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EPOXY HYDANTOINS AS MATRIX RESINS

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Summary

The physical properties of amine-cured hydantoin epoxy resins have been investigated and compared to the state-of-the art MY 720/Eporal resin system used in advanced carbon fiber composites. Tensile strength and fracture toughness of castings of the hydantoin resins cured with methylenedianiline are significantly higher than the MY 720 control castings. Water absorption of an ethyl, amyl hydantoin formulations was found to be relatively low (2.1% at equilibrium) and Tg's were about 160°C, approximately 15° below the final cure temperature. These compounds are candidates for matrix resins for composites with improved structural properties.

Two series of urethane and ester-extended hydantoin epoxy resins were synthesized to determine the effect of crosslink density and functional groups on properties. Castings cured with methylenedianiline, or with hexahydrophthalic anhydride were made from these compounds and evaluated. The glass transition temperatures, tensile strengths and moduli, and fracture toughness values were all found to be much lower than that of the simple hydantoin epoxy resins. Using a methylene bishydantoin epoxy with a more rigid structure gave brittle, low-energy fractures, while a more flexibile, ethoxy-extended hydantoin epoxy resin gave a very low Tg.

INTRODUCTION

The objective was to develop new matrix resins for improved structural properties of graphite fiber composites. The epoxy resin used in graphite composites for aerospace applications is N,N,N'N'-tetraglycidyl-4,4'-methylenedianiline (ARALDITE MY 720*). MY 720 formulated with 4,4'-diaminodiphenylsulfone (Eporal*, or DDS) hardener is the basis of the resin system which is widely used in graphite composites, e.g., Narmco 5208*. Laminates made from these epoxy/graphite systems have many outstanding properties but are deficient in impact strength. It is important to reduce the hidden interior damage to such laminates caused by low energy impact.

The desired improved properties of prepreg and composites with the new matrix resin are as follows:

1. Materials easily and reproducibly formulated to "aerospace quality."
2. Materials easily quality-controlled, and multiple vendor sources readily developed.
3. Prepreg with good tack and drape having a minimum of 30 days out-time at 90°F.
4. A cure temperature in the 250°F-300°F range and a cure cycle of 4 to 6 hours duration.
5. Long-term composite durability from -65 to 180°F.
6. Improved toughness over existing 350°F epoxy materials such as NARMCO 5208/T300.
7. Moisture resistance equal to or better than existing 350°F epoxy materials such as NARMCO 5208/T300.

A solution to the impact resistance problem may lie in the use of matrix resins that display high modulus and high elongation values in neat casting studies. Earlier results at CIBA-GEIGY showed the promise of the hydantoin epoxy class of resins as matrix resins for impact-resistance graphite composites.[1] Other advantageous properties of these resins are relatively high heat distortion temperatures, low viscosities and ease of B-staging and processing.[1,2] Neat castings of two diglycidyl hydantoin resins based on 3,5-dimethyl hydantoin (DMH) and 5-methyl-5-ethyl-hydantoin (MEH), cured with methylene dianiline (MDA) show high modulus and higher elongation than the MY 720/DDS system.

Use of such materials in composites has led to systems with improved impact resistance; a DMH/MDA laminate showed significantly better Gardner impact strength than a MY 720/DDS laminate.[3] The DMH-based resin used in this earlier study, XB 2793, was neither designed nor optimized for composite applications, but chosen for its high modulus and high elongation properties. Modification of the resin structure might improve these properties further.

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* Use of trade names or names of manufacturers in this report does not constitute an official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration.

Numerous structural modifications are feasible with the hydantoin system, as shown in Figure 1.

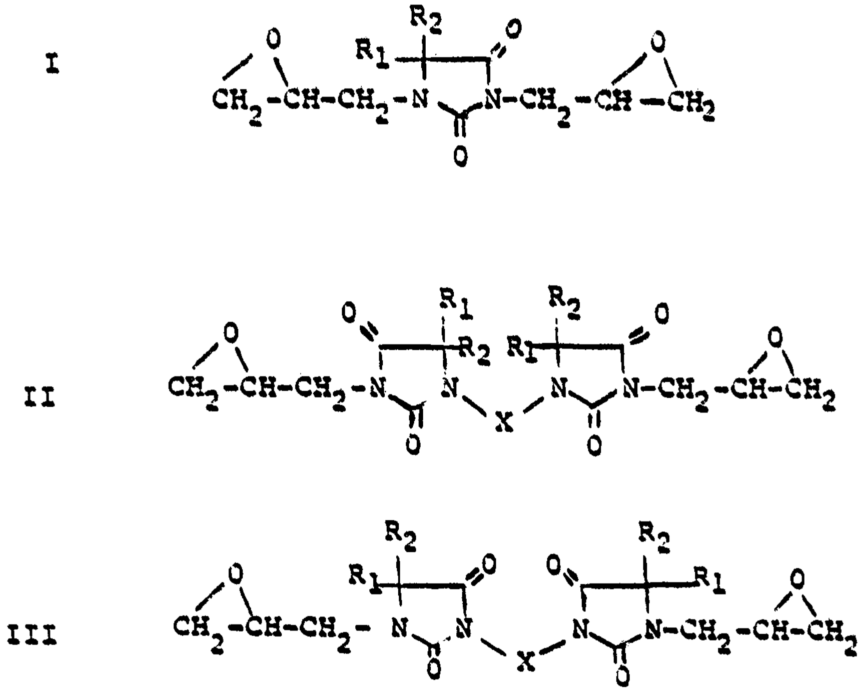


FIGURE 1 - HYDANTOIN EPOXY RESIN STRUCTURES

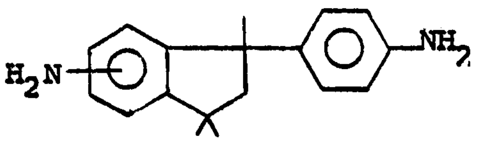
R_1 and R_2 can be alkyl groups such as methyl, ethyl and pentamethylene; X can be methylene, bis-hydroxyethyl esters of various chain lengths, or urethane or urea groups. The curing agent used can also affect properties significantly.

The initial work on this contract was to synthesize and screen selected hydantoin epoxy resins and hardeners and to determine the effect of molecular structure on pertinent properties, e.g., the effect of different side chains on water absorption and the effect of an extended structure (yielding a lower crosslink density) on tensile and fracture toughness properties. These evaluations were to include glass transition and heat distortion temperatures, tensile properties, fracture toughness, impact strength, and water absorption. The compounds which gave the most promising results would be considered candidate matrices for carbon fiber composites.

Experimental Results and Discussion

A. Simple, Non-Extended Hydantoin Epoxides

Clear, void-free castings were made from nine hydantoin epoxy-diamine systems and from four control systems using MY 720 and bisphenol-A diglycidyl ether (DGEBPA) cured with MDA and DDS. The hydantoins used are of the structure I in Figure 1, cured with methylene dianiline (MDA), diaminophenylindane (DAPI, IV, Fig. 2), and DDS. These thirteen systems and their curing conditions are listed in Table I. The ratios used were for stoichiometric equivalent amounts, determined by titration.



IV

Figure 2. Diaminophenylindane (DAPI)

The following measurements were made on the castings described above: Tg via thermomechanical analysis, tensile strength, modulus and elongation at break, fracture toughness, and water pick-up at 60°C (140°F) and 95% R.H. for one-eighth inch thick samples (average of 3 samples). Tensile tests were performed according to ASTM D638, with Type I, 1/8 inch-thick samples. Fracture toughness values were calculated from the results of a compact tensile test (similar to ASTM E399) described by Knott and Met.[4] Samples were prepared from machined neat resin castings about 6 mm thick. Controlled cracks were introduced into slots machined into the samples by tapping a razor blade at their edge (see figure 3). The tensile load needed to propagate the crack was measured on an Instron tester with a cross-head speed of 0.5 mm/min. The strain energy release rate, G_{Ic}, was calculated from the measured critical stress intensity factor, K_{Ic}, using the equation $G_{Ic} = (K_{Ic}{}^2/E)(1-\gamma^2)$. E is Young's modulus from the tensile test and Poisson's ratio, γ , was found to be 0.38 by the simultaneous determination of transverse and longitudinal strains on cured, cast samples.

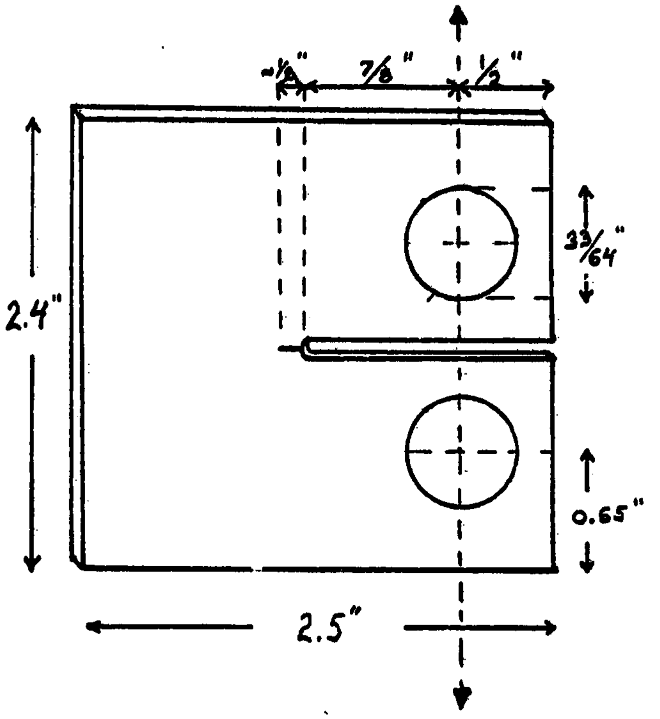


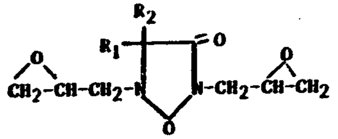
Figure 3. Compact Tensile Test Specimen

Results of the tests on these thirteen systems are given in Table I. Literature values for MY 720 and for NARMCO 5208 are also included for comparison.

In all cases, MDA-cured epoxides exhibited greater fracture toughness values than the corresponding DDS-cured or DAPI-cured epoxides. Tensile strength at break was also generally highest for MDA-cured castings. The bifunctional hydantoin epoxides provided significantly higher tensile elongation and fracture toughness then the tetrafunctional MY 720 and were generally similar in these properties to DGEBPA. Within the series of castings cured with MDA, the methyl, ethyl and the ethyl, amyl hydantoin epoxy resins had the highest fracture toughness values.

Water absorption was lowest with the ethyl, amyl hydantoin systems, especially with the MDA hardener. Tg retention of resin systems in a high humidity environment would be expected to be highest for the latter system.

TABLE I - PHYSICAL AND MECHANICAL PROPERTIES OF AMINE - CURED HYDANTOIN EPOXIDES



FORMULATION a)						TENSILE VALUES					FRACTURE TOUGHNESS			
R_1	R_2	Amine	Tg/TMA (°C)	ΔH (kcal/eq)	Water Absorption (%)	Strength kg/mm^2	(ksi)	Modulus kg/mm^2	(ksi)	Elongation %	K_{Ic} kg/mm$^{3/2}$	(lb/in$^{3/2}$)	G_{Ic} J/m^2	(in-lb/in^2)
CH_3	C_2H_5	MDA c)	160	-	5.7	8.6	(12.2)	246	(350)	3.8	3.63	(1025)	462	(2.59)
C_2H_5	C_5H_{11}	MDA	160	-	2.1	5.9	(8.4)	225	(320)	5.0	2.99	(844)	343	(1.92)
Pentamethylene		MDA	180	-	4.1	7.6	(10.8)	309	(439)	3.3	2.51	(708)	176	(0.986)
MY 720		MDA	175	-	-	5.3	(7.5)	196	(279)	2.9	1.71	(483)	129	(0.722)
DCEBPA		MDA	160	-	-	7.0	(10.0)	211	(300)	4.7	2.76	(779)	312	(1.75)
CH_3	C_2H_5	DAPI d)	164	-	5.7	4.7	(6.7)	344	(489)	1.8	1.71	(483)	73	(0.409)
C_2H_5	C_5H_{11}	DAPI	168	-	2.8	4.1	(5.8)	204	(290)	2.4	1.96	(553)	162	(0.907)
Pentamethylene		DAPI	203	-	3.6	4.6	(6.5)	281	(400)	1.8	1.97	(556)	119	(0.666)
CH_3	C_2H_5	DDS e)	181	19.6	6.7	6.8	(9.7)	352	(501)	2.8	1.53	(432)	57	(0.319)
C_2H_5	C_5H_{11}	DDS	164	20.6	3.3	5.8	(8.2)	246	(350)	3.1	2.22	(627)	173	(0.969)
Pentamethylene		DDS	180	-	4.8	5.4	(7.7)	344	(489)	1.6	2.20	(621)	121	(0.678)
MY 720		DDS	232	28.8	4.4	2.9	(4.1)	337	(479)	0.9	1.52	(429)	59	(0.330)
													$60^{b)}$	(0.336)
NARMCO 5208		DDS	-	-	-	-	-	-	-	-	-	-	82^{6}	(0.459)
DCEBPA		DDS	-	-	-	7.2	(10.2)	232	(330)	3.3	2.61	(737)	254	(1.42)

a) MDA and DAPI cures were at 120 to 175°C; DDS cures were with 1 phr BF_3·MEA and at 120 to 200°C.

b) Value estimated from fracture surface energy data of B. L. Lee et al.[5]

c) 4,4'-methylenedianiline

d) Diaminophenylindane (IV)

e) Diaminodiphenyl Sulfone

B. Urethane-Extended Hydantoin Epoxides

Five urethane hydantoin epoxy resins were synthesized from three different alkyl-substituted hydantoins reacted with toluene diisocyanate and with diphenylmethane diisocyanate, according to the scheme shown in Figure 4. Reactions with isocyanate were carried out as in U.S. Patent No. 3,867,385[7]. The structures are shown on Table II. The methyl, ethyl and the pentamenthylene derivatives showed high (19 to 21 kcal/equivalent) heats of reaction with methylenedianiline (MDA). The ethyl, amyl derivative reacted less fully with MDA, and so it was cured with DDS. As shown in Table II, Tg's were found to be considerably lower than the Tg's found for the simple hydantoin epoxy resins (160° to 180°C).

The urethane resins were high in viscosity and casting was difficult because they reacted when heated to reduce viscosity for deaeration and pouring. However, castings of two of the formulations were made for testing. Results (given in Table II as an average of at least five determinations) showed tensile strengths and moduli and fracture toughness values to be low. Apparently, the conversion to urethanes makes the castings more flexible but does not improve their physical properties.

C. Ester-Extended Hydantoin Epoxides

Four ester-extended hydantoin epoxy resins were prepared from three different alkyl-substituted hydantoins reacted with adipic acid and with sebacic acid as in U.S. Patent No. 3,872,097[8] (shown schematically in Figure 4). The structures are given in Table III. Derivatives of terephthalic acid could not be synthesized, apparently because of very low solubility; a transesterification reaction might have been more successful. As shown in the table, curing was not complete for most of the formulations; soft gummy materials resulted on heating the mixes. It was found that the ester epoxy resins contain about 35 percent of monoglycidyl compound and do not cure effectively with any of the usual diamine hardeners. The adipate of 1-glycidyl, 3-hydroxethyl, 5-methyl, 5-ethyl hydantoin cured well using hexahydrophthalic anhydride (HHPA). Castings were made from these materials, but Tg was found to be very low (56°C), as were the tensile and fracture toughness values.

D. Ureas

Preparation of urea derivatives of hydantoins (to synthesize epoxy resins as shown in Figure 5) was attempted by reacting isocyanates with hydantoins according to the procedure described in the U.S. Patent No. 3,778,439[9]. The reaction was incomplete, leaving 2.3 to 6.5 percent of unreacted isocyanate and 4.5 to 9 percent of unreacted hydantoin. Complete glycidylization of one of these products could not be accomplished; the resulting material had a low epoxy value (75 percent of theory) and a high chlorine content (8.2 percent). No castings were made from these compounds.

Figure 4. SYNTHESES OF BIS(HYDANTOIN) EPOXY RESINS: URETHANES AND ESTERS

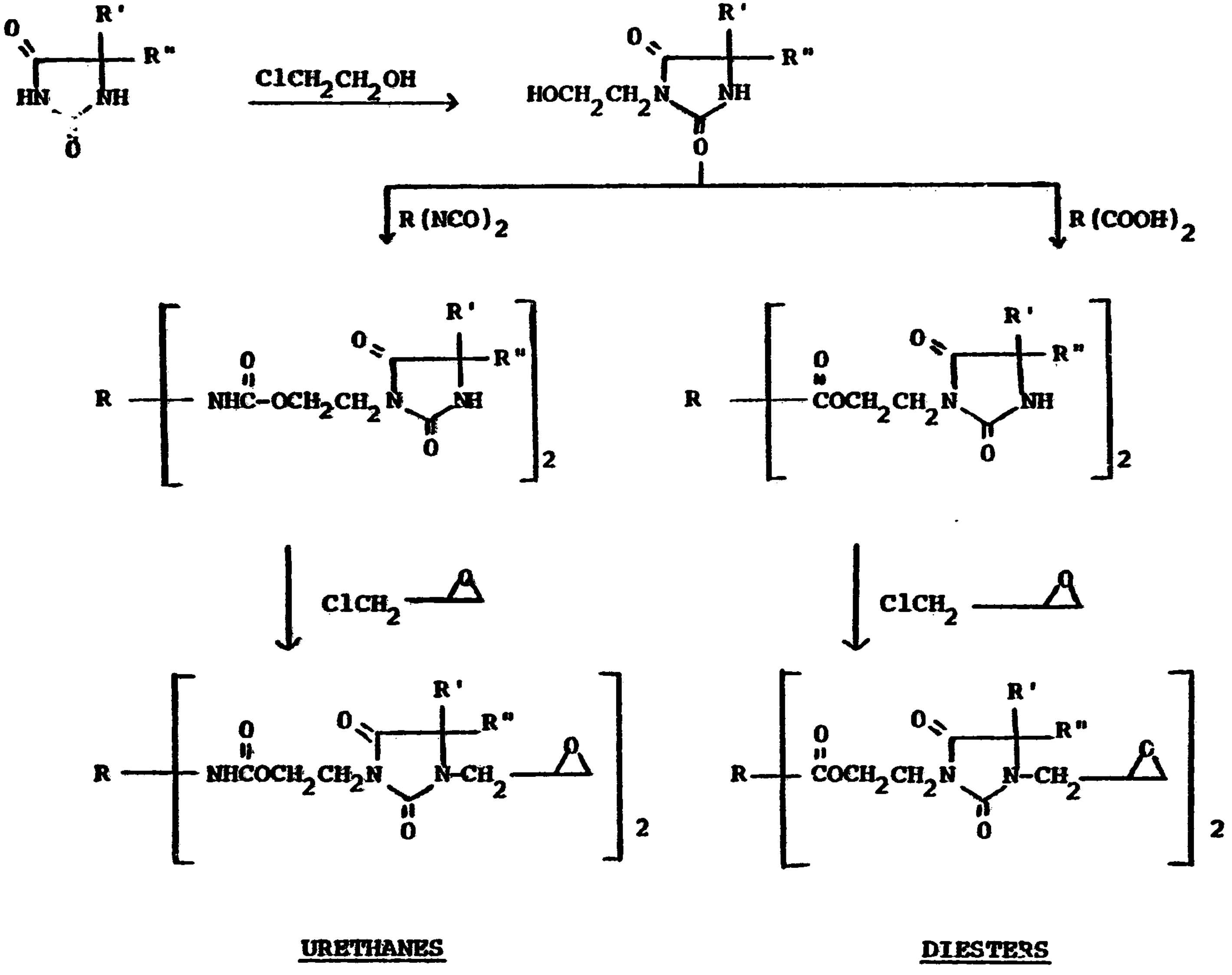
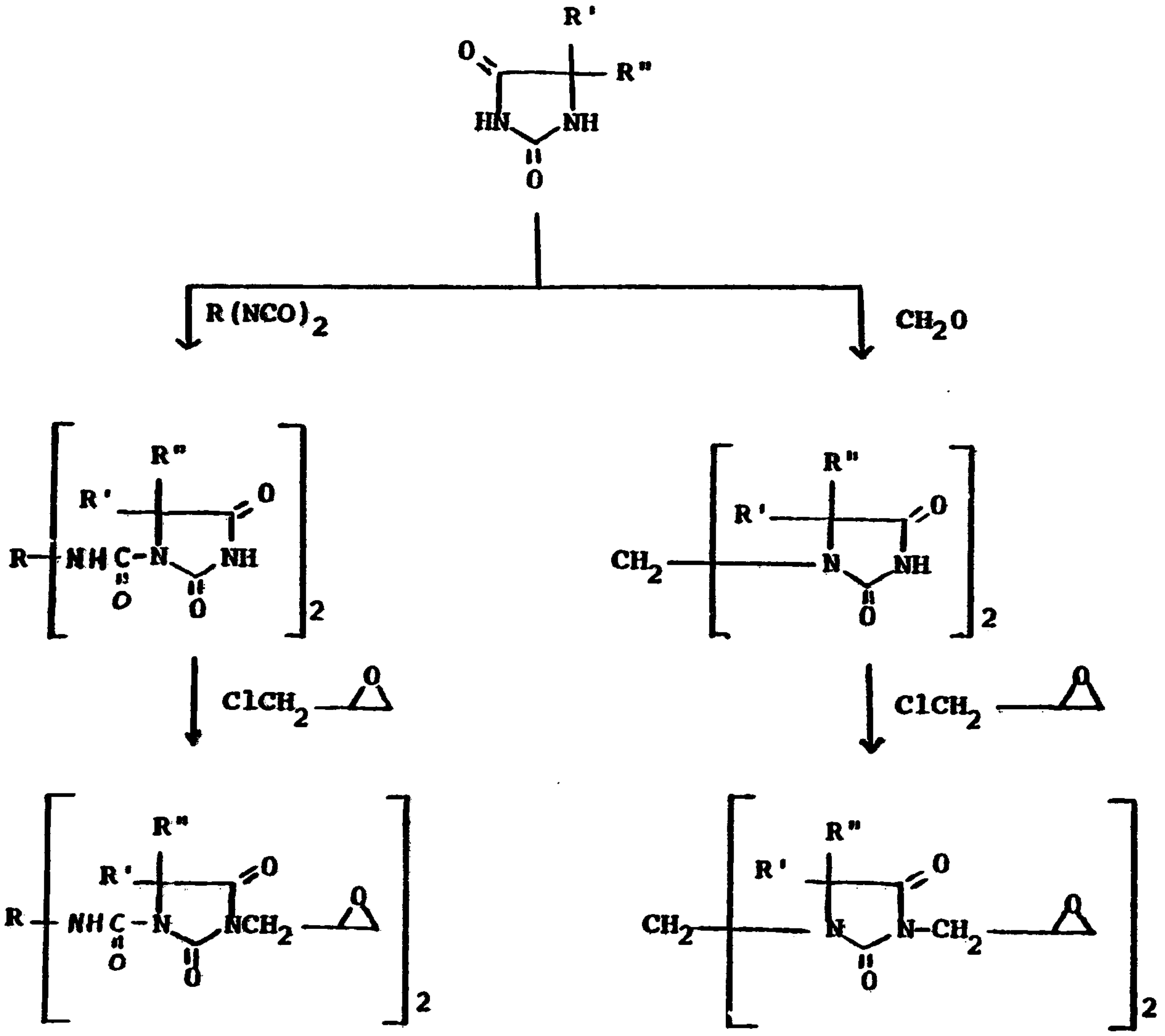


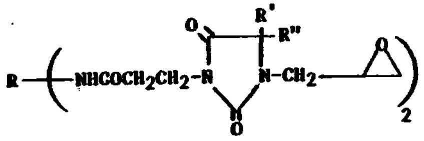
Figure 5. SYNTHESES OF BIS(HYDANTOIN) EPOXY RESINS: UREAS AND METHYLENE-BRIDGED COMPOUNDS

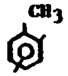
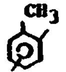
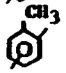


UREAS

METHYLENE BIS(HYDANTOIN) EPOXIDES

TABLE II - PHYSICAL AND MECHANICAL PROPERTIES OF URETHANE - EXTENDED HYDANTOIN EPOXY SYSTEMS



R	R'	R"	CURE AGENT	Δ H (KCAL/EQ)	Tg/DSC (°C)	TENSILE VALUES STRENGTH kg/mm^2(ksi)	MODULUS kg/mm^2(ksi)	ELONGATION (%)	FRACTURE TOUGHNESS K_{Ic} kg/mm$^{3/2}$(lb/in$^{3/2}$)	G_{Ic} J/m^2(in-lb/in^2)
	CH_3	C_2H_5	MDA b)	17.1	113	- -	- -	-	- -	-
	C_2H_5	C_5H_{11}	MDA	10.4	120 a)	4.1 (5.8)	18.6 (26.4)	1.7	0.72 (203)	240 (1.34)
	C_2H_5	C_5H_{11}	DDS c)	17.4	96	- -	- -	-	- -	-
	PENTAMETHYLENE		MDA	20.8	-	- -	- -	-	- -	-
DIPHENYLMETHANE	CH_3	C_2H_{11}	MDA	18.8	105	2.5 (3.6)	17.3 (24.6)	1.0	- -	-
DIPHENYLMETHANE	C_2H_5	C_5H_{11}	MDA	15.9	-	- -	- -	-	- -	-

a) 100°C VIA TMA

b) 4,4' - METHYLENEDIANILINE

c) DIAMINODIPHENYL SULFONE

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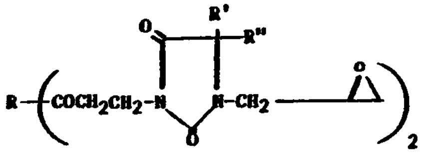
TABLE III - PHYSICAL AND MECHANICAL PROPERTIES OF ESTER - EXTENDED HYDANTOIN EPOXY SYSTEMS



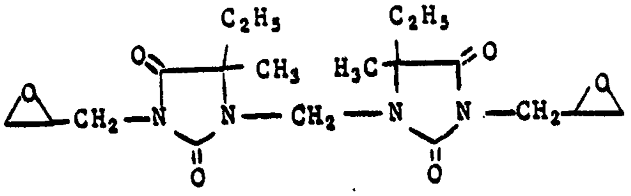
						TENSILE VALUES					FRACTURE TOUGHNESS			
						STRENGTH		MODULUS		ELONGATION	K_{Ic}		G_{Ic}	
R	R'	R"	CURE AGENT	ΔH (KCAL/EQ)	Tg/DSC (°C)	kg/mm^2	(ksi)	kg/mm^2	(ksi)	(%)	$kg/mm^{3/2}$	$(lb/in^{3/2})$	J/m^2	$(in\text{-}lb/in^2)$
$(CH_2)_4$	CH_3	C_2H_5	HHPA a)	21.7	56	2.1	(3.0)	70.3	(100)	0.9	4.74	(1338)	276	(1.55)
$(CH_2)_4$	C_2H_5	C_5H_{11}	MDA b)	NO CURE	-	-	-	-	-	-	-	-	-	-
$(CH_2)_4$	PENTAMETHYLENE		MDA,DDS c)	NO CURE	-	-	-	-	-	-	-	-	-	-
$(CH_2)_8$	CH_3	C_2H_5	HHPA	10.1	33	-	-	-	-	-	-	-	-	-
$(CH_2)_8$	CH_3	C_2H_5	MDA	15.1	47	-	-	-	-	-	-	-	-	-

a) hexahydrophthalic anhydride
b) 4,4'-methylenedianiline
c) diaminodiphenyl sulfone

E. Methylene-Bridged Epoxy Compounds

1. 1,1'-Methylene-Bis(2-Glycidyl,5-Methyl,5-Ethyl Hydantoin) (V)

The diepoxide of 1,1-methylene-bis(5-methyl, 5-ethyl hydantoin), V, Figure 6, was prepared according to the scheme in Figure 5 (details of the synthesis are given in U.S. Patent No. 3,778,439[9]). A white, crystalline product melting at 132-134°C was formed. It was found to cure well at 175°C with MDA; DSC showed 22.8 kcal/equiv. centered at 179°C and a Tg of 160°C. Clear castings were made and samples were cut for tensile and fracture toughness tests. The results of these tests are shown in Table IV, along with the values determined for control samples based on methyl, ethyl hydantoin diepoxide, on MY 720, and on bisphenol A diepoxide, all cured with MDA. The glass transition temperature is reasonably high (160°C) and the tensile values are higher than those for MY 720 and similar to those of the simple hydantoin systems. However, the fracture toughness values are low, similar to those of MY 720 cured with MDA. This bis-hydantoin epoxide appears to undergo a very brittle fracture, similar to that of MY 720 castings. A water absorption test at 60°C and 95 percent relative humidity showed an equilibrium weight gain of 3.2 percent.

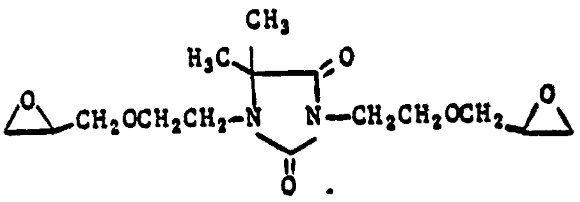


V

Figure 6. 1,1'-Methylene-Bis(2-Glycidyl,5-Methyl,5-Ethyl Hydantoin

2. 1,3-Bis(2'-Glydicyloxyethyl)5,5-Dimethyl Hydantoin (VI)

The ethoxy-extended hydantoin epoxy resin, compound VI, Figure 7, was synthesized by addition of ethylene oxide to 5,5-dimethylhydantoin, followed by glycidylation. It was cast with MDA and cured (Δ H = 12.3 kcal/equiv) at temperatures up to 175°C to make clear eighth-inch thick and quarter-inch thick sheets. Tensile and fracture toughness samples were cut. Test results are given in Table IV. The glass transition temperature is only 70°C, possibly because of the flexible ethoxy groups in the main chain and possibly also because of the lower degree of cure. Tensile and fracture toughness properties are similar to those of the better simple hydantoin systems, although G_{Ic}, at 224 Joules/square meter, is not as high as the best value found for the methyl ethyl hydantoin, 462 J/m^2. Properties of compound VI cured with MDA are also similar to those of a standard bisphenol A epoxy resin, except for Tg, which is considerably lower. Water absorption was relatively high, about 7 percent.



VI

Figure 7. 1,3-Bis(2'-Glycidyloxyethyl)5,5-Dimethyl Hydantoin

TABLE IV. PHYSICAL PROPERTIES OF MDA - CURED EPOXIDES

				TENSILE VALUES		FRACTURE TOUGHNESS	
		Water	Strength	Modulus	Elongation	K_{Ic}	G_{Ic}
EPOXY RESIN	Tg (^oC)	Absorption (%)	kg/mm^2(ksi)	kg/mm^2(ksi)	(%)	kg/mm$^{3/2}$(lb/in$^{3/2}$)	J/m^2(in-lb./in^2)
V	160	3.2	6.5 (9.2)	359 (510)	3.0	1.90 (536)	87 (0.487)
VI	70	7	7.5 (10.7)	299 (425)	4.9	2.79 (787)	224 (1.25)
Methyl, ethyl hydantoin	160	5.7	8.6 (12.2)	246 (350)	3.8	3.63 (1024)	462 (2.59)
MY 720	175	-	5.3 (7.5)	196 (279)	2.9	1.71 (483)	129 (0.722)
Bisphenol A	160	-	7.0 (10.0)	211 (300)	4.7	2.76 (779)	312 (1.75)

Conclusions

Hydantoin epoxy resins cured with MDA exhibit relatively high tensile strengths and fracture toughnesses as compared with MY 720 cured with MDA or DDS. Water absorption of the ethyl, amyl hydantoin cured with any of the three hardeners used is also significantly lower than those of a MY 720/DDS system. Physical properties of these hydantoin systems, especially those cured with MDA, show promise of providing improved matrix resins for composites.

Urethane-extended hydantoin epoxy resins were found to yield lower glass transition temperatures, lower tensile strengths and moduli, and lower fracture toughness than the simple hydantoin epoxy resins. Similarly, ester-extended hydantoin epoxy resins gave lower values for these physical properties. Therefore, no advantage was found in modifying the backbone structure of hydantoin epoxides with flexible urethane or ester groups. A more rigid, methylene bis-hydantoin was made, but was brittle, offering no improvement in fracture toughness. An ethoxy-extended hydantoin epoxy resin was apparently too flexible, giving a low Tg.

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