

Modified ketone resin as an epoxy resin curing agent

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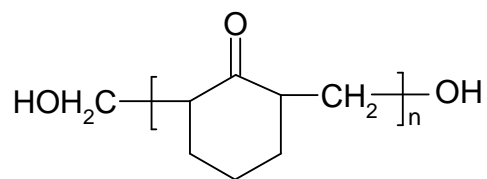
ABSTRACT

Cyclohexanone-formaldehyde (CHF) resin was brominated and the brominated CHF (BCHF) was then reacted with excess hydrazine derivatives. The hydrazinated CHF resin designated as HCHF (i.e. modified ketone resin) were characterized and then applied as epoxy resin curing agents. Thus the curing of commercial epoxy resin namely Diglycidyl Ether of Bisphenol-A (DGEBA) by HCHF was monitored by differential scanning calorimetric (DSC) and from the DSC scan the glass fibre reinforced composites of DGEBA-HCHF systems were prepared and characterized by chemical resistivity and mechanical properties.

Keywords: Epoxy resin, Ketone resins, IR spectral study, Curing of epoxy resins, Hydrazines, DSC, TGA, Composites etc.

INTRODUCTION

Ketone resins are known for the last five decades [1]. Number of reports about aliphatic and alicyclic ketone-formaldehyde resins are found for many commodity applications like paints, foam, adhesives, moulding materials, etc [2-7]. Experimental and kinetic study about KF resinification has been well established by Masahiro Abo et. al. [8]. These authors studied aliphatic and alicyclic ketone-formaldehyde resins. More particularly alicyclic ketone say, cyclohexanone-formaldehyde resin (CHF) has good utility because it has excellent glossy and transparent properties [4,5]. The structure of CHF resin has been well established [8] as;



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

MATERIALS AND METHODS

Materials :

Cyclohexanone-formaldehyde (CHF) resin (Mol.Wt. ~700) and hydrazine derivatives listed in Table-2 were obtained from local market. Diglycidyl ether of bisphenol-A (a commercial epoxy resin) was obtained from local paint industry. Its specification are: epoxy equivalent: 190 and viscosity 40-100 cps.

Glass cloth:- 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.

Preparation of Bromo derivative of CHF (BCHF) resin

The bromination of CHF resin was carried out by the method reported for bromination of ketones [9]. To a solution of 11.0 gm (0.1 mole) CHF resin in 350 ml benzene, a solution of 32 gm Br₂ (0.2 mole) in 75 ml benzene was added dropwise over a period of half an hour. The reaction temperature was adjusted to 20°C during the whole period of reaction. The quantity of Br₂ 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. Anhydrous sodium sulphate was added and the solvent was distilled off under vacuum. The resultant brominated CHF was designated as BCHF resin. The elemental analysis of BCHF resin is given in Table-1.

TABLE – 1: Elemental analysis of BCHF resin

Analysis		C %	H %	Br %
(C ₇ H ₈ OBr ₂) _n (268) _n	Cald.	31.34	2.98	59.7
	Found	31.2	2.8	58.9

\overline{M}_n (VPO) DMF: 1650

SYNTHESIS OF HYDRAZINO FUNCTIONALIZED CHF (HCHF)

To a solution of hydrazine derivative (0.25 mole) (Table-2) in ethanol (100 ml) was gradually added to a solution of BCHF resin (0.1 mole) in tetrahydro furan (THF) with continuous stirring at room temperature. The saturated sodium bicarbonate solution was added as an acid acceptor. The reaction was kept aside till CO₂ gas ceased. The resulting dark brown pasty mass was washed by ethanol, by decantation and then by dry ether and finally air dried. The hydrazino functionalized CHF resin samples were designated as HCHF resins.

FABRICATION OF GLASS FIBRE REINFORCED COMPOSITES

A suspension of epoxy resin-HCHF resin (in ratio of 60:40 by weight) in THF solvent and 2 - 3 drops of pyridine was prepared and well stirred for 5 minutes. The resultant suspension mixture was applied with a brush to a 250 mm x 250 mm glass fibre 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 film release sheet and compressed in a flat platen press under about 70 psi pressure. The prepregs stacked 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 final dimension.

MEASUREMENTS

The C, H and N contents of all the HCHF 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 all the polymer sample were taken in KBr pellet on "Perkin Elmer model No. spectrum one". The number of NH₂ groups were determined by non-aqueous conductometric titration in Formic acid - acetic acid mixture. Perchloric acid in formic acid - acetic acid was used as a titrant. Curing of epoxy - HCHF resin system was carried out by DSC. Universal V 3.0 GTA Instrument was used for this study. The instrument was calibrated using standard indium metal with known heat of fusion (H = 28.45 J/g). Curing was carried out from 30 - 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 Thermo Gravimetric Analysis (TGA) on a Du Pont 950 TGA in air at a heating rate of 10°C min⁻¹. The resistance against chemicals of the composite samples were measured according to ASTM D 543. All mechanical testings were performed using 3 test specimens.

Chemical Resistance

The chemical resistance of the composite was measured according to ASTM D543. The sample size was approximately 20mm × 20mm. The data are furnished in Table – 5.

Mechanical Properties

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

Flexural Strength Test

The measurements of 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 ATSM D790. The crosshead speed was 100mm/min.

Compressive Strength Test

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

Impact Sstrength Test

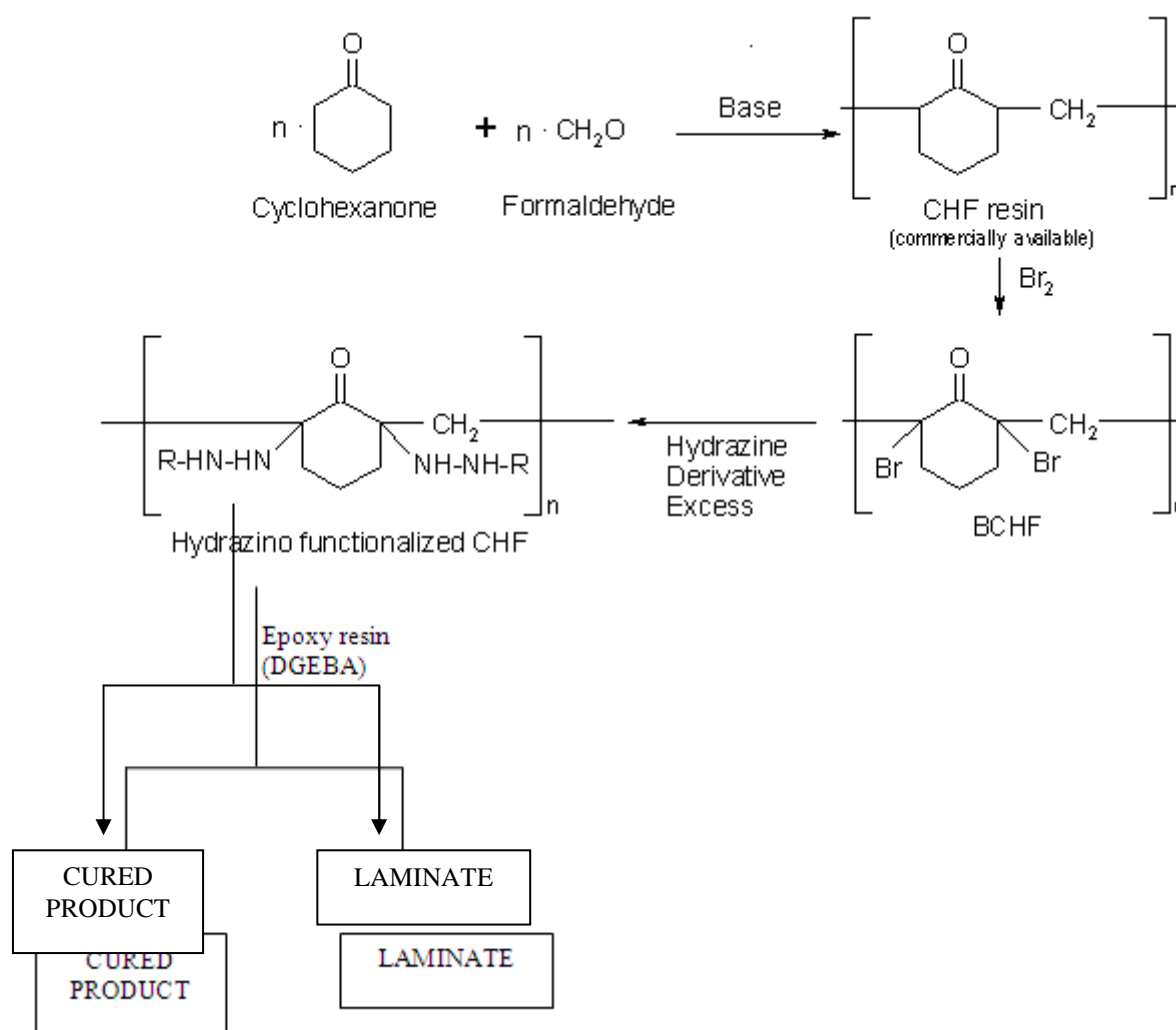
According to the testing method of ASTM D256, the measurements were made through an Izod – tester at room temperature.

Rockwell Hardness Test

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

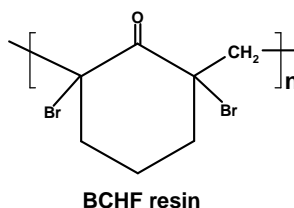
Electrical Testing

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

SCHEME - 1

RESULTS AND DISCUSSION

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



The C,H and Br contents of BCHP also agree with the predicted structure. The bromine content of BCHP polymer indicate that the bromination of terminal OH group could not be exist. This is only possible at higher temperature [11]. The reaction of BCHP with hydrazine and its various derivatives was carried out by simple condensation reaction. The excess hydrazine derivative was used to get HCHF with more amino groups. The HCHF were characterized by 'N' content and NH₂ group estimation by non-aqueous conductometric titration. The results of N contents and NH₂ group determination (Table – 2) are indicates that, around two NH₂ groups are present per repeat unit of HCHF. The inspection of IR spectra of HCHF reveals that, all the IR spectra comprised the spectral features of CHF chain and additional of aromatic and hydrazinic groups. The only discernible difference is that the spectra of HCHF comprises the new bands at 3500, 3300 cm⁻¹ due to the NH₂ groups and bands at 3030,1600,1450 cm⁻¹ due to aromatic breathing. As the HCHF resin contains NH₂ group , these resins were tried for curing of epoxy resin. The commercial resin namely diglycidyl ether of bisphenol-A (DGEBA) was used for curing study. The HCHF-DGEBA systems were monitored on DSC. From the DSC thermograms the kick off temperature (Tk), peak temperature (Tp) and final temperature (Tf) for curing system were evaluated and the activation energy was calculated. The data are furnished in Table - 3.

TABLE – 2: Characterization of hydrazino cyclohexanone - formaldehyde (HCHF Resins)

HCHF resin sample	Molecular formula	Molecular weight of repeating unit	Elemental analysis					
			C %		H %		N %	
			Cald.	Found	Cald.	Found	Cald.	Found
HCHF-1	C ₇ H ₁₄ ON ₄	170	49.41	49.2	8.23	8.1	32.94	32.7
HCHF-2	C ₁₉ H ₂₂ ON ₄	322	70.80	69.4	6.83	5.9	17.39	17.2
HCHF-3*	C ₁₉ H ₂₀ Cl ₂ ON ₄	391	58.31	58.2	5.11	5.0	14.32	14.1
HCHF-4**	C ₁₉ H ₂₀ Br ₂ ON ₄	480	47.50	46.7	4.16	4.0	11.66	11.4
HCHF-5	C ₂₁ H ₂₆ ON ₄	350	72.00	71.8	7.42	7.3	16.00	15.7
HCHF-6	C ₁₉ H ₂₀ O ₃ N ₆	412	55.33	55.1	4.85	4.7	20.38	20.1
HCHF-7	C ₁₉ H ₁₈ O ₃ N ₈	502	45.41	45.2	3.58	3.4	22.31	22.2

* %Cl Cald : 18.15 Found : 18.0

** %Br Cald : 33.33 Found : 33.1

Hydrazine and its derivatives used :

- | | |
|------------------------------------|--------------------------------|
| 1 : Hydrazine | 2 : Phenyl hydrazine |
| 3 : 4 – Chlorophenyl hydrazine | 4 : 4 – Bromophenyl hydrazine |
| 5 : 4 – Methyl phenyl hydrazine | 6 : 4 – Nitro phenyl hydrazine |
| 7 : 2,4 – Dinitro phenyl hydrazine | |

TABLE – 3: DSC Curing of epoxy resin ; DGEBA - HCHF Resin

DGEBA-HCHF SAMPLE	Curing temp. (T °C)			Activation Energy (Ea) KJ/Mole
	T _k	T _p	T _f	
HCHF - 1	110 °C	135 °C	152 °C	123
HCHF - 2	108 °C	125 °C	155 °C	120
HCHF - 3	97 °C	126 °C	157 °C	122
HCHF - 4	110 °C	124 °C	155 °C	129
HCHF - 5	95 °C	130 °C	150 °C	125
HCHF - 6	112 °C	136 °C	151 °C	130
HCHF - 7	108 °C	125 °C	159 °C	126

TABLE – 4: TGA of unreinforced DGEBA - HCHF cured material

Cured Samples	% Weight loss at various temperature °C				
	250°C	300°C	450°C	600°C	750°C
URC-1	3.44	12.12	63.49	75.39	88.37
URC-2	4.01	11.89	63.02	75.69	88.93
URC-3	4.00	12.13	63.47	75.41	88.87
URC-4	3.61	11.87	63.13	74.88	87.89
URC-5	4.12	11.98	63.16	75.53	88.88
URC-6	4.34	11.99	63.17	74.88	89.13
URC-7	3.01	10.10	65.11	72.87	83.92

TABLE – 5: Chemical, mechanical and electrical properties of glass reinforced composites of epoxy resin HCHF resin system

Composites Sample	Chemical resistance %		Flexural Strength (Mpa)	Compressive Strength (Mpa)	Impact Strength (Mpa)	Rockwell Hardness (R)	Electrical Strength Kv mm ⁻¹
	Thickness	Weight					
C-1	1.4	1.3	280	340	315	120	18.7
C-2	1.4	1.3	278	347	320	111	19.0
C-3	1.5	1.5	274	348	330	110	22.0
C-4	1.1	1.2	286	350	285	130	22.5
C-5	1.3	1.3	280	348	285	128	22.6
C-6	1.2	1.2	278	300	275	125	25.7
C-7	1.2	1.2	270	333	270	126	21.5

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, 25mm, 10ply., Resin content: 40% curing temp. 145±3°C; Time 7 hrs; pressure : 60-70 psi. Composite size : 250mm x 250mm x 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).

The HCHF-DGEBA cured products were also monitored for TGA and the TGA data are shown in Table-4. The results show that the cured products start their degradation in the range of 250°C -750°C. The degradation is rapid after the temp. 400°C, and the cured products were lost completely beyond 650 °C. The glass fibre reinforced composites (GRC) of HCHF-DGEBA were also prepared based on DSC data (i.e. 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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