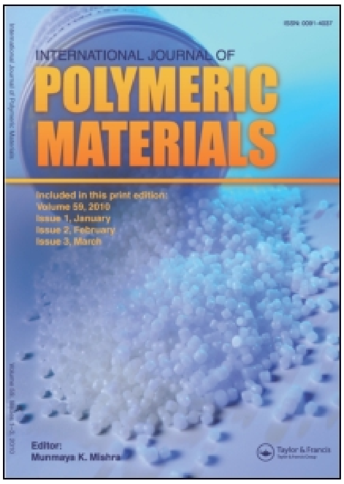

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Synthesis, Characterization and Glass Reinforced Composites of Acetone-Formaldehyde – Resorcinol Resins

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Acetone-Formaldehyde (AF) resin having methylol groups (—CH_2OH) has been prepared and condensed with resorcinol (R) in the presence of alcoholic alkali catalyst at varying ratios of AF:R; 1:1, 1:1.5 and 1:2. The resultant AF–R resins were characterized by elemental analysis, IR spectral studies, number average molecular weight ($\overline{Mn}$) estimated by non-aqueous conductometric titration and thermogravimetry. The curing study of AF–R resins with Hexamethylenetetramine (HMTA) was monitored by Differential Scanning Calorimetry (DSC) and kinetic parameters were evaluated. The glass reinforced composites based on AF–R–HMTA system have also been prepared and characterized.

Keywords: Acetone-Formaldehyde (AF) resin; Acetone-Formaldehyde–Resorcinol (AF–R) resin; Thermogravimetric analysis (TGA); Differential Scanning Calorimetry (DSC); Infra-Red (IR) spectroscopy; Glass fibre Reinforced Composites (GRC); non-aqueous conductometric titration

INTRODUCTION

The study of acetone-formaldehyde resignification is well established [1–5]. The AF resins, having two to three — CH_2OH groups, found many applications such as for corrosion protection of building materials and metallic surface, ion exchange resin, adhesive, binder *etc.* [6–8]. Like resol (having — CH_2OH self curable groups), AF

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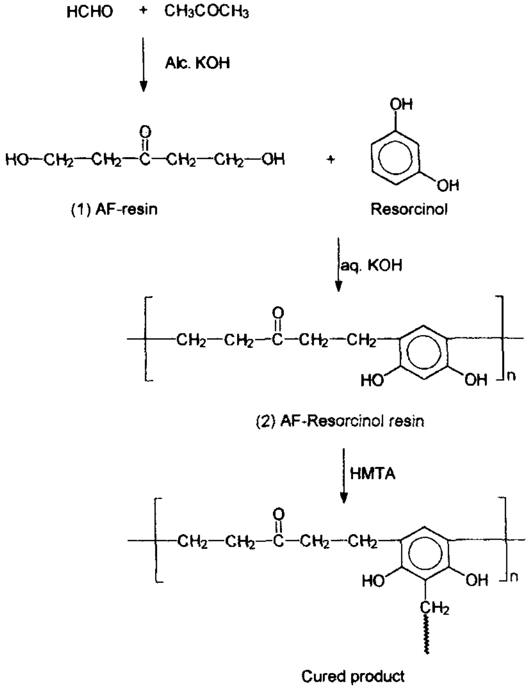
* Corresponding author.

resins (*i.e.*, having — CH_2OH groups) may afford the condensation with phenolic derivatives. The present authors have carried out the work in this direction [9, 10]. In continuation of this work [9] (*i.e.*, studies of AF–phenol condensation) the present communication comprises the synthesis and studies of AF–resorcinol condensation. The resins were studied for their curing characteristic with Hexamethylenetetramine on DSC. The glass reinforced composite fabrication has also been carried out. The whole work is drawn in the Scheme-I.

EXPERIMENTAL

Materials

All the chemicals used were of laboratory grade. Acetone-Formaldehyde (AF) resin was prepared by the method reported in our earlier communication [9].



SCHEME I

Synthesis of Acetone-Formaldehyde–Resorcinol Resin

The AF resin and resorcinol in a molar ratio of 1:1, 1:1.5, 1:2 respectively were refluxed in tetrahydrofuran solvent using 1% KOH of the total weight of the reactant for 1 hr. Resulting solution is poured immediately in distilled water to give dark brown, thick resin and was washed several times with distilled water to remove unreacted reactants. The yields were 85–90%. The details about all three resins are furnished in Table I.

Composite Fabrication

A typical method of fabrication for composites is given below.

A suspension of freshly prepared AF–R resin (II) and Hexamethylene tetramine in tetrahydrofuran was prepared and was stirred well for 5 min. The suspension mixture was applied with a brush to a 250 mm x 250 mm fibre glass cloth and the solvent was allowed to evaporate. The 10 dried prepregs prepared this way were stacked one on top of another and pressed between steel plates coated with a Teflon film release sheet and compressed in a flat platen press under about 70 psi pressure. The prepreg stacks were cured by heating at 90°C for 1 hr. and post cured at 95 ± 3°C for 1 hr. 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.

TABLE I Characterization of AF–R resins

Molar ratio of AF:R Resin system	*Elemental analysis*				*Non-aqueous conductometric titration*	
	C(%)		*H(%)*			
	Calc.	*Found*	*Calc.*	*Found*	$\overline{DP}$	$\overline{Mn}$
1:1	68.75	68.10	6.25	6.10	5	1000
1:1.5	68.75	68.30	6.25	6.02	3	580
1:2	68.75	68.25	6.25	6.09	2	385

MEASUREMENTS

The C, H contents were estimated by means of a Carlo Earba C, H, N, S, P elemental analyzer (Italy). The IR spectra were taken in KBr pellets using a NICOLETT-400 DR FTIR spectrophotometer.

Non-aqueous conductometric titration of AF and AF – R resins was carried out in pyridine against standard sodium methanolate in pyridine as titrant. The $\overline{Mn}$ value of each sample was calculated according to the method reported [11].

Curing of AF – R: Hexamethylenetetramine system was carried out by differential scanning calorimetry. A Du Pont 900 DSC was used for this study. The instrument was calibrated using standard materials *i.e.*, Indium metal ($\Delta H = 28.45\,Jg^{-1}$) with known heats of fusion. Curing was carried out using a single heating rate ($10\,K\,min^{-1}$). The sample weight for this investigation was in the range of 4 – 5 mg an empty cell was used as a reference.

Cured samples were subjected to Thermogravimetric analysis (Du Pont 950 thermogravimetric analyzer) in air at a rate of $10\,K\,min^{-1}$.

All the chemical, mechanical and electrical tests of the prepared composites were conducted according to ASTM methods following the method reported in our earlier publication [12].

RESULTS AND DISCUSSION

The AF condensation has been performed by our reported method [9]. The resultant AF resin is colorless thick liquid. As commercial resol having —CH_2OH groups for post curing '*insitu*' reaction, the AF resin having two active —CH_2OH groups is used for further condensation with resorcinol.

The AF – R condensation products were in form of dark brown thick liquid. The freshly prepared products are soluble in most polar organic solvents, but on longer storage they slightly harden and decrease solubility. It was observed that in absence of resorcinol, AF under similar condition remains relatively intact. It will, however, crosslink at elevated temperature (about 130 – 150°C). The elemental analysis of all the resins are consistent with the predicted structure (Scheme-I). A typical IR spectrum of self cured AF – R resin is shown in Figure 1. The

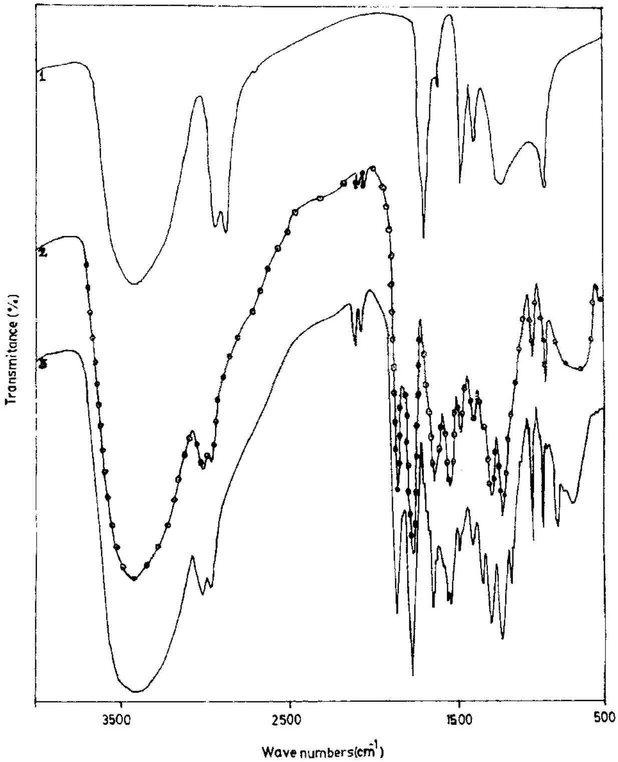
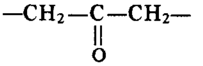


FIGURE 1 IR spectra of 1. AF, 2. AF–R and 3. AF–R–HMTA resins.

IR spectra of all the three resins comprises important bands due to AF moiety and aromatic moiety. The broad bands appeared from 2900 to 3500 cm^{-1} with inflections at 2890, 2940 and 3400 cm^{-1}. This is due to resorcinol groups. The first two inflections may be associated with asymmetric and symmetric stretching vibration of — CH_2 — and  $-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-$ systems. The bands at 770 and 840 cm^{-1} may be attributed to adjacent H-atoms or 1,2- or 1,4-substituted aromatic ring. The band at 1710 cm^{-1} may be attributed due to $>C{=}O$ group. Hence on the basis of these observations and the reactive sites present in the concern monomers (*i.e.*, AF and resorcinol) the most probable structure of such AF–R resin is shown in Scheme I.

The $\overline{Mn}$ values of all three resins estimated by non-aqueous conductometric titration are shown in Table I. The values indicate that the $\overline{Mn}$ decreases with the increase in molar proportion of resorcinol.

Since the produced AF – R resin can react with curing agents like Hexamethylenetetramine(HMTA), the cure reaction of AF – R – HMTA was studied for the ratio of AF:R:HMTA; 1:1:1, 1:1.5:1, 1:2:1 respectively. The data obtained from DSC scans are given in Table II. The DSC thermograms show, that all cured AF – R – HMTA systems gave a single exotherm peak in the range of 81 – 110°C. Here the curing temperature and time are reduced compared to AF – Phenol [9] and AF – m – Cresol [10]; reported earlier by us. This might be due to higher reactivity of resorcinol. The typical DSC thermogram is shown in Figure 2. The Kick-off temperature (T_i), peak exothermic temperature (T_p) and temperature of completion (T_f) were obtained from the DSC thermograms. The activation energy (E_a) values for such system (Tab. II) do not vary widely, which indicates that AF – R is more reactive towards the hexamethylenetetramine. The kinetic parameters E_a (activation energy) and n (order of reaction) were calculated by assuming that the curing reaction obeys Arrhenius-type kinetics and the peak maximum represents a point of constant conversion at a heating rate of $10\,\mathrm{K\,min^{-1}}$.

To obtain information about the properties of the unreinforced cross-linked materials, cured samples were prepared using the same proportions and temperatures as presented in Table III. The unreinforced cured AF – R – HMTA samples were prepared at 95 ± 3°C for 2 hrs. These products are dark brown in color and are very brittle. They form powders under normal hand pressure and are insoluble in all common organic solvents. The IR spectra of all three cured products resemble those of AF – R resin. The only noted difference is that the spectra comprise more intense bands due to — CH_2 — group

TABLE II Curing characteristics of AF – R – Hexamethylenetetramine (HMTA) system at $10\,\mathrm{K\,min^{-1}}$

Molar ratio of AF:R:HMTA resin system	*Kick off temp.* T_i (°C)	*Peak temp.* T_p (°C)	*Final temp.* T_f (°C)	*Activation energy* (E_a) *KJ mol*$^{-1}$	*Reaction order* '*n*'
1:1:1	85	99	110	28.8	1.7
1:1.5:1	81	95	109	28.3	1.7
1:2:1	80	92	102	27.3	1.8

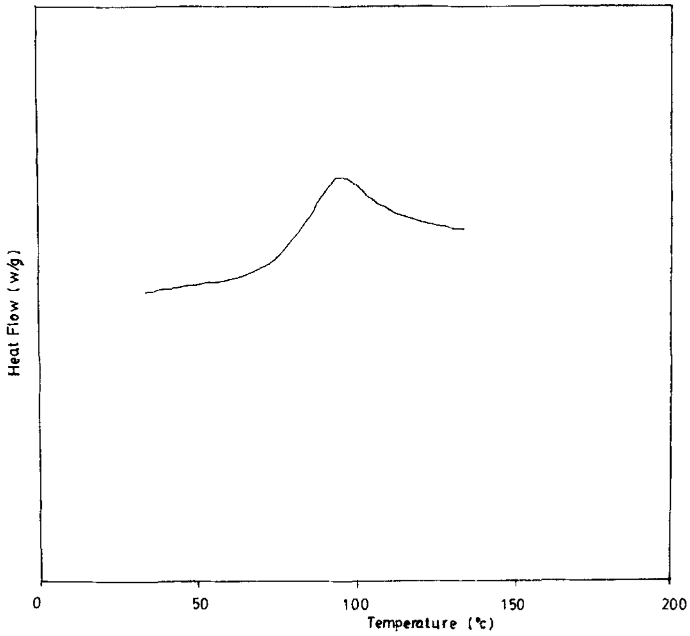


FIGURE 2 DSC thermogram of AF:R:HMTA system (1:2:1).

TABLE III TGA of unreinforced AF:R:Hexamethylenetetramine (HMTA) cured materials

Molar ratio of AF:R:HMTA resin system	*Percent weight loss at °C from TGA*					
	150	200	300	400	500	550
1:1:1	10.5	20.0	31.0	41.0	86.0	95.0
1:1.5:1	11.0	19.0	33.0	44.0	85.0	97.0
1:2:1	12.5	20.0	32.0	47.0	90.0	98.0

and a weak band around 1940 cm^{-1} due to 1,2,3,5-tetra substituted benzene ring system [13], Typical *TG* curves of unreinforced cross-linked materials is shown in Figure 3. The *TG* data are shown in Table III. It shows that they all degrade in a single step, and that their decomposition starts around 100°C. Degradation becomes faster between 150 and 450°C. The weight loss was about 97% at 530°C in all cases. Comparison of the thermal properties of the thermal properties of the AF-R-HMTA with AF-Phenol-HMTA [9] and AF-m-Cresol-HMTA [10] reveals that AF-R-HMTA cured

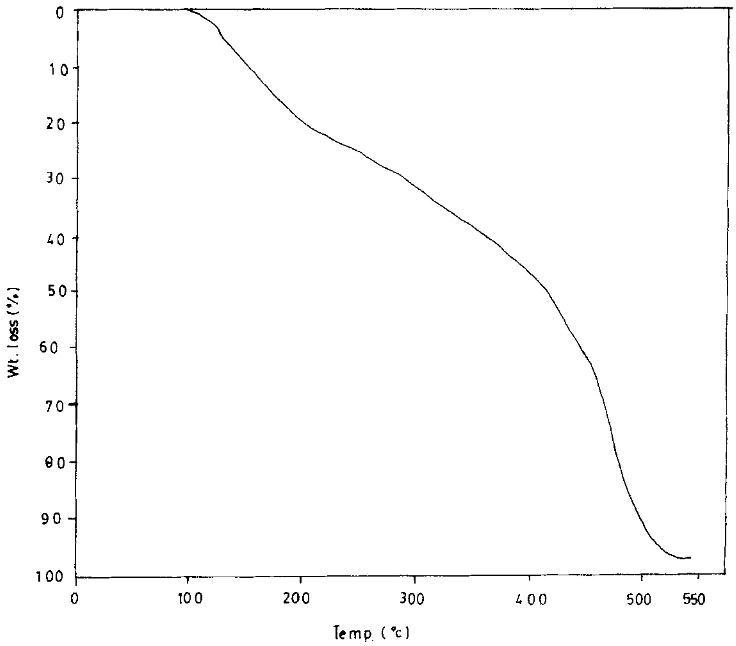
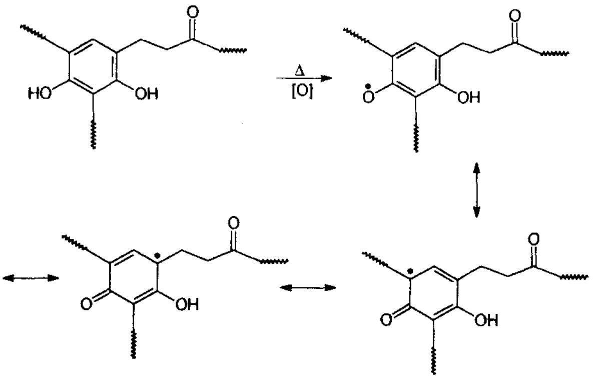


FIGURE 3 TG thermogram of AF:R:HMTA system 1:2:1 (———).

materials are less stable. This may be due to thermooxidation reactions in the polymer chain which arise due to the dehydrogenation of — OH groups and the formation of the new carbonyl groups of their acidic or quinoid type radicals [14] as shown in Scheme II.



SCHEME II

TABLE IV Mechanical and chemical properties of glass-reinforced AF:R:Hexamethylenetetramine (HMTA)

Composites [a] (*Molar ratio of AF:R:HMTA*)	*%Change on exposure to 25% (W/V) NaOH* [b]		*Density* $g\ ml^{-1}$	*Flexural strength (Mpa) (ASTM-D-790)*	*Compressive strength (Mpa) (ISO-method)*	*Impact strength (Mpa) (ASTM-D-256)*	*Rockwell hardness (R) (ASTM-D-785)*	*Electrical strength (in air) (kV/mm)*
	Thickness	*Weight*						
1:1:1	1.15	1.5	1.21	281	283	282	109	18.6
1:1.5:1	1.1	1.35	1.23	290	290	290	110	18.9
1:2:1	1.0	1.41	1.25	292	292	293	112	19.3

[a] Conditions Reinforcement: E glass cloth; plain weave, 25 mm; 10 ply. Resin content 40 ± 2 Wt%; curing temperature, 95 ± 3°C, time 2 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 mineral acid (25% V/V).

The glass reinforced composites based on AF – R – HMTA systems have also been prepared at 95 ± 3°C in the form of dark brown sheets. The specific gravity of all composites is in the range 1.21 – 1.25 (Tab. IV). Examination of chemical resistance test reveal that all composites have remarkable resistance to organic solvents and concentrated acid (25% V/V). However, the concentrated alkali (25% W/V) cause changes in their thickness and a weight loss of about 1.0 – 1.15. The composites had good mechanical properties, and the electrical strength of all the composites was in range of 18.3–18.9 kV mm^{-1}. It was also observed that the produced composites have better alkali resistivity than those of commercial novolac/resol based composites.

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