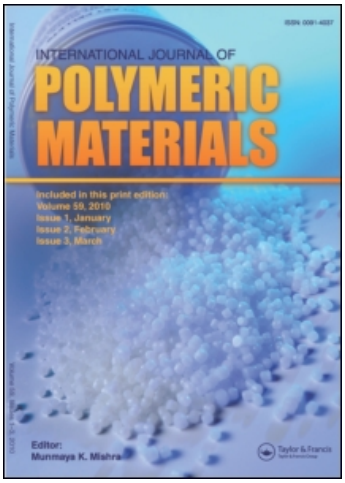

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Synthesis, Characterization and Glass/Carbon Reinforcement of Acetone-Formaldehyde-1,5-Dihydroxynaphthalene-Epoxy Resin System

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Acetone-formaldehyde (AF) resin containing the methylol group ($-CH_2OH$) has been prepared and condensed with 1,5-dihydroxynaphthalene (DN) in the presence of an alcoholic alkali catalyst at varying ratios of AF:DN: 1:1, 1:1.5 and 1:2, respectively. The resultant AFDN resins were characterized by elemental analyses, IR spectral studies, and number average molecular weight determined by the nonaqueous conductometric titration method. Further reaction of the AFDN resins was carried out with different epoxy resins (i.e., DGEBA, DGEBC and DGEBF). The curing of these resins was monitored by differential scanning calorimeter (DSC) and their kinetic parameters have been evaluated. Based on DSC thermograms both glass and carbon fiber-reinforced composites have been laminated and characterized for chemical, mechanical and electrical properties. The unreinforced cured resins were subjected to thermogravimetric analysis (TGA).

Keywords acetone-formaldehyde-1,5-dihydroxynaphthalene (AFDN) resin, acetone-formaldehyde (AF) resin, carbon fiber-reinforced composites (CFRC), glass fiber-reinforced composites (GFRC)

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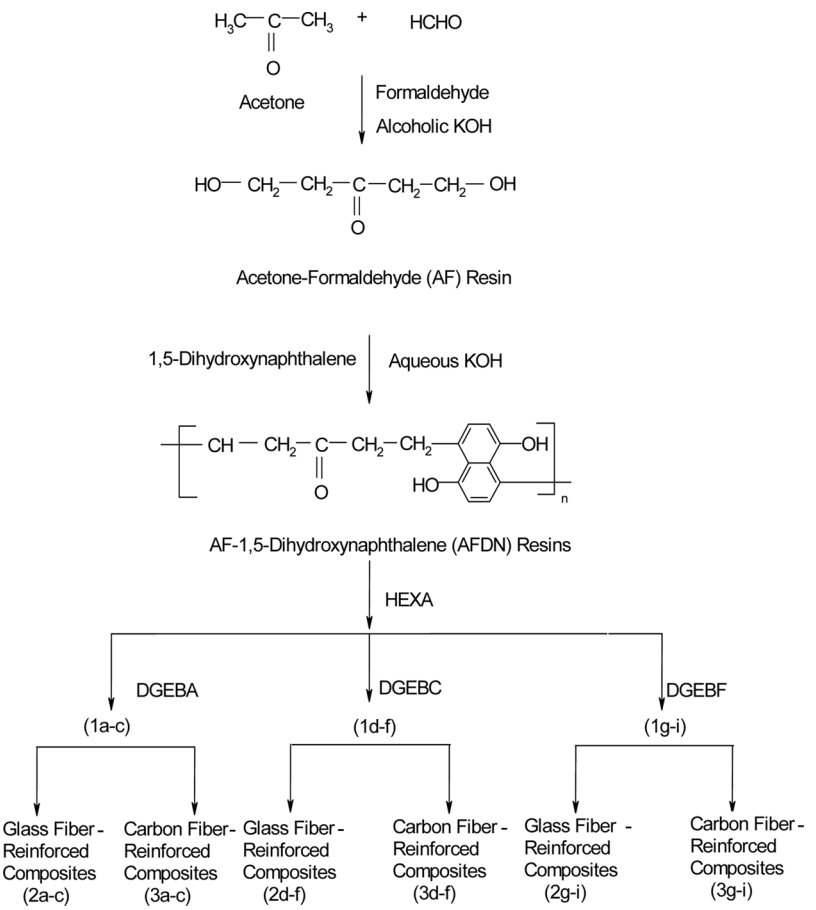
INTRODUCTION

The study of acetone-formaldehyde resinification is well established [1–3]. The AF resin, having two to three methylol groups ($-CH_2OH$), has found many applications, such as for corrosion protection of building materials and metallic surfaces, ion exchange resin, adhesive, binder, and the hydraulic seal of oil wells [4–6]. Like resol (having $-CH_2OH$ self-curable groups), such AF resin (i.e., having $-CH_2OH$ groups) may afford condensation with phenol derivatives. Such aspects have been reported from our laboratory in this direction [7–10]. In extension of this work [7–10], it was thought interesting to study the acetone-formaldehyde-1,5-dihydroxynaphthalene (AFDN) resinification with different epoxy resins (i.e., DGEBA, DGEBC and DGEBF) and their glass and carbon reinforcement.

Hence the present article comprises synthesis, characterization, glass and carbon reinforcement of the AFDN-epoxy resin system. Based on DSC



Scheme 1: Synthesis steps.

thermograms, both glass and carbon fiber-reinforced composites were laminated and characterized for chemical, mechanical and electrical properties. The whole work is scanned in Scheme 1.

EXPERIMENTAL

Materials

The specifications of all epoxy resins are as follows:

Epoxy equivalent weight of diglycidylether of bisphenol-A (DGEBA), 190

Epoxy equivalent weight of diglycidylether of bisphenol-C (DGEBC), 210

Epoxy equivalent weight of diglycidylether of bisphenol-F (DGEBF), 160

E-type glass-woven fabric (0.25 mm thick) was obtained from Unnati Chemicals, India. Carbon fiber (12 K) was obtained from Reliance, IPCL, Vadodara, India. All other chemicals were of pure grade.

Preparation of Acetone-Formaldehyde Resin

Acetone-formaldehyde (AF) resin has been prepared by following the method reported in our earlier communication [7]. The general procedure is as follows:

A mixture of acetone (1 M) and formaldehyde (0.66 M) with 5% alcoholic KOH was heated at 40–50°C with constant stirring for 15 minutes. The resultant mixture was cooled to room temperature. The so-called resin obtained was a colorless thick liquid. It was neutralized by formic acid. Preliminary characterization of acetone-formaldehyde (AF) resin is furnished in Table 1.

Preparation of Acetone-Formaldehyde-1,5-Dihydroxynaphthalene (AFDN) Resin

The AF and 1,5-dihydroxynaphthalene (DN) in molar rations of 1:1, 1:1.5, and 1:2 respectively, were refluxed in dioxane solvent using 2.5% KOH of the

Table 1: Preliminary characterization of acetone-formaldehyde (AF) resin.

Molecular formula		**$C_5H_{10}O_3$**	
Elemental Analysis		%C	%H
	Calc.	50.84	8.47
	Found	50.01	8.30
Solubility		Soluble in water (2 g in 10 ml)	
No. of –OH group		1.98	

Table 2: Characterizations of AFDN resins.

Molar ratio of AFDN resins	Color and State	Elemental analysis calc./ (found) %C	%H	Nonaqueous conductometric titration *DP	$\overline{Mn}$
1:1	Brown Pasty Mass	74.38 (74.28)	5.78 (5.67)	8	1936
1:1.5	Brown Pasty Mass	74.38 (74.30)	5.78 (5.69)	6	1452
1:2	Brown Pasty Mass	74.38 (74.27)	5.78 (5.69)	3	726

*DP = Degree of Polymerization.

total weight for 2 h. The resulting solution is then poured immediately into distilled water and washed several times with distilled water in order to remove unreacted reactants. The yields of resins were 85, 87, and 90%, respectively. Characterization of AFDN resins is furnished in Table 2.

Preparation of AFDN-Epoxy Resin Curing System

An AFDN-epoxy resin system was prepared by mixing AFDN resin and epoxy resin (DGEBA) in different proportions (as shown in Table 3). To this mixture the catalyst Hexamethylenetetraamine (HEXA) (0.5% of weight of AFDN resin) was added under continuous stirring and stirred well for 15 minutes to form a homogeneous system.

Similarly, other AFDN-epoxy resin systems for different epoxy resins like DGEBC and DGEBF were prepared by using the same method and conditions used for DGEBA.

Three different AFDN-epoxy resin systems were prepared by using different proportions of AFDN and epoxy resins (i.e., DGEBA, DGEBC, and DGEBF as shown in Table 3).

Composite Fabrication

Glass and carbon fiber composites were prepared by the same method. The preparation method of glass fiber-reinforced composites and carbon fiber-reinforced composites is given briefly as follows:

The composites were prepared by using E-type glass fiber. Suspensions of AFDN-epoxy resin systems were prepared in tetrahydrofuran (THF). The mixture was applied with a brush to a 200 mm × 200 mm glass cloth and the solvent was allowed to evaporate. The ten dried prepregs prepared in this way were then stacked one on top of another and pressed between steel plates coated with a Teflon release sheet and compressed under 70 psi pressure. The prepreg stacks

Table 3: Curing characterizations of AFDN-epoxy resin systems.

Epoxy resins	Compositions		Designation	Kick-off temp. Ti(°C)	Peak temp. Tp(°C)	Final temp. Tf (°C)	Activation energy (Ea) KJ/mol	Order of reaction 'n'
	AFDN	Epoxy resin						
DGEBA	60	40	1a	144	167	186	62.1	1.9
	50	50	1b	149	169	190	62.4	1.8
	40	60	1c	154	170	196	62.7	1.7
DGEBC	60	40	1d	139	161	178	61.4	1.9
	50	50	1e	142	162	184	61.6	1.9
	40	60	1f	148	165	188	61.9	1.8
DGEBF	60	40	1g	137	156	172	60.2	1.9
	50	50	1h	139	158	178	60.7	1.8
	40	60	1i	143	162	183	61.1	1.7

were cured by heating in an autoclave oven at $180 \pm 5^{\circ}C$ for 5 hours. The composites so obtained were cooled to 45–50°C before the pressure was released.

Carbon fiber-reinforced composites (CFRC) were prepared by using 30 tows (12 K) of carbon fiber. Then by following a similar method and molding conditions as above, carbon fiber-reinforced composites were laminated.

ANALYSIS AND CURING

Analysis

The C, H contents were estimated by means of Thermofinagan 1101 Flash Elemental Analyzer (Italy). The IR spectra of all the samples were taken in KBr pellets on a Nicolet 760 D spectrophotometer. The number average molecular weight was estimated by using nonaqueous conductometric titration method [11].

Curing

A Du Pont 900 DSC was used for the curing study of AFDN-epoxy resin curing systems. The instrument was calibrated using standard indium metal with known heat of fusion ($\Delta H = 28.45\,J/g$). Curing was carried out using a single heating rate of 10°C/min in air. The sample weight for this investigation was in the range of 4–5 mg along with an empty reference cell.

Thermogravimetric analysis (TGA) of AFDN-epoxy resin curing systems have been carried out using a Du Pont 950 thermogravimetric analyzer at a heating rate of 10°C/min in air. The sample weight for this investigation was in the range of 4–5 mg.

COMPOSITE CHARACTERIZATION

All the chemical, mechanical and electrical tests on composites were conducted according to ASTM methods (as listed below) using three specimens for each test.

Chemical Resistance Test

ASTM D 543-67 was used to measure the chemical resistance of the composites towards sodium hydroxide, organic solvents and mineral acids.

Mechanical and Electrical Testing

(1) The flexural strength was measured according to ASTM D 790.

(2) The compressive strength was measured according to ASTM D 695.

(3) The impact strength was measured according to ASTM D 256.

(4) The Rockwell hardness was measured according to ASTM D 785.

(5) The electrical strength was measured according to ASTM D 149.

RESULTS AND DISCUSSION

The AF resin, having two active methylol groups (–CH_2OH groups) per molecule, was used for further condensation with 1,5-dihydroxynaphthalene (DN) following the same reported method [7]. The AFDN condensation product was a brown, pasty mass. The freshly prepared products were soluble in most organic solvents, but on longer storage they slightly harden. It was observed that in the absence of 1,5-dihydroxynaphthalene, acetone-formaldehyde (AF) resin under similar conditions remained relatively intact. The AFDN-epoxy resin systems for different epoxy resins (i.e., DGEBA, DGEBC, and DGEBF) were prepared as per Table 3.

The elemental analysis of all the AFDN resins was found to be consistent with their predicted structures. Number average molecular weight ($\overline{Mn}$) of all three resins, estimated by nonaqueous conductometric titration [11], indicate that $\overline{Mn}$ decreases with increasing molar proportion of DN. The results of elemental analysis, number average molecular weight ($\overline{Mn}$) and degree of polymerization (DP) are furnished in Table 2. Typical IR spectra for all the resins were found to be consistent with the ones expected from the structures of resins.

The curing study of AFDN-epoxy resin systems was carried out on DSC. The data obtained from DSC thermograms for all AFDN-epoxy resin systems give a single exothermic peak in the range of 137 to 195°C. The activation energy (Ea) values for these systems did not vary widely. The results of curing temperature with activation energy (Ea) and order of reaction are furnished in Table 3.

The unreinforced cured AFDN-epoxy resin samples were prepared at 180 ± 5°C for 5 hours. They crumbled to a powder under normal hand

Table 4: TGA of unreinforced cured AFDN-epoxy resin systems.

	%Weight loss at various temperature °C from TGA					
Designation	**200**	**300**	**400**	**500**	**600**	**700**
1a	2.9	32.1	41.6	49.8	72.3	87.4
1b	2.8	30.8	40.1	48.2	68.4	85.2
1c	2.6	29.7	38.6	42.4	61.3	81.5
1d	3.8	35.4	44.3	52.6	74.6	89.6
1e	3.6	34.6	43.8	51.8	73.8	88.4
1f	3.2	33.3	42.6	50.3	72.9	87.8
1g	3.9	37.4	46.8	54.9	76.3	92.4
1h	4.2	36.8	46.1	54.1	75.4	91.3
1i	4.6	36.1	45.7	53.4	74.8	90.2

Table 5: Chemical, mechanical and electrical properties of glass fiber-reinforced composites of AFDN-epoxy resin systems.

Glass fiber-reinforced composites	% Loss on exposure to 25% (W/V) NaOH		Density g/cm^3	Flexural strength (MPa)	Compressive strength (MPa)	Impact strength (MPa)	Rockwell hardness (R)	Electrical strength (in air) (kV/mm)
	Thickness	Weight						
2a	1.13	1.11	1.25	287	288	286	110	18.9
2b	1.12	1.10	1.26	290	294	290	115	19.8
2c	1.11	0.9	1.27	294	298	295	119	20.3
2d	1.14	1.12	1.25	284	285	281	107	18.7
2e	1.14	1.12	1.25	286	291	286	111	19.5
2f	1.13	1.11	1.26	289	293	290	114	20.1
2g	1.15	1.13	1.25	280	280	278	103	18.6
2h	1.15	1.13	1.25	281	287	283	109	19.3
2i	1.14	1.12	1.24	286	288	285	112	19.9

Table 6: Chemical, mechanical and electrical properties of carbon fiber-reinforced composites of AFDN-epoxy resin systems.

Carbon fiber-reinforced composites	% Loss on exposure to 25% (W/V) NaOH		Density g/cm^3	Flexural strength (MPa)	Compressive strength (MPa)	Impact strength (MPa)	Rockwell hardness (R)	Electrical strength (in air) (kV/mm)
	Thickness	Weight						
3a	1.15	1.13	1.23	278	279	276	101	18.6
3b	1.14	1.13	1.24	281	283	281	105	19.5
3c	1.13	1.0	1.24	285	288	286	109	20.1
3d	1.16	1.14	1.23	278	276	272	100	18.5
3e	1.15	1.14	1.23	278	281	278	101	19.3
3f	1.15	1.13	1.24	280	285	281	104	19.5
3g	1.17	1.15	1.24	270	271	272	98	18.4
3h	1.17	1.15	1.25	273	277	273	100	19.1
3i	1.15	1.13	1.25	274	278	275	103	19.6

pressure, and were insoluble in all common organic solvents. TG data are shown in Table 4 for unreinforced cured resin samples and show that they all degrade in a single step and their decomposition started around 200°C. The rate of decomposition becomes faster in the range of 300 to 600°C. The product was lost completely beyond 700°C. The glass fiber-reinforced composites based on AFDN-epoxy resin systems were also prepared at 180 ± 5°C for 5 hours. Chemical resistance tests revealed that all composites had remarkable resistance to organic solvents and concentrated acids (25% V/V). However, the concentrated alkali (25% W/V) caused losses in their thickness and weight (as shown in Tables 5 and 6). Results shown in Tables 5 and 6 suggest that both glass and carbon-reinforced composites have good chemical, mechanical and electrical properties.

CONCLUSIONS

The following conclusions have been made:

(1) Ease of preparation of acetone-formaldehyde (AF) resin, AFDN resins and AFDN-epoxy resin system.

(2) Ease of the preparation of glass and carbon-reinforced composites from AFDN-epoxy resin system.

(3) Glass fiber-reinforced composites have better chemical, mechanical and electrical properties than carbon fiber-reinforced composites. This is due to the unidirectional fibers in carbon fiber-reinforced composites.

REFERENCES

[1] Borodkina, N. I., and Frolov, S. S. *Zh.Priki.Khim* **36**, 408 (1963).

[2] Hayano, H., and Fujita, K. *Japan Kanzei Chuo Bunsekishoho* **18**, 89 (1978).

[3] Skoda, A. I., Mravec, D., and Ilavski, J. *Chem. Prum.* **39**, 575 (1989).

[4] Okay, O., and Schindlbauer, H. *Angew. Makromol. Chem.* **127**, 203 (1984).

[5] Kuznetsova, O. N., Sakhapova, V. P., Arkhireev, V. P., and Kadyrov, R. R. *Polymer Sci. Series D* **1**, 249 (2008).

[6] Gillera, M. F. U.S. Patent, 4,034,012 (1977).

[7] Patel, H. S., and Dixit, B. C. *High Performance Poly.* **9**, 153 (1997).

[8] Patel, H. S., and Dixit, B. C. *Inter. J. Poly. Mater.* **40**, 29 (1998).

[9] Patel, H. S., and Dixit, B. C. *Inter. J. Poly. Mater.* **42**, 309 (1998).

[10] Patel, H. S., and Dixit, B. C. *Poly. and Poly. Compo.* **8**, 255 (2000).

[11] Patel, H. S., and Patel, B. K. *Inter. J. Poly. Mater.* **56**, 312 (2009).