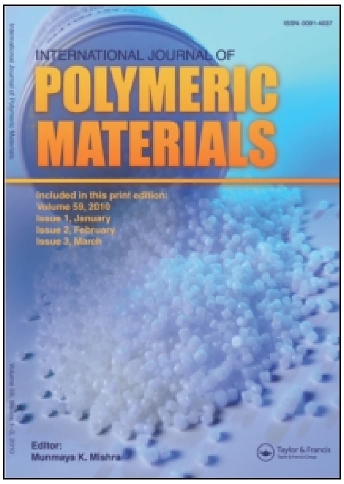

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Amino Benzoic Acid-Formaldehyde Condensates as Epoxy Curing Agent

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Each 2-, 3- and 4-aminobenzoic acid (AB) was polycondensed with formaldehyde (F) in the presence of an aqueous acid catalyst. The resulting polymer samples, ABF, were employed as a curing agent for curing of epoxy resin, namely diglycidyl ether of bisphenol-A (DGEBA). Triethylamine (EA) was used as a catalyst for accelerating curing reaction. The curing study was established kinetically by differential scanning calorimetry. The cured-DGEBA-ABF samples (unreinforced) were characterized by intrared (IR) spectroscopy, thermogravimetry and chemical resistivity.

KEY WORDS Aminobenzoic acid (AB), triethyl amine (TEA), curing reaction, chemical resistivity.

INTRODUCTION

Curing of epoxy resins by amine and anhydride functional groups containing compounds has been extensively studied.[1,2] The simultaneous curing of epoxy resin by two different functional groups containing compound has not been developed so far and only a few patents[3–5] have been reported. The author, however, has recently reported[6] the effects of curing epoxy resin of DGEBA using 4-aminobenzoic acid as a bifunctional curing agent.

In continuation of this work,[6] this paper describes the curing of DGEBA by ABF (2-, 3-, 4-aminobenzoic acid-formaldehyde) condensated. The study has been done kinetically using a differential scanning calorimeter. The cured DGEBA-ABF samples were studied for thermogravimetric analysis and chemical resistivity.

RESULTS AND DISCUSSION

The objective of the work reported here is to synthesize 2-aminobenzoic acid-formaldehyde [ABF-1], 3-aminobenzoic acid-formaldehyde [ABF-2] and 4-aminobenzoic acid-formaldehyde [ABF-3] condensation polymers. The synthesis of ABF 1 & 3 were carried out using the method reported earlier.[7–8] The same method was followed for the synthesis of ABF-2. The structural parameters of all three

TABLE I

Curing characteristics of epoxy resin systems using triethylamine catalyst

Resin System	Ratio (%wt/wt)	Ti^{a} (^{o}C)	Tp^{b} (^{o}C)	Tf^{c} (^{o}C)	Ea^{d} Kcal /mol	n^{e}
DGEBA-(ABF-1)	0.7:0.3	111	149	171	39.4	0.96
	0.9:0.1	120	158	182	42.0	1.1
DGEBA-(ABF-2)	0.7:0.3	107	132	158	32.8	1.02
	0.9:0.1	114	143	170	36.2	0.98
DGEBA-(ABF-3)	0.7:0.3	95	118	151	30.8	1.01
	0.9:0.1	108	125	160	33.4	0.99

[a] Temperature ofinitiation of curing.

[b] Temperature of peak exotherm.

[c] Temperature of completion of curing,

[d] Energy of activation

[e] order of reaction

TABLE II

TGA of unreinforced epoxy cured materials

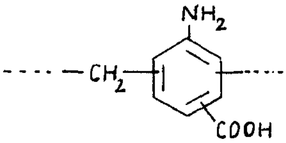
Resin System	Ratio	To	T_{10}	Tmax	IPDT^{a}
DGEBA-(ABF-1)	0.7:0.3	158	251	392	455
	0.9:0.1	115	249	388	450
DGEBA-(ABF-2)	0.7:0.3	164	261	403	470
	0.9:0.1	160	255	398	461
DGEBA-(ABF-3)	0.7:0.3	177	278	428	488
	0.9:0.1	165	271	418	477

polymers samples agreed with those reported.[7] The synthesized polymer samples were used as a curing agent and triethyl amine (TEA) was used as a catalyst (1% on the basis of weight of DGEBA) to cure the epoxy resin, namely, DGEBA. The study was carried out for the different systems of DGEBA:ABF are listed in Table I.

The data obtained from the differential scanning calorimetry scans (DSC) run at 10°C/min are given in Table I. The cure reaction of DGEBA:ABF-1 was studied for two different stoichiometric ratios namely 0.9:0.1 and 0.7:0.3 for all the three systems. DSC thermograms revealed that in presence of TEA all the resin systems gave single exothermic peak in the range of 108 to 182°C. The single exothermic peak proves that the rate of reaction of the reactive groups (i.e. amino, carboxylic) present in the epoxy resin:curing agent:catalyst system occur simultaneously. From the DSC thermograms, the initial curing temperature (*Ti*), peak exothermic temperature (*Tp*) and temperature of completion of cure (*Tf*) were obtained. The kinetic parameters such as *E* (activation energy) and *n* (order of reaction) were calculated assuming that the curing reaction obeys Arrhenius type kinetics and that the peak maxima represents a point of constant conversion for each system.

To obtain information about the properties of unreinforced crosslinked epoxy resins, the resin systems shown in Table II were cured isothermally. Infrared (IR) spectra of unreinforced cured products clearly showed disappearance of the oxirane ring. The unreinforced cured epoxy samples were analyzed for their thermal stability by thermogravimetry analysis (TGA). The results obtained revealed that resins degrade in a single step and start their decomposition at around 240°C. The rate of decomposition increases between 300°C and 400°C. The cured resin decomposes 90% at around 480°C.

The thermal stability of the resin system may be accounted for by the aromatic character of both the epoxy resin as well as the curing agents. The chain molecules of ABF-1, ABF-2 and ABF-3 are comprised of the repeating unit



It is likely that intramolecular hydrogen bond formation may take place between neighboring—COOH groups as well as between adjacent —NH_2 groups. Intramolecular H—bond formation may contribute in the thermal stability of the resin systems. The integral procedural decomposition temperature (IPDT) data calculated by Doyle's method[8] shown in Table II also reflects the thermal stability of the resin systems.

The samples of each unreinforced epoxy resin system listed in Table III were put in 100 ml standard reagents (water, 25% NaOH, 25% HCl, acetone) for seven days. After exposure to chemical reagents, each sample was examined on the basis of physical properties like discoloration, loss of gloss and change in weight. The data obtained for percentage weight loss (after 7 days) are presented in Table III. The weight change data falls in the range of 1 to 4.9% indicating no substantial effect of water acetone, HCl or NaOH.

TABLE III

Chemical resistivity of the unreinforced cured epoxy resin

Resin System	Ratio	% wt. loss after seven days			
		Water	25%NaOH	25%HCl	Acetone
DGEBA:(ABF-1)	0.7:0.3	1.90	4.80	2.10	1.15
	0.9:0.1	2.11	4.90	2.15	1.19
DGEBA:(ABF-2)	0.7:0.3	1.80	4.71	2.01	1.12
	0.9:0.1	1.92	4.76	2.14	1.16
DGEBA:(ABF-3)	0.7:0.3	1.75	4.55	1.98	1.09
	0.9:0.1	1.78	4.58	2.03	1.16

EXPERIMENTAL

Materials

All the chemicals used were of laboratory grade. The commercial epoxy resin, namely diglycidyl ether of bisphenol-A (DGEBA) was obtained from Sympol Products Pvt. Ltd., Ahmedabad, India. Specifications of epoxy resin are: epoxy equivalent weight; 190–210; viscosity at 25°C: 4–10 p; density at 25°C: 1.16–1.17 g/cm^2.

Measurements

Infrared (IR) spectroscopy. IR spectra of the cured epoxy resin systems were taken on a Perkin Elmer spectrophotometer.

Epoxy resin curing. The epoxy resin (DGEBA) and curing agents (ABF-1, ABF-2 and ABF-3) were mixed in the promotion (listed in Table I), and cure temperatures were determined by differential scanning calorimetry (DSC) using a DuPont 900 differential scanning calorimeter at a single heating rate (10 c/min).

Thermogravimetric analysis (TGA) of the cured samples. Thermogravimetric analysis was performed on the cured samples using a DuPont 951 thermogravimetric analyser. The thermograms were obtained at a heating rate of 10°C/min. The experiments were made in a static air atmosphere.

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