Thermochimica Acta, 220 (1993) 261–270
Elsevier Science Publishers B.V., Amsterdam

Thermal behavior of 4-maleimidophenyl glycidyl ether resins

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(Received 26 June 1992; accepted 8 September 1992)

Abstract

A novel epoxy–maleimide resin 4-maleimidophenyl glycidyl ether (MGE), was prepared from 4-aminophenol. Characterization was carried out by estimation of the epoxy equivalent and by IR and ^{1}H-NMR spectroscopy. The MGE resin was cured by heating above 250°C. A decrease in the curing temperature was observed after the addition of a stoichiometric or non-stoichiometric amount of an aromatic diamine. The values of the curing temperature and the heat of the polymerization reaction (ΔH) were independent of diamine concentration but depended on the structure of the diamine. The char yield of the cured resins at 800°C in a nitrogen atmosphere ranged from 25% to 40%, which is much higher than the values reported for epoxy resins.

INTRODUCTION

Bismaleimide-modified epoxy resins, which can be processed like conventional heat cured epoxy resins, have been investigated [1–6]. The driving force behind these investigations was to develop resin formulations having the excellent high temperature performance expected from bismaleimides along with a toughness greater than that of high temperature epoxy resin systems currently in use [7, 8].

In an earlier paper, we reported the curing behavior of bismaleimide epoxy blends [9]. Curing temperatures of these blends were lower than those of bismaleimides. During the curing of such a thermoset blend system, two types of reactions might take place:

(a) curing of the two resins independent of each other thereby leading to

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possible formation of interpenetrating networks of epoxy and bismaleimides; and

(b) co-curing of epoxy and bismaleimides.

It is difficult to distinguish between these two curing processes in this type of resin system. Therefore it was considered of interest to examine the curing behavior of a low molecular weight precursor having both an epoxy and a maleimido group. We now report the curing behavior of a novel resin based on 4-aminophenol, in which maleimide and epoxy groups are an integral part of the polymer backbone.

4-Aminophenol is a bifunctional monomer which can be used for the synthesis of oligomers with ordered structures [10]. Several polymers based on 4-aminophenol have been reported [10–12]. However, no studies have been carried out on the glycidyl ether of 4-maleimidophenol. In the present work, the curing behavior of such a resin with aromatic diamines is reported.

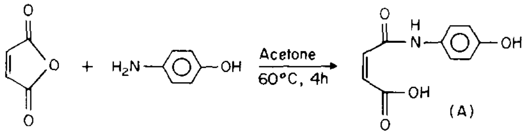
EXPERIMENTAL

Materials

4-Aminophenol (Fluka Chemie AG)[1] was purified by recrystallization from methanol. Acetone (E. Merck) was kept overnight over anhydrous sodium sulfate, refluxed and distilled. Epichlorohydrin and acetic anhydride (BDH) were freshly distilled. Anhydrous sodium acetate was obtained by fusion. 4,4′-Diaminodiphenylmethane, DDM (Fluka AG), was recrystallized from water. 4,4′-Diaminodiphenyl ether, DDE (Fluka AG), was used as received.

Synthesis of 4-maleimidophenyl glycidyl ether resin (MGE)

Equations (1)–(3) show the steps involved in the synthesis.



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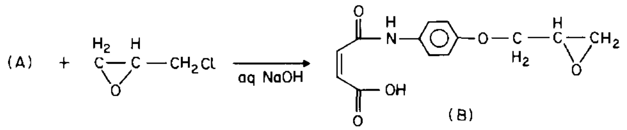
[1] Identification of a commercial product is made only to facilitate experimental reproducibility and to describe adequately the experimental procedure. In no case does it imply endorsement by NIST or imply that it is necessarily the best product for the experiment.



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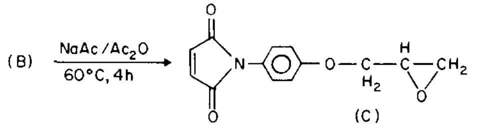

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4-Aminophenol (12 g, 0.11 mole) was added to 45.5 ml of dry acetone placed in a three necked round bottom flask fitted with a reflux condenser and a nitrogen gas inlet tube. Nitrogen was passed through the reaction mixture and the temperature was raised to 60°C. Maleic anhydride (12.6 g, 0.13 mole) in 30 ml of acetone was added to the reaction mixture with stirring. The reaction was carried out for 4 h. The precipitated *N*-(4-hydroxyphenyl)maleamic acid (A) was collected by filtration (75% yield): IR (KBr) 1706 cm^{-1} ($\nu_{C=O}$, α,β-unsaturated acid), 1660 cm^{-1} ($\nu_{C=O}$, α,β-unsaturated amide); ^{1}H-NMR (DMSO-d_6) $\delta = 6.36$ ppm (q, –CH=CH–), 6.72 ppm (d, 2H, phenyl), 7.44 ppm (d, 2H, phenyl), 10.37 ppm (s, –COOH).

A 15 g amount of the crude product (A) was mixed with a solution containing 6.4 g of NaOH (0.16 mole) in 66 ml of water. The reaction mixture was stirred at room temperature for 30 min. Epichlorohydrin (12.3 g, 0.13 mole) was added and the reaction mixture was stirred for 1 h. The temperature was raised to 70°C and the reaction was continued for 3 h. The reaction mixture was neutralized with dilute HCl and the precipitate (B) obtained was filtered off and dried (58% yield): IR (KBr) 1706 ± 2 cm^{-1} ($\nu_{C=O}$, α,β-unsaturated acid), 1660 cm^{-1} ($\nu_{C=O}$, α,β-unsaturated amide), 1252, 904 and 830 cm^{-1} (ν_{C-O}, epoxide); ^{1}H-NMR (DMSO-d_6) $\delta = 4.02$ ppm (epoxide), 6.36 ppm (q, –CH=CH–), 6.96 ppm (d, 2H, phenyl), 7.56 ppm (d, 2H, phenyl). The residual proton signal of DMSO-d_6 interferes with the protons of the oxirane ring; correct integration was thus difficult for these protons.

Cyclodehydration of B was achieved by using fused sodium acetate and acetic anhydride. For this purpose, 7.5 g of B was dissolved in 17 ml of acetone, and 6.6 g of anhydrous sodium acetate and 34 ml of freshly distilled acetic anhydride were added to the reaction mixture. The solution was refluxed at 60°C for 4 h. The mixture was then cooled and added to ice cold water. The precipitate (C) was collected by filtration, washed with sodium bicarbonate solution and then dried under vacuum (88.7% yield). The spectral properties of the product are given in the next section.

An alternative procedure for conversion of A to B was also carried out in which 15 g of A was dissolved in a solution containing 6.0 g of NaOH in 60 ml of water. The resulting solution was added dropwise in 30 min, with continuous stirring, to epichlorohydrin (7.24 g) kept in a flask at 70°C. The reaction mixture was further stirred for 1.5 h, cooled and then neutralized with dilute HCl. The precipitate (B) obtained was filtered off and dried (73.6% yield). This method gave a higher yield. Cyclodehydration of B was effected by using fused sodium acetate and acetic anhydride. An oily product was obtained which was then dissolved in chloroform, the solution was filtered and the product was precipitated in petroleum ether.

CHARACTERIZATION

Infrared spectra were recorded on a Bio-Rad Digilab-FTS-40 FTIR spectrophotometer. ^{1}H-NMR spectra were recorded on a JEOL-JNM-FX 100 FT NMR spectrometer using $CDCl_3$ or DMSO-d_6 as solvent and tetramethylsilane as an internal standard.

The epoxy equivalent was determined according to a method reported in the literature [13]. The curing behavior of the resin with diamines was monitored by differential scanning calorimetry in the range 50–300°C by using a Du Pont 9900 thermal analyser having a 910 DSC module. A heating rate of 10°C min^{-1} was used.

The thermal stability of the uncured and cured resins was determined by use of a Du Pont 1090 thermal analyzer having a 951 TG module. A sample size of 11 ± 2 mg and a heating rate of 10°C min^{-1} were used.

Blending of MGE resin with aromatic diamines

The curing of the epoxy group of MGE was achieved by using an aromatic diamine, i.e., DDM or DDE, in a molar ratio of 4:1 (epoxy/diamine stoichiometric amounts). However, the maleimido group is capable of undergoing Michael-type nucleophilic addition to the double bond. Hence, it is possible to utilize the amine in curing of the epoxy as well as the maleimido group. Therefore curing was also attempted using non-stoichiometric amounts of resin. The blending of the resin and the amine was carried out in acetone–methyl ethyl ketone solution using the molar ratios 4:1, 4:1.5, 4:1.75 and 4:2. After a homogeneous solution was obtained, the solvent was removed under reduced pressure.

RESULTS AND DISCUSSION

MGE was obtained as a brown resin in an overall yield of 38%. The epoxy equivalent of the resin was 253 ± 6, which agrees fairly well wih the theoretical value of 245. In the IR spectrum of the resin, characteristic peaks of different functional groups were at 1784 and 1717 cm^{-1} ($\nu_{C=O}$, imide); 1229, 960 and 836 cm^{-1} (ν_{C-O}, epoxide) (Fig. 1).

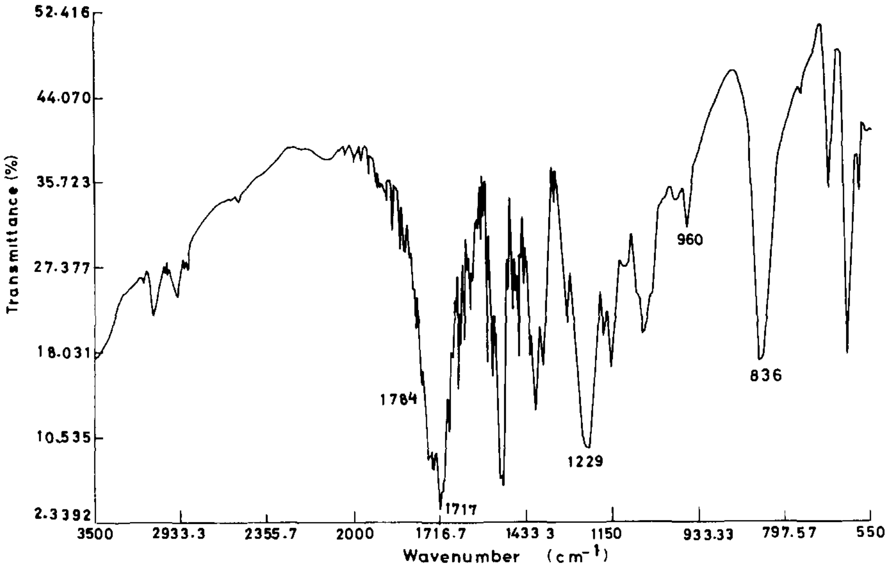


Fig. 1. Infrared spectrum of MGE resin.

In the ^{1}H-NMR spectrum of MGE in $CDCl_3$, the characteristic chemical shifts δ were 2.16 (3H, $-\underset{\diagdown\,O\,\diagup}{CH_2-CH}-$), 4.2 (2H, ether $-CH_2-$), 7.02 ($-CH{=}CH-$ and 2H, phenyl) and 7.32 ppm (2H, phenyl). A broad signal corresponding to less than 0.3 proton was observed around 5.35 and may be due to opening of the epoxide to give –OH.

In the DSC scan of MGE (Fig. 2), no melting peak was observed. However, an exotherm with two maxima was present in the range 252–330°C, with peak positions at 286 and 320°C.

MGE is a monomer with an electron deficient double bond and an

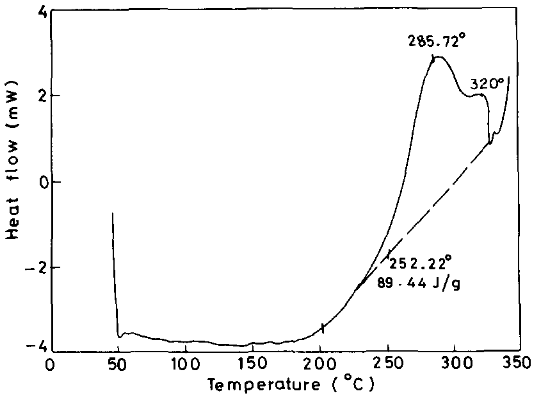
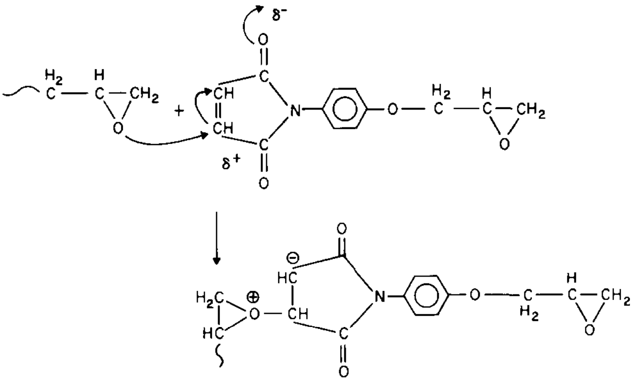


Fig. 2. DSC scan of MGE resin.

electron donor oxygen of the oxirane ring. Therefore the oxirane ring may also participate in this polymerization by an ionic mechanism to yield an oxonium ion, as depicted in eqn. (4).



(4)

The carbanion can readily react with the maleimido double bond. Thus the bimodal exotherm may be attributed to radical as well as ionic polymerization of MGE.

From the DSC exotherms, the temperature of onset of the curing reaction T_i, the peak temperature, T_{max} and the temperature at the end of the curing T_f were determined. The heat of the polymerization reaction ΔH was obtained by taking the area under the exothermic transition. The effect of the nature of the amine and its concentration on the curing exotherm is obvious from the results summarized in Table 1 (see also Fig. 3). In the presence of an amine, the exothermic peak temperature was reduced by at least 100°C. However, no significant change in the onset of the exotherm was observed on increasing the amine content. Similarly, the ΔH value was independent of the amine concentration. The structure of the amine, on the

TABLE 1

Curing characteristics of MGE resin with aromatic diamines

Resin system	Molar ratio of MGE and diamine	Designation	Curing characteristics			ΔH ($J\ g^{-1}$)
			T_i (°C)	T_{max} (°C)	T_f (°C)	
MGE	–	MGE	252	286	330	89
MGE-DDM	4:1	MEM	103	164	221	69
	4:1.5	MEM50	105	162	219	57
	4:1.75	MEM75	103	161	217	46
	4:2	MEM100	107	165	237	51
MGE-DDE	4:1	MEE	152	182	213	31
	4:2	MEE100	153	186	217	46

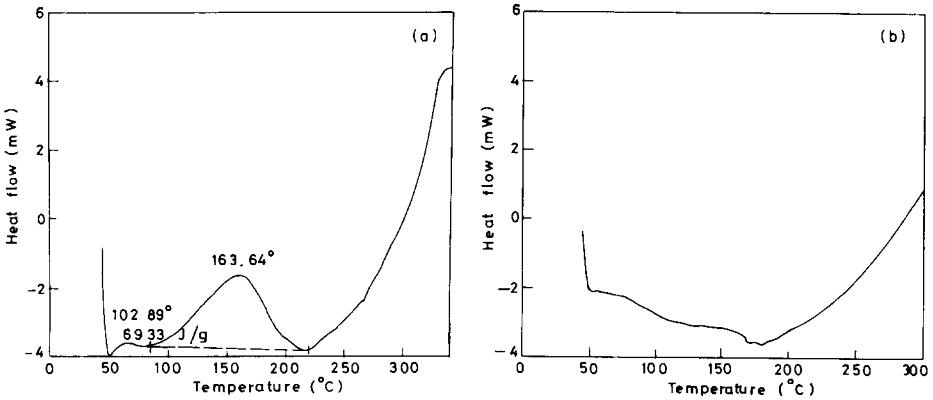


Fig. 3. DSC scan of MEM: (a) uncured; (b) iosthermally cured.

other hand, influenced the curing characteristics. There were changes in T_i and in T_{max} when DDE was used instead of DDM.

The isothermal curing in air of the neat MGE resin was carried out at 250°C, that of the MGE–DDM (MEM) formulation at 165°C, and that of the MGE–DDE (MEE) resin at 185°C, each for 30 min. During this isothermal curing, about 2–5% weight loss was observed.

The thermogravimetric trace of the neat uncured MGE resin and that of the MGE resin cured at 250°C for 1 h are shown in Fig. 4. In the uncured MGE resin, a two step decomposition was observed and the char yield at 800°C was 32%. On curing, the degradation started above 350°C. The weight loss at low temperatures (in the range 257–330°C) was not observed in this case. It is quite likely that at lower temperatures the oxirane ring underwent scission in the uncured resin but not in the cured resin (see eqn. (4)). Hence, only the weight loss associated with the breakdown of the maleimido group above 350°C was observed.

The results of the thermogravimetric analysis of the MGE resin cured

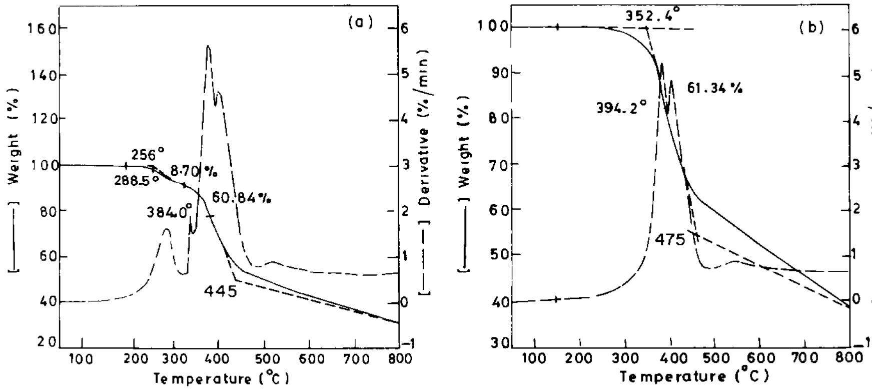


Fig. 4. Thermogravimetric traces of MGE: (a) uncured; (b) isothermally cured.

TABLE 2

Thermal behavior of MGE resin

Resin designation		T_i (°C)	T_{max} (°C)	T_f (°C)	Char yield at 800°C (%)
MGE	UC[a]	257	289	330	
		360	384	445	32
	C[b]	352	394	475	39
MEM	UC	311	396	478	35
	C	329	398	482	37
MEM50	UC	324	391	467	35
	C	325	394	470	–
MEM75	UC	325	389	471	36
	C	330	392	460	34
MEM100	UC	329	391	463	32
	C	329	383	466	35
MEE	UC	334	419	465	25
	C	342	421	470	26
MEE100	UC	340	407	465	27
	C	342	434	480	28

[a] UC = Uncured sample. [b] C = Sample cured at 250°C (MGE), 165°C (MGE–DDM) or 185°C (MGE–DDE) for 30 min before recording TG traces.

with a varying concentration of the diamine are summarized in Table 2 (see also Fig. 5). These results indicate that the cured resin was stable up to 300°C and started losing weight thereafter. Compared with the neat MGE resin (cured), the addition of an amine resulted in a decrease (10–30°C) in the initial decomposition temperature. The T_{max} values were highest for the MEE resin formulations. The char yields however, were lowest in these resins when compared with the MGE or MEM formulations. The isothermal heating (165 or 185°C) for 30 min of the MGE resin containing a

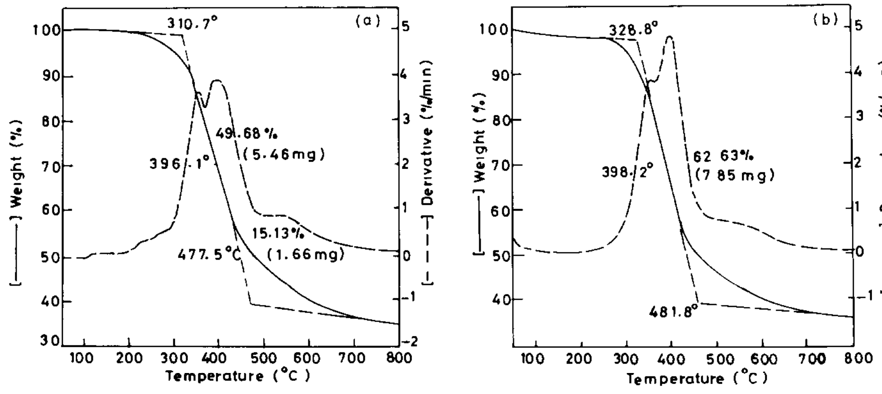


Fig. 5. Thermogravimetric traces of MEM: (a) uncured; (b) isothermally cured.

diamine did not affect the thermal stability. In situ curing of the MGE–diamine formulation during the TG experiment may be responsible for this observed behavior.

A comparison of this novel resin with the conventional resin consisting of the diglycidyl ether of bisphenol A (DGEBA) and 3,3′-diaminodipenyl sulfone (DDS) shows significant dissimilarities in thermal behavior. An increase in the concentration of the diamine in the DGEBA–DDS system resulted in an increase in thermal stability [14]. The char yield in most cases was around 10%.

In the MGE resin system, however, the concentration of the diamine did not affect the degradation temperature, but the structure of the diamine affected both the degradation temperature and the char yield. Moreover, the MGE resin cured with DDM or DDE had higher thermal stability and higher char yield (i.e., 25–40%) than the conventional DGEBA resin cured with DDS.

CONCLUSION

On the basis of these studies, it is concluded that 4-maleimidophenyl glycidyl ether resin formulations are more stable than the state-of-the-art epoxy resins. This may be due to the presence of the maleimido group in the backbone.

ACKNOWLEDGMENTS

The Department of Science and Technology (Government of India) and the National Institute of Standards and Technology, USA are gratefully acknowledged for sponsoring this work and providing a fellowship to L.C.

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