

## Alkylbenzene-Maleic Anhydride Photoadducts as Dianhydrides for Epoxies and Polyimides

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### Synopsis

Dianhydrides from ethylbenzene, cumene, and branched C<sub>5</sub>-C<sub>6</sub> alkylbenzene-maleic anhydride photoadducts have a surprisingly high solubility in epoxy resins. Dianhydrides from benzene, toluene, and *n*-C<sub>10</sub>-C<sub>12</sub> alkylbenzene adducts, which are homologs of the above, were not soluble. Epoxies cured with the ethylbenzene and cumene dianhydride adducts had higher heat distortion temperatures and flexural strengths than epoxies cured with two commercial monoanhydrides. High-melting polyimides were also obtained with these two new dianhydrides.

### INTRODUCTION

Dianhydrides have been reported to be useful as epoxy curing agents<sup>1,2</sup> and in the preparation of polyimides.<sup>2,3</sup> Pyromellitic dianhydride (PMDA) is the simplest dianhydride used for these purposes.<sup>1-3</sup> The major disadvantage of PMDA as an epoxy curing agent is its low solubility and high reaction rate in epoxy resins. Often, the resin gels before all the PMDA dissolves. Recently, other dianhydrides have been developed which are more soluble in epoxy resins. These materials form cured products which are comparable to PMDA resins.<sup>2,4</sup>

We have found that the dianhydrides prepared from ethylbenzene, cumene, and branched C<sub>5</sub>-C<sub>6</sub> alkylbenzene-maleic anhydride photoadducts<sup>5</sup> are very soluble in epoxy resins and form good cured products. Dianhydrides prepared from benzene, toluene, and benzene substituted with alkyl chains of seven and higher carbons were not soluble. While this work was in progress, others<sup>6</sup> reported that the benzene-maleic anhydride photoadduct formed polyimides with excellent high-temperature properties when treated with various diamines. We found that the dianhydrides from ethylbenzene and cumene adducts also formed good polyimides.

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## EXPERIMENTAL

### Materials

The dianhydrides were prepared by the photochemical addition of maleic anhydride to alkylbenzene.<sup>5</sup> Nadic methyl anhydride (NMA) and tetrahydrophthalic anhydride (THPA) were purchased from Allied Chemical Company. DER-332, a bisphenol epoxy resin, and DEN-438, an epoxy novolac, were purchased from Dow Chemical Company. Hexamethylenediamine (HMDA) and 4,4'-diaminodiphenyl ether (DAPA) were purchased from Eastman Kodak.

### Epoxy Castings

Epoxy castings of DER-332 and ethylbenzene (EBMA) and cumene (CMA)-maleic anhydride photoadducts were prepared by dissolving 0.4 equiv. of the photoadduct in 1.0 equiv. of the epoxy. When dissolved, 0.4 equiv. of phthalic anhydride was added. The resulting liquid was poured between 1/8-in. casting frames and cured at 160°C. for 24 hr. For comparison purposes, DER-332 was cured with 1 equiv. of NMA and 1 equiv. of THPA. Test results are given in Table I.

TABLE I  
Properties of Anhydride-Cured Epoxy Resins<sup>a</sup>

	EBMA	CMA	NMA	THPA
Barcol hardness	40	35	32	35
Heat distortion temp., °F.	230	210	156	195
Flexural strength, psi	18,000	19,000	16,000	15,000
Flexural modulus, psi × 10 <sup>-5</sup>	4.9	5.5	5.2	3.5
Impact strength, ft.-lb./in. <sup>b</sup>	3.3	3.3	2.6	4.4

<sup>a</sup> Dow DER-332

<sup>b</sup> Izod unnotched.

EBMA and CMA were also soluble in the epoxy novolac, DEN-438; however, no castings were prepared. The dianhydride from branched C<sub>5</sub>-C<sub>6</sub> alkylbenzene was also soluble in the two epoxy resins, but insufficient dianhydride was available for preparation of castings. Dianhydrides prepared from benzene, toluene, and *n*-C<sub>10</sub>-C<sub>13</sub> alkylbenzene were not appreciably soluble in DER-332 or DEN-438.

### EBMA-DAPE Polyimide

To a rapidly stirred mixture of 5 g. (0.025 mole) of 4,4'-diaminophenyl ether in 90 g. *N,N*-dimethylacetamide at ambient temperature was slowly added 7.55 g. (0.025 mole) of ethylbenzene-maleic anhydride photoadduct.

A rise in the relative viscosity was observed during this addition. The resulting light-brown solution was poured into a flat dish and evaporated in a vacuum oven at 70°C. and 20 mm. Hg. The temperature was then raised to 140°C. for 4 hr. The dark solid that formed was quite brittle, melting point >600°C., molecular weight about 300,000.\*

### CMA-HMDA Polyimide

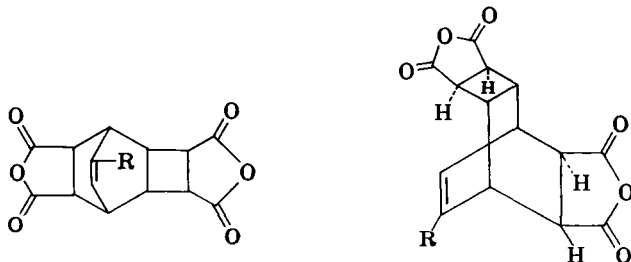
The same procedure as above was followed. The mixture of dianhydride and diamine was found to be heterogeneous. Small samples were placed in aluminum dishes (50-mm. diameter) and heated as described above. The resulting films had a melting point of 430–450°C. The infrared spectrum of the films showed some acid and amide bands, indicating incomplete reaction. One of the films (0.12-mm. thick) had a tensile strength of 1083 psi and an initial modulus of  $20.83 \times 10^3$  psi with a 25% elongation at the breaking point.

### RESULTS AND DISCUSSION

The test results (Table I) show that the two soluble dianhydrides are potentially useful epoxy hardeners. Heat distortion temperature and flexural strength are improved over two commercial monoanhydrides. The heat distortion values are somewhat inferior to those reported for resins cured with pyromellitic dianhydride (200°C.), but in this work only one dianhydride formulation was tried. Other formulations are undoubtedly possible which will give higher heat distortion temperatures.

The polyimides formed are comparable to those reported by Tabushi and co-workers for the benzene-maleic anhydride adduct.<sup>6</sup> As in the case of polyimides from pyromellitic dianhydride, extremely tough and high-melting polymers were obtained.<sup>3</sup>

It is not obvious from the structure of the dianhydride<sup>5,10</sup> why the ethylbenzene and cumene adducts should be so soluble in epoxy resins or epoxy novolacs. It is probable that the intermediate alkyl groups ( $R = C_2H_5$  to  $C_6H_{13}$ ) give the compound just the right amount of nonpolar character to offset the polar anhydride groups. The methyl group then does not possess enough and the higher alkyl groups have too much nonpolar character.



\* The molecular weight was estimated from a measurement of the concentration dependence of the reduced specific viscosity of solutions of the polymer in dimethylacetamide at 25°C. by using the procedure of Chinnai.<sup>7</sup>

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### Résumé

Les dianhydrides obtenus par photoaddition d'anhydride maléique à de l'éthylbenzène, du cumène et de l'alcoylbenzène avec branches latérales en C<sub>5</sub>-C<sub>6</sub> présentent une solubilité surprenante dans les résines époxy. Les dianhydrides au départ de benzène, toluène et d'alcoylbenzène C<sub>10</sub>-C<sub>12</sub> qui sont les homologues des précités n'étaient pas solubles. Les époxy traités avec les produits d'addition de dianhydride et de cumène avaient des températures de distorsion thermiques plus élevées et des forces à la flexion plus grandes que les époxy traités avec les monoanhydrides commerciaux. Les polyimides de haut point de fusion furent également obtenus avec ces deux nouveaux dianhydrides.

### Zusammenfassung

Dianhydride aus Äthylbenzol, Cumol und verzweigten C<sub>5</sub>-C<sub>6</sub>-Alkylbenzol-Maleinsäureanhydrid-Photoaddukten besitzen eine überraschend hohe Löslichkeit in Epoxyharzen. Die homologen Dianhydride aus Benzol, Toluol und *n*-C<sub>10</sub>-C<sub>12</sub>-Alkylbenzoladdukten waren nicht löslich. Mit Äthylbenzol- und Cumol-Dianhydridaddukten gehärtete Epoxyharze besaßen höhere Hitzeverformungstemperaturen und Biegefestigkeiten als mit zwei handelsüblichen Monoanhydriden gehärtete Epoxyharze. Schliesslich wurden mit diesen beiden neuen Dianhydriden auch hochschmelzende Polyimide erhalten.

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