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Synthesis and thermal characterization of a one component maleimide-epoxy resin

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Summary

A one component resin based on *N*-(*p*-carboxyphenyl)maleimide (CPMI) and allyl glycidal ether (AGE) was synthesized. The resin showed comparable thermal cure transitions to those of Matrimid 5292™. The polymer of CPMI-AGE was dark red to brown and very brittle.

Introduction

Maleimide polymers have applications in the area of composites due to their excellent thermal stability, chemical resistance, and mechanical properties. Maleimide based epoxy resins have been proposed as materials in the aerospace industry in applications such as hypersonic aircraft, reusable space planes, and missiles. Bismaleimide resins (BMI) are attractive for composites because the maleimide moieties have unsaturated end groups that undergo thermal addition polymerization without by-product elimination that can lead to the formation of voids within the composite. The major shortcoming of BMI systems is brittleness, which results in low damage tolerance and poor processing characteristics.[1] Thus, commercial systems, such as Ciba-Geigy's Matrimid 5292™, incorporate a second difunctional component, such as diallyl bisphenol A, to introduce toughness into the resin and to allow cure of the resin through multi-step reactions. Although the exact mechanisms of cure have not been established, reactions believed to occur in these systems include the intermolecular "ene" reaction between the maleimide and the allyl species, etherification by dehydration, Diels-Alder reactions,

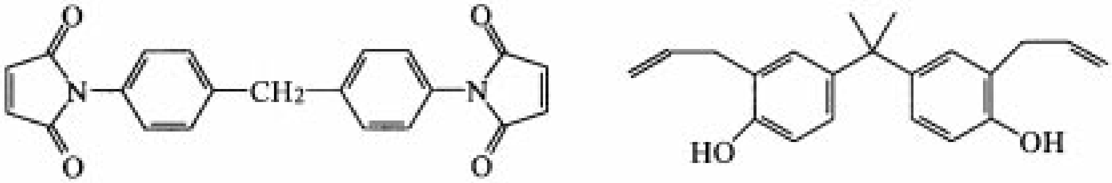

Figure 1: Matrimid 5292™ components

homopolymerization of maleimide groups, and alternating vinyl copolymerization.[2,3]
A compound containing both a maleimide unit and an allyl ether group has been synthesized. This compound was designed to allow cure reactions analogous to those of Matrimid 5292™, but in a simplified, one-component resin system. The ether linkages and the higher aliphatic content within the monomer were also expected to impart additional degrees of flexibility to the crosslinked resin for improved toughness.

Experimental

Materials and Methods

N-(p-carboxyphenyl)maleimide (CPMI) was synthesized according to a previously published procedure.[4] All reagents were used without further purification except where noted. Allyl glycidyl ether (AGE), tetrahydrofuran (THF), and triethylamine (TEA) were purchased from the Aldrich Chemical Co. Methylene chloride (Optima Grade) and acetic anhydride were purchased from Fischer Chemical Co. The two-component resin system, 4,4'-bismaleimido-diphenyl-methane (BMPM)/O,O'-diallyl bisphenol A (DABPA) (Matrimid 5292™), was purchased from Ciba-Geigy. THF was distilled over calcium hydride prior to use. Thermal cure was conducted on a differential scanning calorimeter (DSC) (TA Instruments 2920 DSC module with a 2100 data station) at a heating rate of 10°C/min under nitrogen atmosphere. Differential thermal analyses (DTA) and thermogravimetric analyses (TGA) were performed on a TA Instruments Simultaneous TGA-DTA 2960 module with a 2100 data station at a heating rate of 20°C/min under nitrogen atmosphere.

Monomer synthesis.

To a 100 mL three-neck round bottom flask fitted with a reflux condenser, an N_2 inlet, and rubber septa, CPMI (4.34 g, 20 mmol) and THF (20 mL) were charged and stirred under N_2, then heated to THF reflux until the solution became homogenous. AGE (2.37 mL, 20 mmol) and TEA (0.55 mL, 4 mmol) were added via syringe. Upon addition of these reagents, the solution color changed from yellow to light orange. After 6 h, the solution became red and was removed from heat. Upon cooling, the viscous, dark red solution was stirred with 20 mL 5% HCl solution and extracted with 40 mL CH_2Cl_2. The CH_2Cl_2 layer was separated and evaporated using a rotary-evaporator (Büchi Rotovapor). The isolated red product was dried under reduced pressure at 65°C for 12 h. Monomer structure was confirmed by solution ^1H and ^{13}C NMR (Bruker ACE 200) (solvent: dimethylsulfoxide-d_6). ^1H NMR (ppm): 1.19, 2.43, 2.61, 3.61, 3.94, 4.94, 5.01, 5.12, 5.25, 6.92, 7.49, 8.09; ^{13}C NMR (ppm): 66.8, 67.41, 71.20, 71.42, 116.53, 126.20, 128.73, 129.97, 134.85, 135.20, 135.54, 166.8, 169.56. FTIR (KBr disk) (cm^{-1}): 3478, 3087, 2938, 1783, 1719, 1610, 1542, 1514, 1381, 1280, 1179, 1111, 930, 853, 773. Monomer solubility was insoluble in all common organic solvents tested and showed limited solubility in some high boiling solvents upon heating. The monomer did not melt prior to the onset of polymerization.

Polymer synthesis.

CPMI-AGE was solubilized in minimal amounts of DMSO and cured thermally under reduced pressure at various temperatures (150°C, 160°C, 170°C, 180°C, and 200°C) for 24 h.

Thermal cure occurred at and above 170°C. The resulting polymers were brittle and red in color. Polymer structure was determined using solid state ^{13}C NMR and FT-IR. Thermal characterization was carried out using TGA, DTA, and DSC. The obtained polymer was insoluble in all organic solvents tried, even after heating.

Results and Discussion

Reactions of epoxide rings can be catalyzed by either base or acid.[5] It was initially believed that the reaction of CPMI and AGE would be self-catalyzed by the acid protons of the CPMI. However, attempts at reaction without added catalysts were unsuccessful. TEA was used as a basic catalyst to promote the reaction between the carboxylic acid and the epoxide ring. The adduct of CPMI and AGE was thus synthesized according to Figure 2.

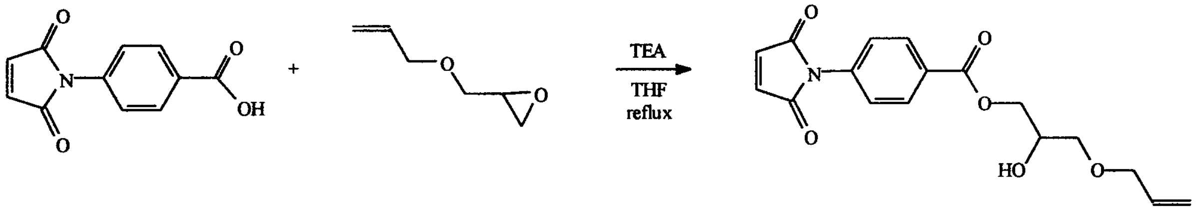

Figure 2: Synthesis of CPMI-AGE

The monomer was expected to undergo initial thermal cure through a combination o processes with the initial phase of cure being an "ene" reaction between the electron poor maleimide double bond of one moiety and the electron rich allyl double bond of a second monomer. It was also expected that this monomer would undergo etherification through the hydroxyl moieties and Diels-Alder chemistry after the "ene" reaction had taken place. Thermal homopolymerization of the maleimide moieties and alternating copolymerization aided by charge transfer interactions between the maleimide and allyl double bonds were also possible.[3,6] They confirm both the monomer structure and polymer cure. The disappearance of the epoxy carbon peaks (43.3 ppm and 50.4 ppm) and the appearance of the tertiary carbon peak (71.5 ppm) and carbon α to the carbonyl peak (71.2 ppm) verify that reaction has taken place between the CPMI and AGE. Solid state ^{13}C NMR of the polymer (cured at 170 °C under reduced pressure) shows only a small degree of residual unsaturation in the allyl region. The near quantitative conversion of the allyl double bonds indicates that

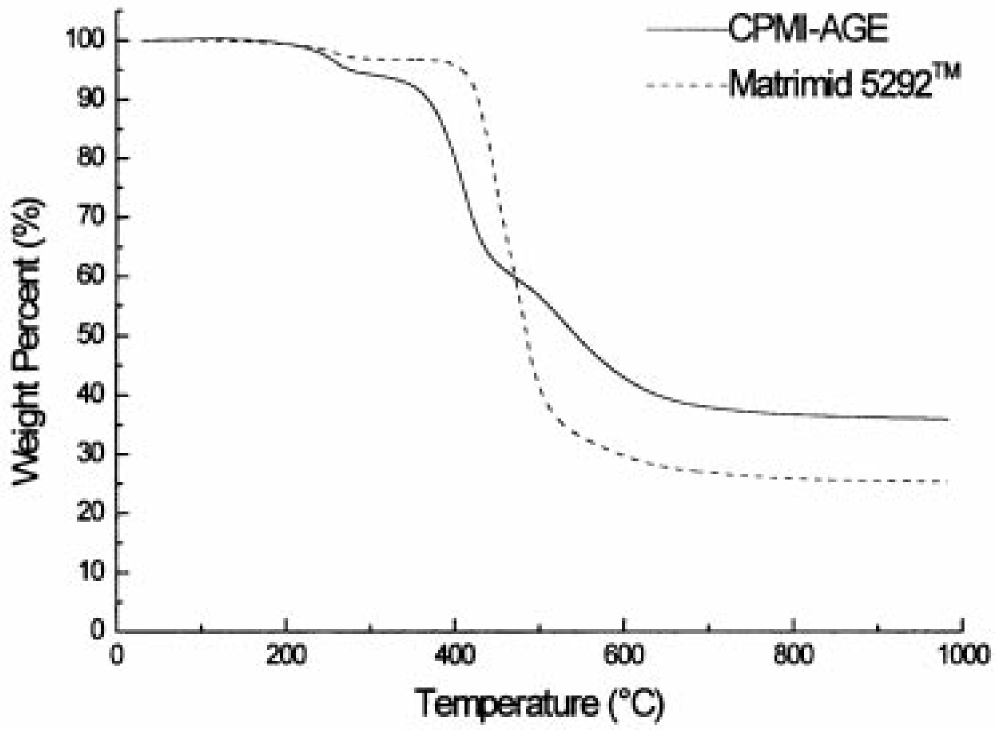

Figure 3: TGA Thermograms of CPMI-AGE and Matrmid 5292

alternating copolymerization and the "-ene" reaction are favored over maleimide homopolymerization. TGA thermograms of CPMI-AGE and Matrimid 5292™ resins are shown in Figure 3. Both Matrimid 5292™ and CPMI-AGE undergo an initial weight loss at 205 °C. This weight loss probably corresponds to the loss of adsorbed water, although dehydration of the hydroxyl groups of CPMI-AGE may give ether linkages. Decomposition (reported as 5% weight loss after initial weight loss) for the CPMI-AGE adduct begins at 375 °C. The thermal stability is slightly less than that of Matrimid 5292™, perhaps due to higher aliphatic content in the CPMI-AGE resin.

DTA and DSC were used to monitor cure with increasing temperature. The DTA traces of the CPMI-AGE adduct and Matrimid 5292™ multi-component resin during curing are shown in Figure 4. Both systems exhibit an exotherm corresponding to initial weight losses shown by TGA. The exothermic peak at

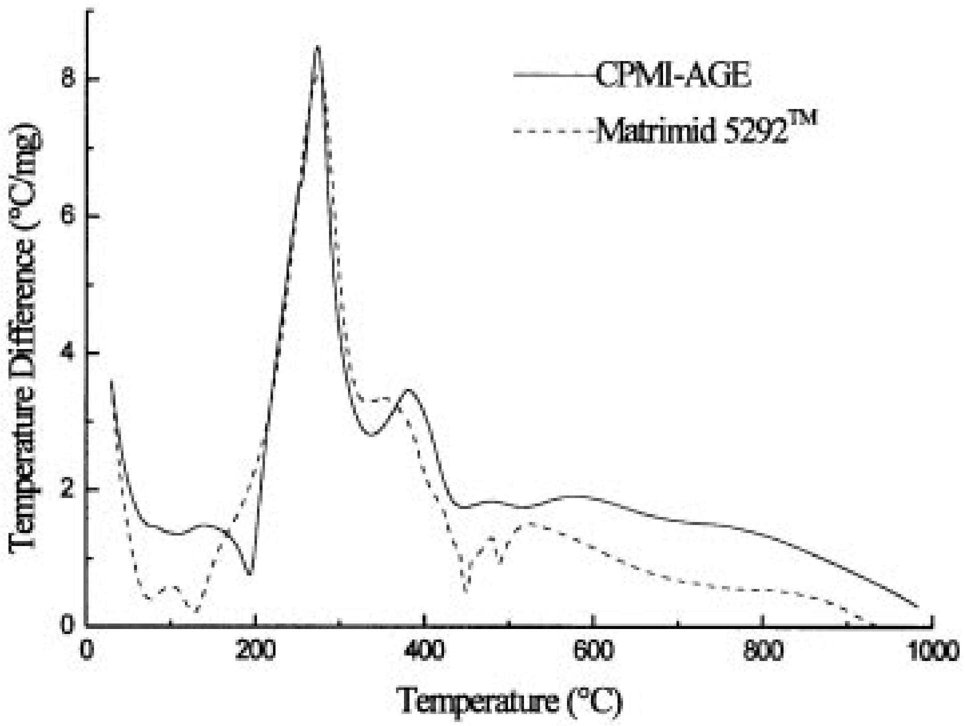

Figure 4: DTA Thermograms of CPMI-AGE and Matrimid 5292™

255 °C in both DTA and DSC thermograms is attributed to multiple cure reactions of the resins. The exact nature of' these cure reactions is unknown, but it is speculated that, in addition to the etherification reaction indicated by TGA, they include the "ene" reaction which is reported to occur in the Matrimid 5292™ system at this temperature.[2,7] Thermal homopolymerization of the maleimide double bond is not believed to significantly contribute to the cure reactions. This was determined by thermal characterization of the analogous *N*-phenyl-maleimide, in which significant thermal polymerization does not occur below 300 °C.

The exothermic transition in the DSC scan of the CPMI-AGE adduct, shown in Figure 5, beginning at 200 °C is comparable to the cure exotherm seen in the Matrimid 5292™ system. This exotherm corresponds to the temperature of initial weight loss seen by TGA and to the exotherm seen in DTA. This evidence suggests that the cure behavior of this monomer is similar to that of the two component system. The lower

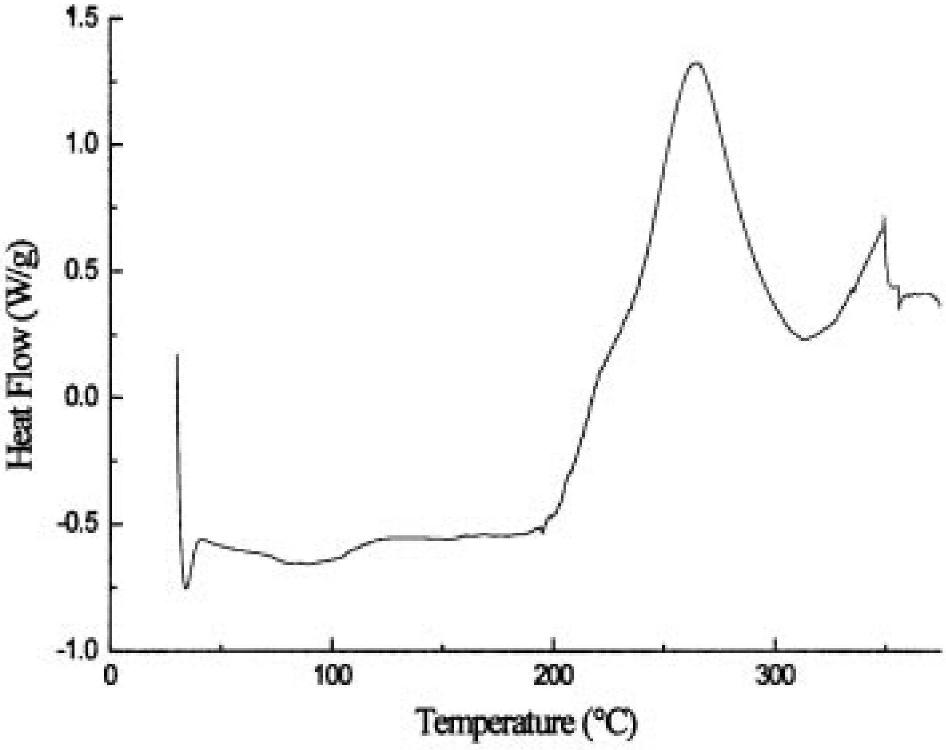

Figure 5: DSC Thermogram of CPMI-AGE

temperature shoulder seen in the DSC thermogram is also seen in the Matrimid system. This shoulder was attributed to small amounts of maleimide homopolymerization.[2] In this system, no significant maleimide homopolymerization is believed to occur based on thermal characterization and cure of *N*-phenylmaleimide, which does not exhibit a cure exotherm at the temperature of the shoulder in the DSC thermogram. The exothermic peak at 255 °C corresponds to the temperature regime of the etherification reaction as well as the temperature at which the "ene" reaction becomes significant. It is important to note that by both DTA and DSC, the monomer does not exhibit a melting transition prior to the onset of cure reactions.

Although thermal polymerization of CPMI-AGE was accomplished with satisfactory results, attempts at formation of composites have thus far proved unsuccessful. Carbon-fiber composites with high rigidity have been synthesized, but the necessity of adding solvent to get desirable carbon-matrix interactions negates the benefit of using a simplified one-component system. Suggested improvements to this system include lengthening the aliphatic chain of the ester linkage in the adduct to allow enhanced mobility of the molecule and greater flow at lower temperatures. An ideal one-component resin would flow below polymerization reactions begin to occur to allow optimized contact of the resin with the fibers of the composite.

Conclusions

A monomer based on CPMI and AGE was designed to allow polymerization and crosslinking based mainly on the "ene" reaction between the maleimide functionality and the allyl functionality of the monomer. Weight loss corresponding to etherification via dehydration was also observable by TGA. Exothermic transitions in both DTA and DSC correspond to ether formation and the "ene" reaction. Thermal studies indicate that this adduct undergoes cure in a similar manner to Ciba-Geigy's Matrimid 5292™ bismaleimide resin.

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