conditioning of the glass surfaces. Samples

were cured 2 h at 85°C followed by 2 h at 150°C. After curing, samples were machined to ASTM D638 specifications and stored in a desiccator until use.

Tensile properties were determined according to ASTM D638 using an Instron tensile tester equipped with a 500 kg load cell.

T_g s were determined using a Dupont DSC 910 attached to a 9900 data analysis system. All samples were scanned under nitrogen atmosphere at a rate of 10°C/min.

Densities of cured resins were obtained by accurately weighing rectangular solids which were precision-machined from expended tensile specimens. Approximate dimensions of the specimens were $1 \times 1 \times 0.32$ cm; accurate dimensional measurements were obtained using a micrometer.

RESULTS AND DISCUSSION

DAIPB/DAEB Blends

Mixtures of DAIPB and DAEB ($10 \leq \text{wt \% DAEB} \leq 40$) appear to be true eutectic solutions rather than supercooled liquids. They have remained in liquid form at room temperature for over one year in our laboratories.

Tensile properties and T_g s of resins cured with DAIPB/DAEB blends are shown in Table I. Properties of MPD-cured resins are also included for reference. The results show a steady increase in tensile strength of the cured resin as the proportion of DAEB is increased, with a maximum of 82 MPa occurring at about 70/30 (wt/wt) DAIPB/DAEB. This represents a 40–50% improvement in strength compared with resins produced from either diamine alone. In fact, the 70/30 blend produces strength, elongation, and modulus values virtually identical to those attained with MPD. The reason for this surprising synergistic effect is unknown at this time, but dynamic mechanical analyses, to be reported at a later date, may provide some insight. T_g s obtained with the blends were slightly depressed (4–8%) in relation to the individual diamines and to MPD, but no definite trend could be discerned.

As shown in Table II, cured-resin densities for DAIPB/DAEB blends were all found to be approximately the same and virtually identical to that obtained with MPD.

TABLE I
Mechanical Properties of Epoxy Resins Cured With DAIPB/DAEB Blends

DAIPB/DAEB (wt/wt)	T_g (°C)	Tensile property		
		TS (MPa)	Elongation (%)	Modulus (GPa)
100/0	167	54	3.4	2.1
90/10	155	59	3.2	2.1
80/20	161	66	4.6	2.0
70/30	154	82	5.6	2.1
60/40	157	72	4.1	2.1
0/100	163	59	3.5	2.1
MPD	167	82	5.7	1.9

TABLE II
Densities of Epoxy Resins Cured With DAIPB/DAEB Blends

DAIPB/DAEB (wt/wt)	Density (g/cm ³)
100/00	1.13
90/10	1.17
80/20	1.16
70/30	1.16
60/40	1.16
0/100	1.17
MPD	1.16

ATBN Rubber Modification of DAIPB

Properties of the rubber-modified resins are shown in Table III. Very low levels of rubber incorporation were chosen to attempt to increase strength without significantly affecting other properties such as modulus and T_g . It can be seen in Table III that T_g decreases steadily with increasing rubber incorporation; the transition was also observed to broaden and become less well-defined. Substitution by one or two percent ATBN caused very little change in the tensile properties of cured resins. Substitution in the 3–5% range did produce an increase in tensile strength and elongation, and a decrease in modulus as expected. Unfortunately, the data did not present a clear trend, and it is difficult to speculate whether the tensile strength maximizes at 3 or 4% ATBN or whether it might continue to increase with greater incorporation of ATBN. In either case, the direction of the T_g is unambiguous, and it was

TABLE III
Mechanical Properties of Rubber-Modified Epoxy Resins

DAIPB/ATBN (wt/wt)	T_g (°C)	Tensile property		
		TS (MPa)	Elongation (%)	Modulus (GPa)
100/0	167	54	3.4	2.1
99/01	162	61	4.0	1.9
98/02	156	50	3.4	2.1
97/03	153	73	7.1	1.8
95/05	148	62	6.2	1.4

TABLE IV
Densities of Rubber-Modified Epoxy Resins

DAIPB/ATBN (wt/wt)	Density (g/cm ³)
100/00	1.13
99/01	1.16
98/02	1.15
97/03	1.14
95/05	1.12

felt that further increases in rubber content would produce an unacceptably low T_g .

In general, the density of the rubber-modified resins decreased with increasing ATBN content as shown in Table IV. This is expected due to the increasing hydrocarbon content of the cured resin, and is also presumably due to an increase in free volume associated with the flexible ATBN component.

CONCLUSIONS

A systematic investigation of the properties of epoxy resins cured with diaminoisopropyl benzene (DAIPB)/diaminoethyl benzene (DAEB) blends and DAIPB/amine-terminated butadiene nitrile rubber (ATBN) blends was conducted. The results indicated that a 70/30 (wt/wt) blend of DAIPB/DAEB yields cured resin tensile properties comparable to those of *m*-phenylene diamine, and much higher than those obtained with either individual diamine. T_g s for resins cured with DAIPB/DAEB blends were slightly lower than those obtained with either MPD or the individual diamines. DAIPB/DAEB blends exist as liquids at room temperature, which is a significant advantage for an epoxy curing agent.

DAIPB, substituted with 3–5% ATBN, produced resins of higher tensile strength than DAIPB alone. However, the T_g s of the cured resins decreased with increasing ATBN content; and in addition, the transition broadened, indicating increasing heterogeneity of the sample.

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