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Lower-Curing-Temperature PMR Polyimides

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LOWER-CURING-TEMPERATURE PMR POLYIMIDES

by

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ABSTRACT

Studies were performed to achieve a lower-curing-temperature PMR Polyimide. The use of m-aminostyrene as the end-cap instead of the monoalkyl ester of 5-norbornene-2,3-dicarboxylic acid was investigated in typical PMR formulations. Model compound studies were also performed. Differential scanning calorimetry studies were performed on model compounds and neat resins to establish their melting and curing characteristics. The elevated temperature weight loss characteristics of neat resins and graphite fiber composites were determined. The room temperature and short-time 260°C (500°F) mechanical properties of the composites were also determined. The use of m-aminostyrene end-caps reduced the final cure temperature of PMR resins by about 55°C (100°F), but the composites prepared with these resins are limited to use temperatures of about 260°C (500°F).

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INTRODUCTION

PMR Polyimides are achieving acceptance as processable high temperature resistant polymer matrix materials. Prior to the development of PMR Polyimides (ref. 1, 2) high temperature resistant polymers were regarded as laboratory curiosities. The commercialization of prepreg materials based on the PMR Polyimide designated as PMR-15 has made it possible to design

and fabricate structures for use at temperatures up to 316°C (600°F) (ref. 3), or nearly twice the use temperature of epoxy resins. PMR Polyimides possess excellent processability. They exhibit excellent flow characteristics, and when properly processed by either autoclave or press molding, the cured composites are defect free. PMR Polyimides employ norbornenyl end-caps, which require high temperatures for the thermally induced addition crosslinking reaction. Thus, the major limitation of PMR Polyimides is that the final cure needs to be conducted at temperatures in the range of 288°-316°C (550° to 600°F), preferably at the higher temperature. These cure temperature requirements exceed the temperature capabilities of many autoclave facilities which were acquired for curing of epoxy matrix composites. A lower-curing-temperature PMR Polyimide would be more compatible with existing facilities and should lead to even wider usage.

The purpose of this study was to investigate the effectiveness of an alternate end-cap, m-aminostyrene, for reducing the cure temperature requirements of PMR Polyimides. Thermal analysis studies of model compounds and neat resins prepared with m-aminostyrene were performed. The elevated temperature weight loss characteristics of neat resins and graphite fiber composites were determined. The room temperature and short-time 260°C (500°F) mechanical properties of the composites were also determined.

EXPERIMENTAL PROCEDURE

MONOMERS

The monomers used in this study are shown in Table I. The m-aminostyrene (MAS) and p-aminostyrene (PAS) were synthesized from the corresponding

nitrostyrenes by reduction with zinc/ammonium chloride in aqueous acetone according to the method of Boyer and Alul (ref. 4). The p-nitrostyrene was prepared by dehydrobromination of β-(p-nitrophenyl)-ethyl bromide (ref. 5). The dimethyl ester of 3,3'4,4'-benzophenonetetracarboxylic acid (BTDE) and the dimethyl ester of 4,4'-(hexafluoroisopropylidene) bis (phthalic acid) (HFDE) were synthesized by refluxing a suspension of the corresponding dianhydride in a calculated amount of anhydrous methanol until the solid had dissolved and then for an additional two hours to give a 50 weight percent (w/o) solution of BTDE or HFDE. The dianhydrides, as well as 4,4'-methylenedianiline (MDA) and p-phenylenediamine (PPDA), were obtained from commercial sources.

MODEL COMPOUNDS

The model compounds described in this study are shown in Figure 1. The monoimide I was prepared by heating a 50 w/o methanol solution of equimolar amountsof MAS and monomethyl phthalate at 150°C (302°F) under nitrogen for 1 hour to yield a brownish liquid which solidified on cooling. Crystallization of the crude product from equal volumes of acetone/methanol gave a 70% yield of product, m.p. 101°-103°C (214°-217°F).

The bisimide II was prepared by the same procedure as the monoimide I, using a 2:1 molar ratio of MAS:BTDE. The product, obtained in 97% yield, exhibited a softening point at ~150°C (302°F), but did not melt completely.

MOLDING POWDERS AND POLYIMIDE PLUGS

Monomers in the desired stoichiometric ratios were dissolved in methanol at a solids loading of 50 w/o and the solution was heated under nitrogen for 1 hour at 150°C (302°F). The dry solid was ground into a

fine powder. The molding powder (approx. 1.5g) was placed into a circular matched metal die (diameter 1 in.) at room temperature. The assembly was heated to 260°C (500°F) at a rate of 5°C (9°F) per minute. A pressure of 1750 psi was applied, and temperature and pressure were maintained for one hour.

INSTRUMENTAL MEASUREMENTS

Infrared (IR) spectroscopy was performed using a commercial grating IR spectrophotometer. Differential scanning calorimetry (DSC) measurements were performed in a commercial pressure DSC cell under 250 psi of nitrogen at a heating rate of 10°C (18°F) per minute. Thermal mechanical analyses (TMA) of molded resin plugs were performed using a penetration probe at a heating rate of 10°C (18°F) per minute. The probe was loaded with a 5 gram weight. Weight loss of the resin plugs was determined by isothermal exposure of three replicate specimens at 288°C (550°F) in a forced draft oven with an air change rate of 100 cm^3 per minute.

COMPOSITE FABRICATION

Pregreg solutions were prepared at room temperature by dissolving the monomers in the desired stoichiometric ratios in anhydrous methanol to form 50 w/o solutions. Pregreg tapes were made by drum-winding and impregnating Hercules HTS graphite fiber with the monomer solutions to yield pregregs containing 45 w/o monomers and 55 w/o fiber. The prepreg tapes were dried on the rotating drum for 2 hours at 50°C (122°F) to reduce the volatile content to approximately 12 w/o. The tapes were removed from the drum, cut into 3 by 3 inch plies, and stacked unidirectionally, 8 plies thick. Vacuum bagged, press cured laminates were fabricated using a ½ inch caul plate. The prepreg stack was wrapped with a porous Teflon glass peel ply.

Two plies of bleeder cloth (style 181E glass fabric) were then placed on the stack. The bagging material was 1 mil Kapton which was sealed to the caul plate with a silicone sealant. A vacuum of 5 in. Hg was applied, and the assembly was heated to 149°C (300°F) at 2.8°C (5°F) per minute. After a 90 minute hold a 149°C (300°F), a vacuum of 20 in. Hg and a pressure of 200 psi were applied, and heating was resumed at 2.8°C (5°F) per minute to 260°C (500°F). Final cure temperature and pressure were maintained for 90 minutes.

In the press cure method, the prepreg stack was placed in a preforming mold and staged at 121°C (250°F) for 2 hours under a pressure of approximately 0.1 psi. The staged prepreg stack was placed into a matched metal die preheated to 121°C (250°F). The temperature was increased to 204°C (400°F) at a rate of 5°C (9°F) per minute and a pressure of 500 psi was applied. The temperature was increased to 260°C (500°F), and maintained for 1 hour. After removal from the press, all composites were postcured by increasing the temperature to 288°C (550°F) at a rate of 5°C (9°F) per minute, and then maintaining 288°C (550°F) for 16 hours.

COMPOSITE TESTING

Prior to specimen preparation, the laminates were inspected for porosity using an ultrasonic C-scan technique. Flexural strength tests were performed using a three point loading fixture with a fixed span of 2 inches. The rate of center loading was 0.05 inches per minute. The thickness of the laminates ranged from 0.075 in. to 0.085 in., resulting in a span/depth ratio of 24 to 27. Interlaminar shear strength tests were conducted at a constant span/depth ratio of 5. The mechanical properties are the average of three replicates. The flexural property vales were normalized to 55 volume percent

(v/o) fiber. The fiber content of the laminates was determined by digestion with sulfuric acid/hydrogen peroxide. Weight loss of the laminates was determined as described in the Instrumental Measurements section.

RESULTS AND DISCUSSION

Model Compound Studies

A preliminary study of curing conditions was performed using the model compounds shown in Figure 1. Model compound I was prepared by heating equimolar amounts of m-aminostyrene and monomethyl phtalate for 1 hour at 150°C (302°F). Model compound I was also prepared by the reaction of m-aminostyrene with phthalic anhydride to yield the intermediate amide-acid, which was then thermally dehydrated to yield the monoimide. The ester-acid reaction was preferred because it was desired to simulate the reaction commonly employed in PMR polyimide chemistry.

Attempts to prepare the isomeric model compound by reaction of p-aminostyrene with either monomethyl phthalate or phthalic anhydride were unsuccessful. When the reaction was carried out at temperatures below 130°C, the products exhibited very weak imide bands in the infrared (IR) spectra. At reaction temperatures in the 135°-150°C (275°-302°F) range, the products were glassy, amorphous solids. IR spectroscopy indicated the presence of strong imide bands, but vinyl bands were absent. This indicated that vinyl polymerization and imide formation had occurred simultaneously.

Model compound II was prepared without difficulty by reaction of m-aminostyrene and the dimethyl ester of 3,3'4,4'-benzophenonetetracarboxylic acid (BTDE).

Figure 2 shows the differential scanning calorimetry (DSC) scan of model compound I. In addition to the melting endotherm at 100°C (212°F), the compound exhibited two reaction exotherms at 142°C and 192°C (278°F and 378°F). The DSC scan of bisimide II is shown in Figure 3. It can be seen that there was a significant increase in the temperature at which cure occurred, compared with the monoimideI. The increase in cure temperature can be attributed to the further stiffening and decreased mobility due to the presence of two cyclic imide groups. Nevertheless, the 235°C (455°F) exotherm is still substantially lower than the cure exotherm (maximum at ~340°C (644°F) exhibited by the PMR polyimides using a norbornenyl end-cap (ref. 6). Thus, the results of the model compound studies warranted further studies with fully formulated polyimide precursors using the m-aminostyrene end-cap.

Neat Resin Studies

Molding powders were prepared from three different monomer combinations using the m-aminostyrene end-cap. The monomer stoichiometry is listed in Table II. Molding powder A is the vinyl-end-capped analog of PMR-15, and C is the analog of the second generation PMR-II.

Figure 4 shows the DSC scans of the molding powders. All three samples exhibited a softening endotherm which initiated at 140°-150°C (284-302°F). This was immediately followed by a curing exotherm. This absence of distinctly separated softening and curing events is in contrast to the behavior observed for norbornenyl-end-capped PMR resins (ref.6). The lack of widely separated thermal events is no doubt responsible for the limited flow which was observed for these resins.

Based on the observed curing maxima in the DSC scans, the temperature of 260°C (500°F) was selected for resin and composite fabrication.

The properties of the three molded resins are listed in Table III. The higher densities of resin compositions B and C reflect the contribution of the trifluoromethyl groups.

The transition temperatures shown in Table III were determined with a thermal mechanical analysis (TMA) apparatus using a penetration probe. Without a postcure, the glass transition temperatures(Tg) of the three resins were considerably lower than the Tg of PMR-15 resin. Attempts were made to increase the Tg by postcuring the resins in air for 16 hours at 260°C (500°F) and 288°C (550°F). Postcure at 288°C (550°F) resulted in a significant increase of the Tg. No further increase in Tg was observed when the specimens were postcured at 316°C (600°F).

Figure 5 shows the TMA scans of resin composition B. It can be seen that above its Tg the resin exhibited a softening temperature (T_s) as reflected by penetration of the probe into the resin specimen. The softening persisted even after postcure at 288°C (550°F), in contrast to the behavior exhibited by PMR-15 resin.

The resins exhibited good thermo-oxidative stability at 288°C (550°F). This is reflected by the comparatively low weight loss, shown in Table III. The weight loss of the resins ranged from 6.1% to 6.9% after 1000 hours in air at 288°C (550°F). For comparison, PMR-15 resin exhibited a weight loss of approximately 3% after 600 hours in air at 288°C (550°F) (ref. 7).

Composite Fabrication and Testing

Composites were fabricated from the three monomer compositions and Hercules HTS graphite fiber using a simulated autoclave molding technique. For comparison, a press-molded composite was also fabricated using resin composition B (2MAS/3HFDE/2MDA).

Table IV shows the weight loss characteristics of the composites after exposure for 1500 hours in air at 260°C (500°F) and 288°C (550°F). All composites exhibited excellent thermo-oxidative stability, as reflected by the low weight loss at both temperatures. There was essentially no difference in weight loss among the various compositions or type of cure. The weight loss at 288°C (550°F) ranged from 1.9% to 2.9%. This compares to a weight loss of approximately 2.2% exhibited by PMR-15/HTS graphite fiber composites under identical conditions.

Ultra-sonic C-scan examination of the composites indicated that they were defect-free. The mechanical properties of the composites are summarized in Table V. The ambient temperature interlaminar shear strength (ILSS) values of all composites are lower than the ILSS values of PMR-15/HTS graphite fiber composites. The low ILSS values at 260°C (500°F) are probably due to the fact that the tests were performed close to the glass transition temperatures of the composites. The lower ILSS values of the simulated autoclave-cured composition B (2MAS/3HFDE/2MDA) compared to press-cured composition B are probably due to the lower pressures used in the simulated autoclave cure.

The flexural strength of press-cured composition B compares favorably with reported values for press-cured PMR-15/HTS graphite fiber composites (ref. 8). However, the flexural strengths of all of the autoclave-cured

composites are lower than the values reported for autoclave-cured PMR-15/HTS graphite fiber composites (ref. 9). The flexural strengths ranged from 40% (composition C) to 90% (composition B) of the flexural strength of autoclave-cured PMR-15/HTS graphite fiber composites. The flexural modulus values of all composites are also lower than the flexural modulus of PMR-15/HTS graphite fiber composites. Except for the composites mad with composition A, the flexural strength values at 260°C (500°F) were approximately 50% of the corresponding room temperature values. The elevated temperature flexural moduli of composites made with composition A and B (press-cured) compare favorably with their room temperature moduli. The elevated temperature moduli of composites made with composition B (autoclaved) and C were significantly lower than their corresponding room temperature moduli. It should be pointed out, however, that no process optimization studies were conducted in the present investigation. Consequently, there is a need to identify improved processing parameters to achieve higher composite mechanical properties.

CONCLUSIONS

Based on the results of this investigation, the following conclusions can be made:

1. Compared to norbornenyl end-capped PMR polyimides, the use of m-aminostyrene as an end-cap lowers the final cure temperature by approximately 55°C (100°F).

2. However, the use temperature of PMR polyimide composites made with m-aminostyrene as an end-cap is limited to about 260°C (500°F) as compared to a use temperature of 316°C (600°F) for norbornenyl end-capped PMR polyimides.

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TABLE I. - MONOMERS USED FOR POLYIMIDE SYNTHESIS

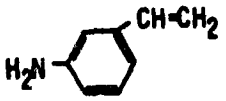
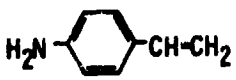
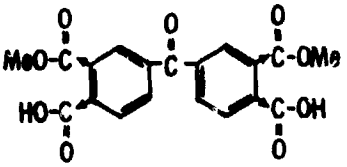
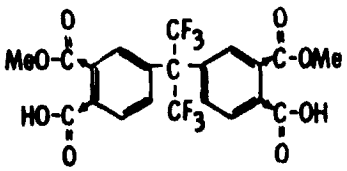
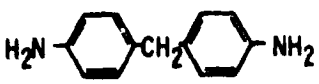
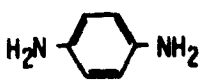
STRUCTURE	NAME	ABBREVIATION
	m-AMINOSTYRENE	MAS
	p-AMINOSTYRENE	PAS
	DIMETHYL ESTER OF 3,3',4,4'-BENZOPHENONE-TETRACARBOXYLIC ACID	BTDE
	DIMETHYL ESTER OF 4,4'-(HEXAFLUOROISOPROPYLIDENE)-BIS (PHTHALIC ACID)	HFDE
	4,4'-METHYLENEDIANILINE	MDA
	p-PHENYLENEDIAMINE	PPDA

TABLE II. - MOLDING POWDERS USED IN POLYIMIDE SYNTHESIS

MOLDING POWDER	MONOMER SYSTEM & STOICHIOMETRY
A	2MAS/3BTDE/2MDA
B	2MAS/3HFDE/2MDA
C	2MAS/2.67HFDE/1.67PPDA

TABLE III. - PROPERTIES OF NEAT POLYIMIDE RESINS

MOLDING POWDER	DENSITY, g/cm^3	TRANSITION TEMP						% WEIGHT LOSS[b]
		NO POSTCURE		260^0 POSTCURE[a]		288^0 C POSTCURE[a]		
		T_g, ^{0}C	T_s, ^{0}C	T_g, ^{0}C	T_s, ^{0}C	T_g, ^{0}C	T_s, ^{0}C	
A	1.338	208	232	257	281	270	301	6.9
B	1.400	222	246	249	268	265	289	6.1
C	1.438	213	266	266	287	274	303	6.7

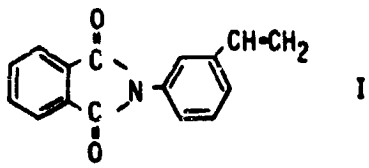
[a]16-hr IN AIR.
[b]DETERMINED ON NONPOSTCURED SPECIMENS AFTER 1000 hr IN AIR AT 288^0 C.

TABLE IV. - COMPOSITE WEIGHT LOSS CHARACTERISTICS AFTER EXPOSURE IN AIR FOR 1500 HOURS

MONOMER STOICHIOMETRY	TYPE OF CURE	FIBER, v/o	% WEIGHT LOSS	
			260^0 C (500^0 F)	288^0 C (550^0 F)
2MAS/3BTDE/2MDA	AUTOCLAVE	60.4	1.6	2.4
2MAS/3HFDE/2MDA	AUTOCLAVE	58.4	1.4	1.9
2MAS/3HFDE/2MDA	PRESS CURE	58.0	1.1	2.6
2MAS/2.67HFDE/1.67PPDA	AUTOCLAVE	68.3	1.2	2.9

TABLE V. - SUMMARY OF PMR POLYIMIDE/HTS GRAPHITE FIBER COMPOSITE PROPERTIES

MONOMER STOICHIOMETRY	TYPE OF CURE	FIBER, v/o	% WEIGHT LOSS	
			260^0 C (500^0 F)	288^0 C (550^0 F)
2MAS/3BTDE/2MDA	AUTOCLAVE	60.4	1.6	2.4
2MAS/3HFDE/2MDA	AUTOCLAVE	58.4	1.4	1.9
2MAS/3HFDE/2MDA	PRESS CURE	58.0	1.1	2.6
2MAS/2.67HFDE/1.67PPDA	AUTOCLAVE	68.3	1.2	2.9



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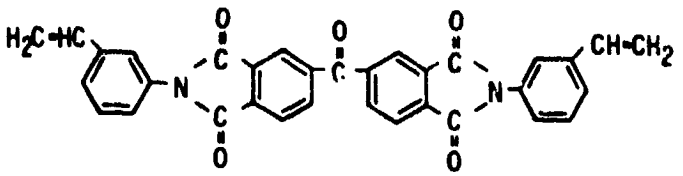

II

Figure 1. - Structures of model compounds.

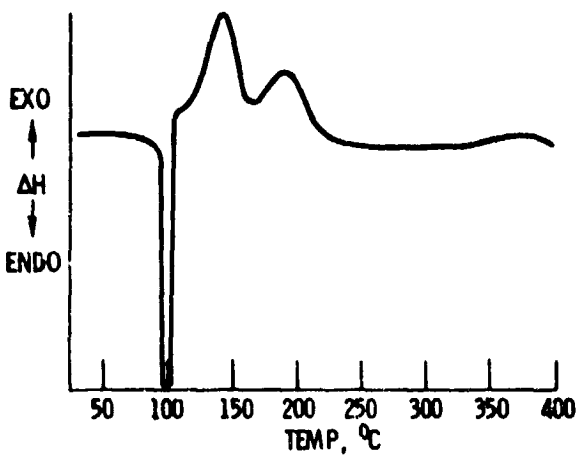

Figure 2. - DSC scan of model compound I.

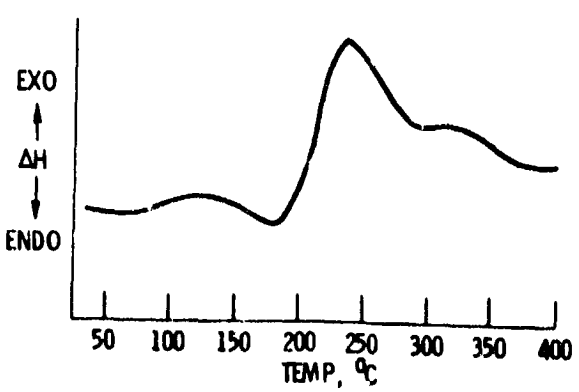

Figure 3. - DSC scan of model compound II.

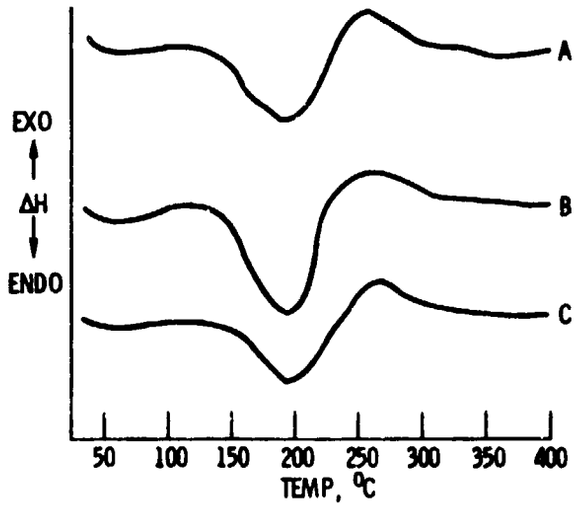

Figure 4. - DSC scans of molding powders.

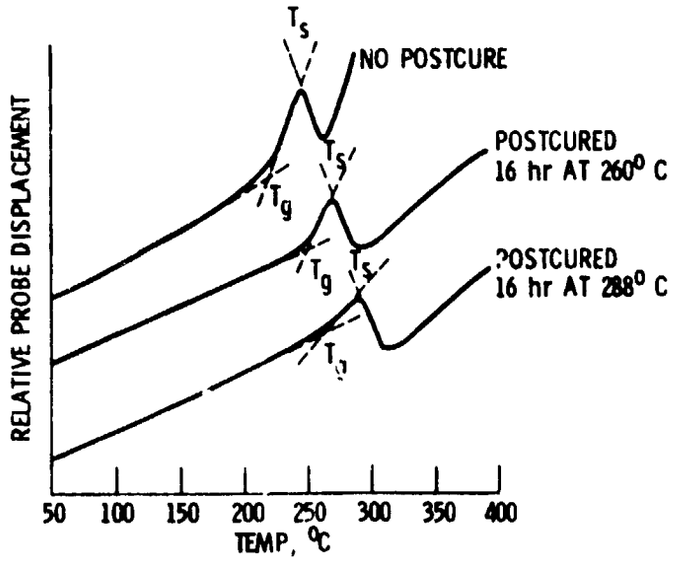

Figure 5. - TMA scans of polyimide resin from 2MAS/3HFDE/2MDA.