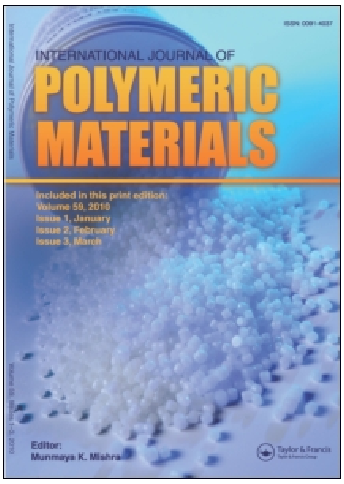

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Modified Cyclohexanone-Formaldehyde Resin as an Epoxy Resin Curing Agent

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Cyclohexanone-formaldehyde (CHF) resin was brominated and the brominated CHF (BCHF) was then reacted with excess aromatic diamines. The aminated CHF resins designated as ACHFs (modified ketone resin) were characterized and then applied as epoxy resin curing agents. Thus, the curing of the commercial epoxy resin diglycidil ether of bisphenol-A (DGEBA) by ACHFs was monitored by differential scanning calorimetric (DSC), based on the the DSC scans, the glass fiber-reinforced composites of DGEBA-ACHF systems were prepared and characterized by chemical resistivity and mechanical properties.

Keywords composites, curing of epoxy resins, diamines, DSC, epoxy resin, IR spectral study, ketone resins, TGA

INTRODUCTION

Ketone resins have been known for the last five decades [1]. Numerous reports about aliphatic and alicyclic ketone-formaldehyde resins exist for many commodity applications like paints, foam, adhesives, and molding materials [2–7]. Experimental and kinetic study about ketone-formaldehyde (KF) resinification has been well-established by Masahiro Abo [8]. This author studied aliphatic and alicyclic KF resins. More particularly, alicyclic ketone, such as cyclohexanone-formaldehyde resin (CHF) has good utility because it has

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The analysis of polymers and composite samples was carried out in neighboring polymer industries. The authors are thankful to Principal Dr. M. V. Hathi, for providing research facilities as well as encouragement for the research work.
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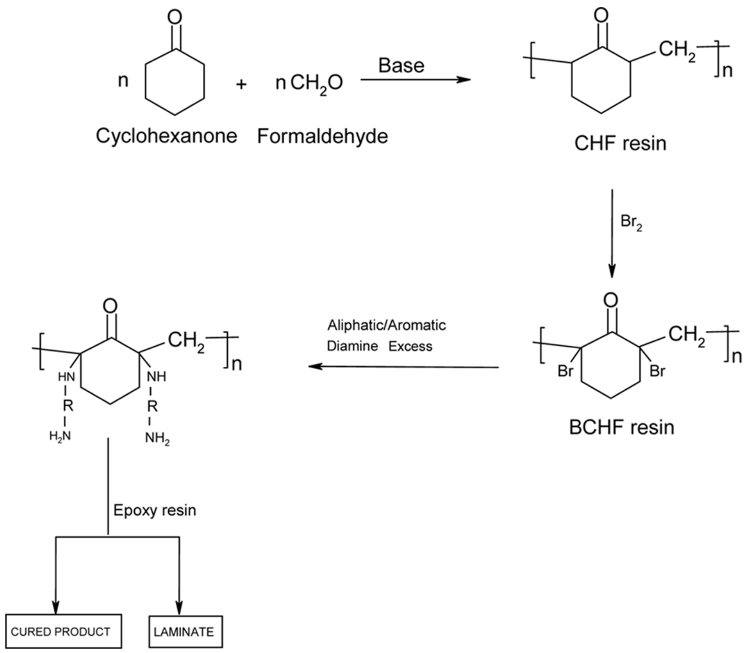
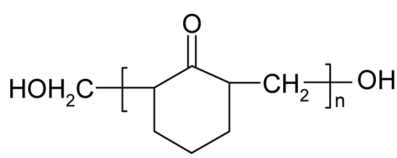


Scheme 1: Preparation Steps.

excellent glossy and transparent properties [4,5]. The structure of CHF resin has been well established [8] as:



One area that has not been reported so far is the modification (i.e., bromination) of such CHF resin. Hence, it was thought interesting to undertake the study of modified CHF resins. The present paper comprises the synthesis of cyclohexanone-formaldehyde (CHF) resin, bromination of CHF resin, and the reaction of such brominated CHF resin with aromatic diamines. The research study is scanned in Scheme 1.

EXPERIMENTAL

Materials

Cyclohexanone-formaldehyde (CHF) resin (mol.wt. ~700) and the diamines were obtained from a local market. Diglycidyl ether of bisphenol-A (a commercial epoxy resin) was obtained from the local paint industry. Its specifications are: epoxy equivalent: 190 and viscosity 40–100 cps. Glass cloth: Satain (212) weave (polyimide compatible) fiberglass woven fabric 0.25 mm thick of 'E' type glass (Unnati Chemicals, India) 270 gm/m^2 was used for laminate preparation.

Preparation of Bromo Derivative of CHF (BCHF) Resin

The bromination of CHF resin was carried out by the method reported for the bromination of ketones [9]. To a solution of 11.0 g (0.1 mole) CHF resin in 350 ml carbon tetrachloride (CCI_4), a solution of 32 g Br_2 (0.2 mole) in 75 ml CCl_4 was added dropwise over a period of 30 min. The reaction temperature was adjusted to 20°C during the whole period of reaction. The quantity of Br_2 added was in excess of the calculated theoretical amount. After the reaction was completed the amount of bromine left unreacted in the reaction mixture was reduced using excess sodium bisulphite solution (5%). The aqueous layer was then separated from the organic layer which contained the desired product. After drying over anhydrous sodium sulphate, the solvent was distilled off under vaccum. The resultant brominated CHF was designated as BCHF resin. The elemental analysis of BCHF resin is given in Table 1.

Aminoarylation of BCHF Resin

A solution of diamine (0.25 mole) (Table 2) in ethanol (100 ml) was gradually added to a solution of BCHF resin (0.1 mole) in tetrahydrofuran (THF) with continuous stirring at room temperature. A saturated sodium bicarbonate solution was added as an acid acceptor. The reaction was kept aside till CO_2 gas ceased. The resulting dark brown pasty mass was washed by decantation evolution from excess ethanol, and then by dry ether and finally air-dried. The aryl aminated CHF resin samples were designated as ACHF resins.

Fabrication of Glass Fiber-Reinforced Composites

A suspension of epoxy resin-ACHF resin (in ratio of 60:40 by weight) in THF solvent and 2–3 drops of pyridine was prepared and stirred well for

Table 1: Elemental analysis of BCHF resin.

Analysis		C %	H %	Br %
$(C_7H_8OBr_2)_n$	Cald.	31.34	2.98	59.7
$(268)_n$	Found	31.2	2.8	58.9

$\overline{Mn}$ (VPO) in DMF: 1650.

Table 2: Characterization of arylaminated cyclohexanone-formaldehyde (ACHF resins).

ACHF resin sample[a]	Molecular formula	Molecular weight of repeating unit	Elemental analysis					
			C %		H %		N %	
			Cald.	Found	Cald.	Found	Cald.	Found
ACHF – 1	$C_{19}H_{22}ON_4$	322	70.8	70.6	6.83	6.7	17.39	17.3
ACHF – 2	$C_{19}H_{22}ON_4$	322	70.8	70.5	6.83	6.5	17.39	17.2
ACHF – 3	$C_{20}H_{24}ON_4$	336	58.4	58.1	9.73	9.6	24.8	24.7
ACHF – 4	$C_{31}H_{30}ON_4$	474	74.88	77.8	6.33	6.2	11.8	11.6
ACHF – 5	$C_{33}H_{34}ON_4$	502	78.88	78.6	6.77	6.5	11.15	11.1
ACHF – 6*	$C_{31}H_{30}O_5N_4S_2$	602	61.79	61.7	4.98	4.8	9.3	9.2

*For Sulfur % Cald: 10.63; Found: 10.5.
[a]Diamines used: 1. 1,3 – Phenylene diamine; 2. 1,4 – Phenylene diamine; 3. 4 – Methyl – 1, 3 – phenylene diamine; 4. Benzidine; 5. 4,4′ – Diamino diphenyl methane; 6. 4,4′ – Diamino diphenyl sulfone.

5 min. The resultant suspension mixture was applied with a brush to a 250 mm × 250 mm glass fiber cloth and the solvent was allowed to evaporate. The 10 dried prepregs prepared in this way were stacked one on top of another and pressed between steel plates coated with Teflon release film and compressed in a flat platen press under about 70 psi pressure. The stacked prepregs were cured by heating at 100°C for 4 hours and post-cured at 130 ± 5°C for 7 hours in an air-circulated oven. The composite so obtained was cooled to 50°C before the pressure was released. Test specimens were made by cutting the composite and machining them to the final dimension.

MEASUREMENTS

The C, H and N contents of the ACHF resins were estimated by the means of TF 1101 flash elemental analyzer (Italy). The bromine content of BCHF polymer was estimated by Carius method [10]. The IR spectra of the polymer samples were taken in KBr pellets on a Perkin Elmer Spectroscope. The number of NH_2 groups were determined by nonaqueous conductometric titration in formic acid – acetic acid mixture. Perchloric acid in formic acid – acetic acid was used as a titrant. Curing of epoxy – ACHF resin system was carried out by DSC. A Du Pont 900 DSC was used for this study. The instrument was calibrated using standard indium metal with known heat of fusion ($\Delta H = 28.45$ J/g). Curing was carried out from 30 to 300°C at 10°C min^{-1} heating rate. The weight of sample for this investigation in the range of 4–5 mg and an empty cell was used as a reference. Cured samples were subjected to thermogravimetric analysis (TGA) on a Du Pont 950 TGA in air at a heating rate of 10°C min.$^{-1}$

Chemical Resistance

The chemical resistance of the composite was measured according to ASTM D543. The sample size was approximately 20 mm × 20 mm.

Mechanical Properties

The mechanical properties were measured on three individual specimens and the average results have been documented.

Flexural Strength Test

The measurements of the flexural strength of composites were carried out on a universal Instron testing machine model number A – 74.37 at room temperature according to the testing method of ASTM D770. The crosshead speed was 100 mm/min.

Compressive Strength Test

The compressive strength was measured according to an IS method. The sample size was 12.5 mm × 12.5 mm.

Impact Strength Test

The impact strength was determined according to the testing method of ASTM D256. The measurements were made through an Izod tester at room temperature.

Rockwell Hardness Test

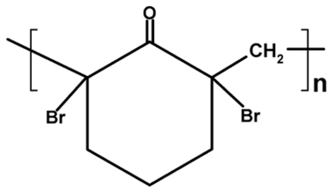
The Rockwell hardness strength was measured according to ASTM D785. The sample size was 25 mm × 25 mm.

Electrical Testing

Dielectric strength measurements were carried out on a high-voltage tester machine oil test set.

RESULTS AND DISCUSSION

The bromination of CHF resin was performed and it was assumed that bromination occured at acidic proton of CHF resin. Thus, the brominated CHF resin (i.e., BCHF) has the following structure:



BCHF resin

The C, H, and Br contents of BCHF also agree with the predicted structure. The bromine content of BCHF polymer indicates that the bromination of the terminal OH group did not occur. This is only possible at a higher temperature [11]. The aryl amination reaction of BCHF with various diamines was carried out by simple condensation reaction. An excess diamine was used to get ACHF with more amino groups. The ACHF were characterized by 'N' content and NH_2 group estimation by nonaqueous conductometric titration. The results of N contents and NH_2 group determination (Table 2) indicate that around two NH_2 groups are present per repeat unit of ACHF. The inspection of IR spectra of ACHF reveals that all the IR spectra comprised the spectral features of the CHF chain and additional aromatic and amine groups. The only discernible difference is that the spectra of ACHF contains new bands at

Table 3: DSC curing of epoxy resin; DGEBA – ACHF resin.

Resin system	Curing temp. (T°C)			Activation energy (EA) J/g
	T_k	T_p	T_f	
ACHF – 1	142°C	158°C	175°C	37.1
ACHF – 2	138°C	152°C	173°C	35.2
ACHF – 3	140°C	153°C	170°C	34.2
ACHF – 4	125°C	145°C	166°C	15.7
ACHF – 5	120°C	140°C	169°C	16.1
ACHF – 6	145°C	162°C	180°C	38.2

Table 4: TGA of unreinforced cured samples of epoxy resin DGEBA – ACHF resins.

Cured samples	% Weight loss at various temperature °C				
	250°C	300°C	400°C	500°C	700°C
1	7	11	22	35	70
2	6	10	22	34	72
3	7	10	20	33	80
4	4.5	9.5	21	34	69
5	4.5	8	20	32	68
6	2	6	16	28	70

Table 5: Chemical, mechanical and electrical properties of glass-reinforced composites of epoxy resin ACHF resin system[a].

Composite sample	Chemical resistance[b] %		Flexural strength (Mpa)	Compressive strength (Mpa)	Impact strength (Mpa)	Rockwell hardness (R)	Electrical strength Kv mm^{-1}
	Thickness	Weight					
1	1.3	1.4	279	355	295	104	18.9
2	1.3	1.4	286	358	285	108	19.1
3	1.5	1.5	286	362	295	115	22.3
4	1.1	1.2	275	355	320	115	22.5
5	1.2	1.2	290	385	325	102	26.1
6	1.3	1.3	291	388	340	121	25.8

[a]Satain (212) weave (polyimide compatible) fiber glass woven fabric 0.25 mm thick of 'E' type glass (Unnati chemicals, India) 270 gm^{-1} was used for laminate preparation, 25 mm, 10ply., Resin content: 40% curing temp. 145 ± 3°C; Time 7 hrs; pressure: 60–70 psi. Composite size: 250 mm × 250 mm × 3.0–3.5 mm.
[b]Chemical resistance to alkali (25% w/v NaOH); composites are unaffected by organic solvents and concentrated acids (25% v/v HCL).

3400, 3300 cm^{-1} due to the NH_2 groups and bands at 3030, 1600, 1500, and 810 cm^{-1} due to aromatic breathing. As the ACHF resin contains NH_2 group, these resins were tried for the curing of epoxy resin. The commercial resin diglycidy ether of bisphenol-A (DGEBA) was used for curing study. The ACHF-DGEBA systems were monitored on DSC. From the DSC thermograms the kickoff temperature (T_k), peak temperature (T_p) and final temperature (T_f) for curing system were evaluated and the activation energy was calculated. The data are furnished in Table 3.

The ACHF-DGEBA cured products were also monitored for TGA and the TGA data are shown in Table 4. The results show that the cured products degrade in the range of 280–700°C. The degradation is rapid above 400°C, and the cured products were lost completely beyond 650°C. The glass fiber-reinforced composites (GRC) of ACHF-DGEBA were prepared based on DSC data (cured temperature). The mechanical, chemical, and electrical properties of GRC are shown in Table 5. The laminates have good chemical resistivity. The mechanical strength of laminates is also quite serviceable.

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