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**HIGH CHAR IMIDE-MODIFIED
EPOXY MATRIX RESINS**

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ABSTRACT

Studies were performed to synthesize a novel class of bis(imide-amine) curing agents for epoxy matrix resins. Glass transition temperatures and char yield data of an epoxy cured with various bis(imide-amines) are presented. The room temperature and 350° F mechanical properties, and char yields of unidirectional graphite fiber laminates prepared with conventional epoxy and imide-modified epoxy resins are presented.

1. INTRODUCTION

The potential electrical problems associated with the release of free carbon fibers into the atmosphere has been discussed (ref. 1). Several approaches are currently being investigated to develop alternate composite materials which will minimize or eliminate the potential problems associated with the accidental release of graphite fibers during or after the burning of graphite fiber reinforced resin matrix composites. A higher char epoxy resin has been identified as a possible approach to solve the fiber release problem. Epoxy resins are the most widely used matrix resins because they are easy to process and because fiber reinforced epoxies have excellent mechanical properties. However, the char yield of state-of-the-art epoxy resins is generally less than 25 percent by weight.

Studies were conducted at the NASA Lewis Research Center to develop a novel type of curing agent, or hardener, for epoxy resins. The purpose of this paper is to describe the synthesis of imide-amine hardeners and to present properties of neat epoxy resins cured with the imide-amine hardeners. The char yields and mechanical properties of graphite fiber reinforced composites fabricated with the imide-modified epoxy resins are also presented.

2. EXPERIMENTAL PROCEDURES

2.1 Monomers

The tetraglycidyl methylene dianiline was purchased from a commercial source under the trade name of Araldite MY 720 (ref. 2). The diamines, 4,4'-methylenedianiline (MDA), 4,4'-sulfonyldianiline (DDS), 4,4'-oxydianiline (ODA), p-phenylenediamine (PDA), and the 4,4'-(hexafluoroisopropylidene)-bis(phthalic anhydride) (6F) were obtained from commercial sources.

A representative procedure for the synthesis of the bis(imide-amine) from MDA and 6F is described below: a solution of 6F (31.08 g, 0.07 mole) in N-methylpyrrolidone (115 ml) was added dropwise during 30 minutes to a stirred solution of MDA (27.72 g, 0.14 mole) in N-methylpyrrolidone (35 ml). The solution was stirred at room temperature for 1 hour, then heated under reflux for 4 hours. The solution was poured into 200 ml of water with rapid stirring. The product was filtered, washed with water, and dried in vacuum at 212° F to yield 55.90 g (99 percent yield).

2.2 Neat Resin Molding

Solutions for molding neat resins were prepared by slowly adding equivalent amounts of the hardeners to a stirred 75 w/o solution of MY 720 resin in methyl ethyl ketone (MEK). The solution was gently heated ($T < 122^{\circ}$ F) during mixing. After clear solutions were obtained, the solutions were stirred at 150° F for 30 minutes to remove the bulk of the solvent. The solutions were then vacuum deaerated and poured into a flat mold made from polished steel plates. The plates were separated and sealed with 0.25 inch Teflon. The filled mold was then vacuum deaerated and placed into an oven preheated to 230° F. After 45 minutes at 230° F, the temperature was raised to 350° F and maintained for 120 minutes. The neat resin castings were then post-cured for 24 hours at 400° F in a forced air oven.

The glass transition temperatures (T_g) of the neat resin castings were determined, before and after post-cure, using a thermomechanical analyzer. Isothermal weight loss measurements in air were performed at 350° F.

2.3 Composite Fabrication

Prepregging solutions were prepared by slowly adding stoichiometric amounts of the hardeners to a stirred solution of MY 720/MEK at 122° F. The MY 720/MEK concentration was calculated to yield a prepregging solution containing 60 w/o resin.

Prepreg tapes were prepared by drum-winding and impregnating Celion 6000 (epoxy finish) graphite fiber with the various MY 720/hardener impregnating solutions to yield prepreg tapes containing 60 w/o fiber. The prepreg tapes were air dried on the drum at 120° F for 1 hr and under ambient conditions for an additional 24 hours. The prepreg exhibited excellent tack and drape and could easily be removed from the peel ply. The prepreg was then cut into 3×8 inch plies and stacked unidirectionally into a matched metal die. Composites were then molded by placing the die into a press at room temperature, applying 15 psi pressure, raising the temperature to 230° F at a rate of 10° F/minute, and holding until resin gelation occurred.

Gelation times at 230° F ranged from 15 to 30 minutes. After gelation, 100 psi pressure was applied and held for 30 minutes. The temperature was then raised to 350° F at a rate of 10° F/minute. After reaching 350° F, temperature and pressure were maintained for 120 minutes. All composites were post-cured for 24 hours at 400° F in a forced air oven.

2.4 Composite Testing

Prior to specimen preparation all laminates were inspected using the ultrasonic C-scan technique. Flexural strength tests were performed using a 3 point loading fixture with a fixed span of 2 inches. The thickness of the laminates ranged from 0.090 to 0.095 inch. The resultant span/depth ratio ranged between 21 and 22. The rate of center loading for flexural testing was 0.05 inch/minute.

Interlaminar shear strength tests were conducted at a constant span/depth ratio of 5 and a loading rate of 0.05 inch/minute. Elevated temperature tests were performed in an environmental heating chamber. For the flexural and shear tests, the load was applied after a 15 minute soak at the test temperature. Forced convection air ovens were used for long-term isothermal exposure of laminates at 350° F. Composite weight measurements were made throughout the exposure times. The air change rate was 100 cubic centimeters per minute.

The properties data presented are averages of 3 or more tests at each condition. Fiber content was determined for all laminates and ranged from 50.4 to 54.9 v/o. For flexural tests, all results were normalized to 55 v/o fiber.

2.5 Char Testing

Aerobic char tests were performed on neat resin and composite specimens in a muffle furnace. Neat resin specimens having dimensions of 1x1x0.25 inch and composite specimens having dimensions of 1x1x0.09 inch were exposed for three minutes at 1500° F. For neat resin, char was determined by weight difference before and after burning. For composites, char residue was determined by subtracting the weight loss of the composite after burning from the as-fabricated resin weight content of the composite.

Anaerobic char testing of neat resins was performed by thermalgravimetric analysis (TGA). The tests were performed in a nitrogen atmosphere using a heating rate of 72° F/minute up to a maximum temperature of 1500° F.

3. RESULTS AND DISCUSSION

3.1 Neat Resins

The structures of the bis(imide-amine) hardeners are listed in table 1. The structures shown are for the 2:1 adducts of the diamine/dianhydride reactions. However, recent gel permeation chromatographic (GPC) analysis of the product from the reaction of MDA and 6F has indicated that the reaction product contained a small quantity of several higher molecular weight oligomers as well as a small quantity of unreacted MDA. All of the bis(imide-amine) hardeners that were used in this study very likely consisted of a mixture of the 2:1 adduct, the higher molecular weight oligomers and unreacted diamine. However, infrared analysis of the reaction product from 6F and MDA did not show absorption bands due to amide or carboxylic acid

functional groups. In addition, GPC analysis did not show the presence of unreacted 6F in the reaction product. Therefore, the only reactive functional groups present in the reaction product are amino groups, and the average molecular weight of the reaction product mixture can be taken to be that of the 2:1 adduct. The molecular weights of the 2:1 adducts were used in calculating the number of equivalents of hardener. Throughout the remaining discussion, the reaction product, or hardener, mixture will be referred to as a bis(imide-amine), and a bis(imide-amine) cured epoxy will be referred to as "epoximide."

The glass transition temperatures of the epoxy and epoximide resins investigated in this study are summarized in table 2. The data show that the use of the bis(imide-amine) hardeners lowered the T_g. The T_g lowering can be attributed either to the increased flexibility conferred by the hexafluoroisopropylidene linkage in the bis(imide-amine) or to the increased distance between crosslinks, or very likely to a combination of both. However, the important point to be made is that the T_g values of all the epoximides investigated are well above the use temperature for the vast majority of fiber reinforced epoxy applications.

The isothermal weight loss characteristics of the epoxy and epoximide resins after 1000 and 2000 hours of exposure in air at 350° F are listed in table 3. The data show that all of the resins exhibited about the same level of thermo-oxidative stability. No beneficial effect of the imide groups was observed within the 2000 hour exposure time period. It is possible that exposure for considerably longer time intervals would discern any effects due to the presence or absence of imide rings.

Table 4 presents the aerobic and anaerobic char yields which were determined at 1500° F for the unreinforced epoxy and epoximide resins. The data clearly show that the epoximide resins exhibited significantly higher char forming characteristics. The aerobic char yields of the epoximide resins were 2 to 3 times higher than the aerobic char yields of MY 720 cured with conventional aromatic diamine hardeners. The percentage increase in anaerobic char yields of the epoximides ranged from approximately 40 percent for MY 720/DDS·BIA (1:1) vs. MY 720/DDS (1:1), to 100 percent for MY 720/MDA·BIA (1:1) vs. MY 720/MDA (1:1). The vastly improved char forming characteristics of the epoximide resins can be attributed to the incorporation of imide molecular structural units in the cured resin by the bis (imide-amine) hardeners.

3.2 Composite Processing

The handling and processing characteristics of the epoximide prepreps compared favorably to those of conventional aromatic diamine/epoxy resins. No difficulty was experienced in preparing prepreg with any of the MY 720/bis(imide-amine) hardener combinations.

Although MEK was used to effect solution of the various bis(imide-amine) hardeners in the epoxy, the results from a few preliminary experiments indicated that the various epoximides could be readily adapted to hot-melt prepreg techniques. The most noticeable difference between the epoximides and the conventionally formulated epoxy resins was that the

former, as expected, exhibited a longer gel time. The increase in gel time is undoubtedly due to the lower reactivity of the bis(imide-amine) hardeners.

3.3 Composite Properties

Table 5 summarizes the T_g and aerobic char yields of Celion 6000 laminates prepared with MY 720 which was cured with 100 percent MDA, 75 percent MDA + 25 percent MDA·BIA, 50 percent MDA + 50 percent MDA·BIA or 100 percent MDA·BIA. As expected, the epoximide laminates exhibited lower T_g values than the MY 720/MDA (1:1) laminate.

The laminate aerobic char yields do not correlate with the neat resin aerobic char yields (see table 4) suggesting a possible resin/fiber interaction. A more significant finding was that essentially the same level of aerobic char yield could be obtained by replacing as little as 25 percent of the MDA with MDA·BIA. Because the synthesis of the bis(imide-amine) uses a rather costly fluorocarbon, this finding strongly suggests a route to obtain high char yields while at the same time minimizing costs. The use of a stoichiometric quantity of a hardener which consists of a mixture of a bis(imide-amine) and its parent diamine would also minimize the reduction in T_g.

Table 6 presents the interlaminar shear strength (ILSS) and flexural strength at room temperature, 350° F, and 350° F after 2000 hours of exposure in air at 350° F of the MDA·BIA epoximide laminates and the MY 720/MDA (1:1) laminates. The room temperature ILSS of epoximide and MDA cured laminates were found to be equivalent. The lower ILSS of the epoximide laminates at 350° F reflects, of course, the somewhat lower T_g values of the epoximides. Except for the epoximide in which 50 percent of the MDA had been replaced by MDA·BIA, the flexural strengths of the epoximide and MDA laminates at room temperature and 350° F are within experimental variation. Both the ILSS and flexural strengths at 350° F after 2000 hours of exposure in air at 350° exhibited increases. These results are probably due to the net effect of degradation and continued crosslinking during prolonged elevated temperature exposure.

The most important point to be noted, however, is that the mechanical properties of the MDA bis(imide-amine) and MDA cured MY 720 laminates appear to be equivalent.

4. SUMMARY OF RESULTS AND CONCLUSIONS

Based on the results of this study, the following conclusions may be drawn:

1. The use of bis(imide-amine) hardeners to cure epoxy resins significantly improves the aerobic and anaerobic char forming characteristics of the cured resin. Compared to epoxy resins cured with conventional diamines there was a 2 to 3 fold increase in aerobic char yield and as much as a 100 percent increase in anaerobic char yield.

2. Prepregs prepared with the bis(imide-amine) hardeners exhibit handling and processing characteristics which are equivalent to those of conventional aromatic diamine/epoxy resins.

3. Graphite fiber/epoxy laminates prepared with bis(imide-amine) hardeners exhibit outstanding aerobic char yields (250 percent improvement). It appears that the high levels of char yields can be obtained by using stoichiometric quantities of hardener mixtures consisting of the bis(imide-amine) and the parent diamine.

4. The bis(imide-amines) can be used to fabricate high quality graphite fiber laminates having mechanical properties which are equivalent to those of conventional graphite fiber/epoxy laminates.

5. REFERENCES

1. Anon., "A Report of Observed Effects on Electrical Systems of Airborne Carbon/Graphite Fibers," NASA TM-78652, 1978.
2. Araldite MY 720, Technical Product Data, Ciba-Geigy Corp.

6. BIOGRAPHIES

6.1 Tito T. Serafini

Dr. Tito T. Serafini is presently Head of the Polymer Matrix Composites Section of the NASA-Lewis Research Center where he has been since 1963. He received his B.S. in Chemical Engineering, M.S. and Ph.D. in Physical Chemistry from Case Institute of Technology; was a member of the Case staff in 1961 and received a post-doctoral fellowship from the University of Turin (Italy) in 1962. His current research is in the areas of polymer synthesis and composite fabrication and characterization. In 1976, he received NASA's highest science award, the Exceptional Scientific Achievement Medal, for his studies which led to the development of PMR polyimides.

6.2 Peter Delvigs

Dr. Delvigs has been a staff member in the Polymer Matrix Composites Section of NASA-Lewis Research Center since 1967. He received a B.A. degree in Chemistry from Case Western Reserve University and a Ph.D. in Organic Chemistry from the University of Minnesota. His current research involves the synthesis and characterization of processable polymer matrix systems for fiber-reinforced composites having improved moisture resistance and char characteristics, as well as improved long-term performance at elevated temperatures.

6.3 Raymond D. Vannucci

Raymond Vannucci has been employed at NASA-Lewis Research Center since 1965. He received a B.S. degree in Engineering from Cleveland State University. Presently he is working as a Materials Engineer in the Polymer Matrix Composites Section. His current research involves the fabrication and characterization of polymer composites.

TABLE 1. - STRUCTURE OF BIS (IMIDE-AMINE) HARDENERS

Structure	Abbreviation
	<p>DDS·BIA</p>
	<p>MDA·BIA</p>
	<p>PDA·BIA</p>
	<p>ODA·BIA</p>

TABLE 2. - GLASS TRANSITION TEMPERATURE OF IMIDE
MODIFIED EPOXY RESINS

Resin/hardener (equivalent ratio)	Glass transition temperature, °F
MY 720/MDA (1:1)	397
MY 720/MDA/MDA·BIA (1:0.5:0.5)	352
MY 720/MDA·BIA (1:1)	334
MY 720/DDS (1:1)	417
MY 720/DDS·BIA (1:1)	316
MY 720/ODA·BIA (1:1)	324
MY 720/PDA·BIA (1:1)	354

TABLE 3. - ISOTHERMAL WEIGHT LOSS OF IMIDE
MODIFIED EPOXY RESINS IN AIR AT 350° F

Resin/hardener (equivalent ratio)	Percent weight loss, hr	
	1000	2000
MY 720/MDA (1:1)	2.6	3.4
MY 720/MDA/MDA·BIA (1:0.5:0.5)	2.4	3.1
MY 720/MDA·BIA (1:1)	1.9	2.6
MY 720/DDS (1:1)	1.6	2.4
MY 720/DDS·BIA (1:1)	2.0	2.7
MY 720/ODA·BIA (1:1)	2.2	3.2
MY 720/PDA·BIA (1:1)	2.1	2.9

TABLE 4. - CHAR YIELDS OF IMIDE MODIFIED EPOXY RESINS

Resin/hardener (equivalent ratio)	Percent char aerobic at 1500° F	Percent char anaerobic at 1500° F
MY 720/MDA (1:1)	13	23
MY 720/MDA/MDA·BIA (1:0.5:0.5)	27	36
MY 720/MDA·BIA (1:1)	38	46
MY 720/DDS (1:1)	15	24
MY 720/DDS·BIA (1:1)	30	33
MY 720/ODA·BIA (1:1)	35	42
MY 720/PDA·BIA (1:1)	35	39

TABLE 5. - GLASS TRANSITION TEMPERATURE AND
AEROBIC CHAR YIELD OF CELION 6000/IMIDE
MODIFIED EPOXY LAMINATES

Equivalent ratio of MY 720/MDA/MDA·BIA	Glass transition temperature, °F	Percent char aerobic at 1500° F
1/1/0	432	18
1/0.75/0.25	392	47
1/0.5/0.5	370	46
1/0/1	365	45

TABLE 6. - MECHANICAL PROPERTIES OF CELION 6000/IMIDE MODIFIED

EPOXY LAMINATES

Equivalent ratio of MY 720/MDA/MDA·BIA	Interlaminar shear strength, ksi			Flexural strength, ^a ksi		
	RT	350° F	350° F/2000 hr	RT	350° F	350° F/2000 hr
1/1/0	13.1	6.7	7.9	245	132	169
1/0.75/0.25	12.3	6.1	7.2	224	113	151
1/0.5/0.5	12.3	5.0	7.2	205	96	144
1/0/1	12.9	5.4	7.1	236	111	164

^aNormalized to 55 v/o fiber.