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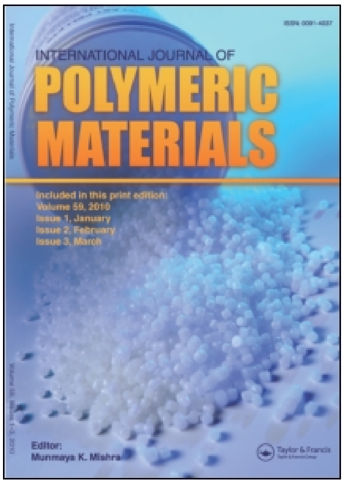

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Synthesis, Characterization and Glass Reinforced Composites of Acetone-Formaldehyde-m-Cresol Resins

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Synthesis, Characterization and Glass Reinforced Composites of Acetone-Formaldehyde-m-Cresol Resins

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

Keywords: Acetone-Formaldehyde (AF) resin; Acetone-Formaldehyde-m-cresol (AF-MC) 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 resinification 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.

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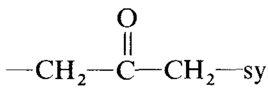
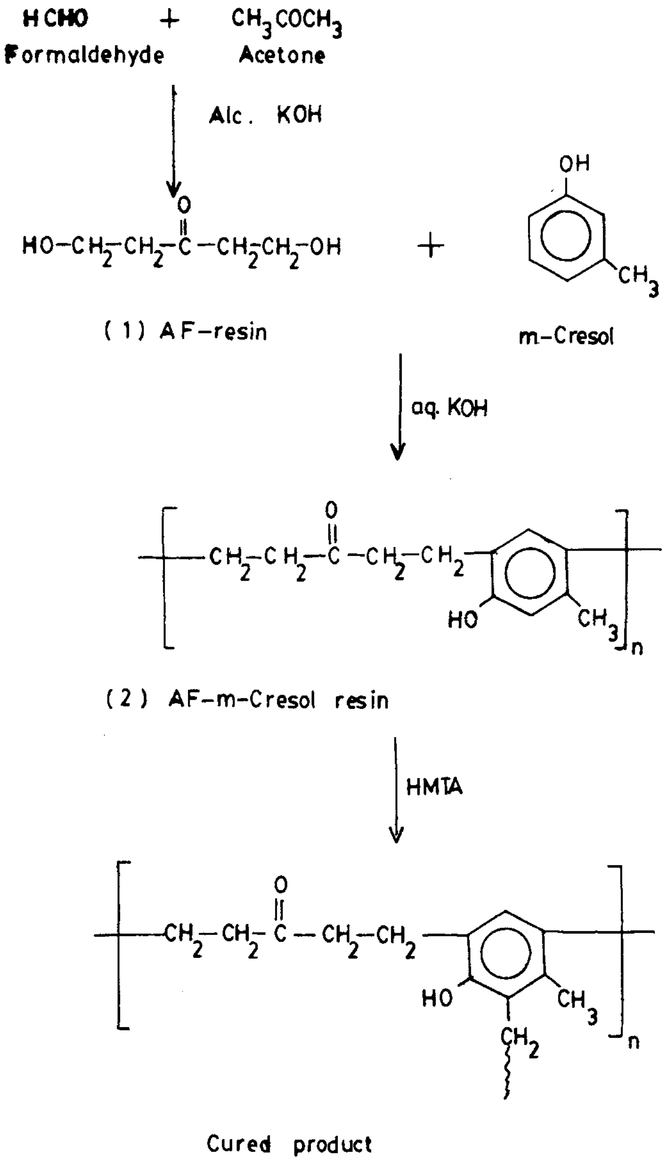
[6–8]. Like resol (having $-CH_2OH$ self curable groups) such AF resin (i.e. having $-CH_2OH$ groups) may afford the condensation with phenolic derivatives. The present authors have carried out the work in this direction [9]. In continuation of this work [9] (i.e. studies of AF-phenol condensation) the present communication comprises the synthesis and studies of AF-m-cresol condensation. The resins were studied for their curing characteristic with Hexamethylenetetramine on DSC. The glass reinforced composite study has also been carried out. The whole work is drawn in the Scheme I.

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 'in situ' reaction, the AF resin having active two $-CH_2OH$ groups is used for further condensation with m-cresol.

The AF-MC condensation product has the form of brown thick liquid. The freshly prepared products are soluble in most polar organic solvents, but on longer storage they slightly harden. It was observed that in absence of m-cresol, AF under similar condition remains relatively intact. It will, however, crosslink at elevated temperature (about 130–150°C). The elemental analyses of all the resins are consistent with the predicted structure (Scheme I). A typical IR spectrum of self cured AF-MC resin is shown in Figure 1. The IR spectra of all the three resins comprises important bands due to AF moiety and aromatic moiety. The broad bands appeared from 2900 to 3600 cm^{-1} with the inflections at 2890, 2950 and 3400 cm^{-1}. This is due to m-cresol groups. The first two inflections may be associated with asymmetric and symmetric stretching vibration of $-CH_3$, $-CH_2-$ and  $-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-$ systems. The bands at 750 and 810 cm^{-1} may be attributed to adjacent H-atoms or 1,2- or 1,4-substituted aromatic ring. The band at 1700 cm^{-1} may be attributed due to $>C{=}O$ group. Hence on the basis of these observations and the reactive sites present in the concerned monomers (i.e. AF and m-cresol) the most probable structure of such AF-MC resin is shown in Scheme I.


HCHO
+
CH3COCH3
Formaldehyde
Acetone
Alc. KOH
HO–CH2–CH2–C(=O)–CH2–CH2–OH
+
OH
CH3
(1) AF-resin
m-Cresol
aq. KOH
O
CH2–CH2–C–CH2–CH2
HO
CH3
n
(2) AF-m-Cresol resin
HMTA
O
CH2–CH2–C–CH2–CH2
HO
CH3
CH2
n
Cured product

SCHEME I

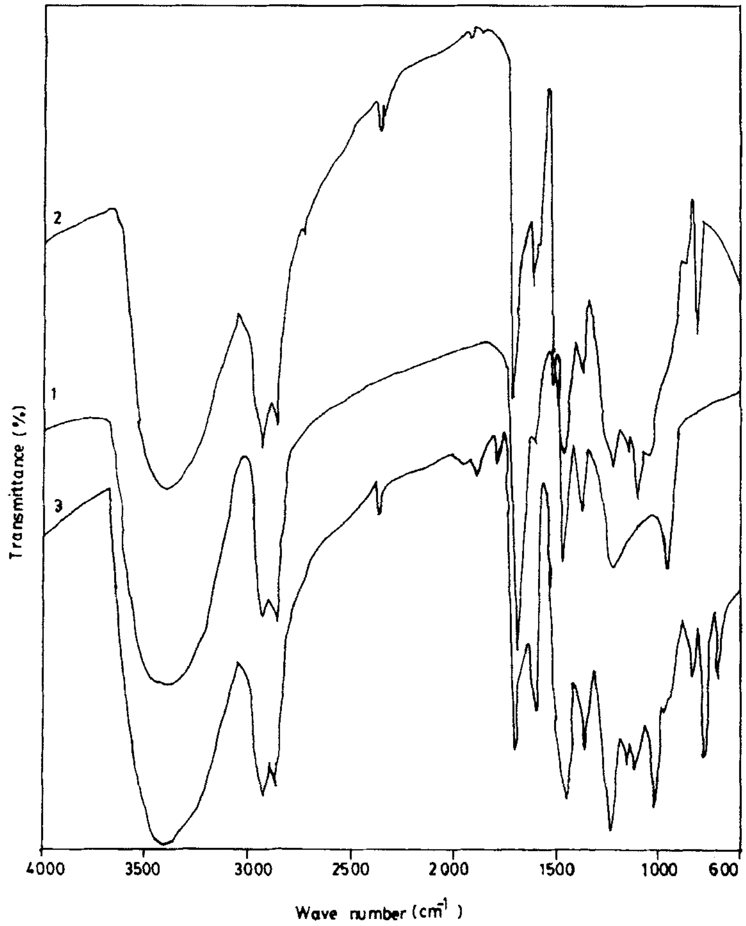


FIGURE 1 IR Sepctra of 1. AF resin (1), 2. AF-MC Resin (2), 3. AF-MC-HMTA resin (3).

The $\bar{M}n$ values of all three resins estimated by non-aqueous conductometric titration are shown in Table I. The values indicate that $\bar{M}n$ decreases with the increase in molar proportion of m-cresol.

Since the produced AF-MC resin can react with curing agents like Hexamethylenetetramine, the cure reaction of AF-MC-Hexamethylenetetramine (HMTA) was studied for the ratio of AF:MC:HMTA; 1:1:1, 1:1.5:1, 1:2:1. The data obtained from DSC scans are given in Table II. The DSC thermograms show, that all cured AF-

TABLE I Characterization of AF-MC resins

Molar ratio of AF:MC Resin system	*Elemental Analysis* *C(%)* *Calc.*	*Found*	*H(%)* *Calc.*	*Found*	*Non aqueous conductometric titration* $\overline{DP}$	$\overline{Mn}$
1:1	75.79	75.6	7.36	7.2	8	1500
1:1.5	75.79	75.7	7.36	7.1	5	900
1:2	75.79	75.6	7.36	7.3	2.2	420

TABLE II Curing characteristics of AF-MC-Hexamethylenetetramine (HMTA) system at 10 K min^{-1}

Molar ratio of AF:MC: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	140	149	182.00	44.1	1.6
1:1.5:1	137	145	178.20	44.52	1.8
1:2:1	135	143	175.00	44.71	1.7

MC-HMTA systems gave a single exotherm peak in the range of 135 to 182°C. 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 thermograms. The activation energy (E_a) values for such system (Table II) do not vary widely, which indicates that AF-MC 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 K min^{-1}.

To obtain information about the properties of unreinforced cross-linked materials, cured samples were prepared using the same proportions and temperatures as presented in Table III. The unreinforced cured AF-MC-HMTA samples were prepared at 145 ± 3°C for 4 hours. These products are dark orange in color and 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-MC resin. The only noted difference is that the spectra comprise more intense bands due to —CH_2—group and a

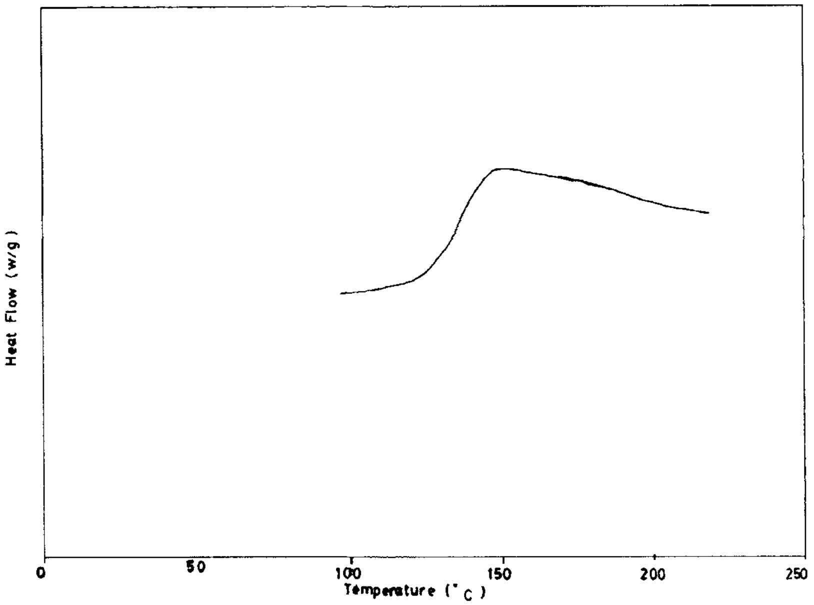


FIGURE 2 DSC thermogram of 1. AF:MC:HMTA (1:1:1) system.

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

Molar ratio of AF:MC:HMTA resin system	*Percent weight loss at °C from TGA*					
	150	*200*	*300*	*400*	*5000*	*550*
1:1:1	1.5	35.0	43.5	52.0	74.0	98.5
1:1.5:1	1.5	34.0	46.5	53.5	70.5	97.0
1:2:1	2.5	27.5	36.5	46.5	85.0	94.5

weak band around 1940 cm^{-1} due to 1,2,3,5-tetra substituted benzene ring system [10]. Typical TG curves of unreinforced crosslinked materials are 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 150°C. Degradation becomes faster between 400 and 500°C. The weight loss was about 94–99% at 550°C in all cases.

The glass reinforced composites based on AF-MC-HMTA systems have also been prepared at 145 ± 3°C in the form of dark brown sheets.

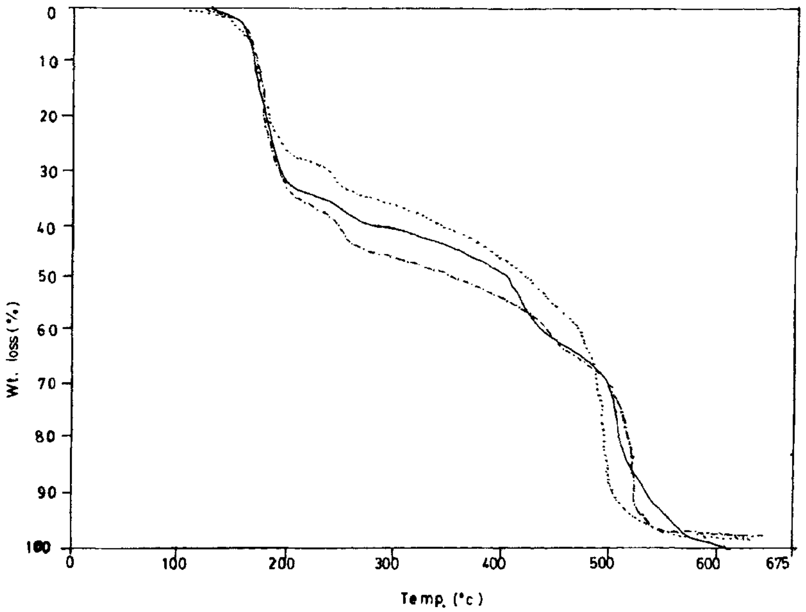


FIGURE 3 TG thermogram of-AF:MC:HMTA Systems 1. 1:1;1 (————), 2. 1:1.5:1 (—·—·—·—), 3. 1:2:1 (-------).

The specific gravity of all composites is in the range 1.20 to 1.24 (Tab. IV). Examination of chemical resistance test reveals 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 0.8–1.5%. The composites had good mechanical properties, and the electrical strength of all composites was in the range of 18.4–19.4 kV mm^{-1}. It was also observed that the produced composites have better alkali resistivity than those of commercial novolac/resol based composites.

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].

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

Composites[a] *(Molar ratio of AF:MC:HMTA)*	*% Change on exposure to 25% (W/V) NaOH*[b]		*Specific gravity*	*Flexural strength (mPa)*	*Compressive strength (mPa)*	*Impact strength (mPa)*	*Rockwell hardness*	*Electrical strength* $(kV\,mm^{-1})$
	Thick-ness	*Weight*						
1:1:1	1.1	1.4	1.20	278	281	279	104	18.4
1:1.5:1	0.9	1.3	1.21	289	288	278	105	19.0
1:2:1	0.8	1.5	1.24	290	289	286	107	19.4

a: Reinforcement, E glass cloth, Plain weave, 25 mm, 10 Ply., Resin content: 40 ± 2 wt. %; molar ratio: AF-MC:H = 1:1 (mol/mol); Curing temperature: 145 ± 3°C; Time 10 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 acid (25% V/V HCl).

Synthesis of Acetone-Formaldehyde-m-Cresol Resin

The AF resin and m-cresol in a molar ratio of 1:1, 1:1.5 and 1:2 were refluxed in the aqueous solution of 2.5% KOH of the total weight for 2 hrs. The supernatant aqueous layer was decanted and resulted resin was washed with a large amount of distilled water to remove unreacted reactants. All three resins obtained were thick brown liquids. The yield were 82 to 92%. The details about all three resins are furnished in Tables I and II.

Composite Fabrication

A typical method of fabrication for composites is given below.

A suspension of freshly prepared AF-MC resin (II) and Hexamethylenetetramine in tetrahydrofuran was prepared and was stirred well for 5 min. The suspension mixture was applied with a brush to a 250 mm × 250 mm fibre glass 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 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 100° for 4 hrs. and post cured at $145 \pm 3°C$ for 6 hrs. 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 contents were estimated by means of a Carlo Erba C, H, N, S, P elemental analyzer (Italy). The IR spectra were taken in KBr pallets using a NICOLET-400 DR FTIR spectrophotometer.

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

Curing of AF-MC: 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 ($\Delta H = 28.45\,\mathrm{J/g}$) with known heats of fusion. Curing was carried out using a single heating rate ($10\,\mathrm{K\ min^{-1}}$). The sample weight for this investigation was in the 4 to 5 mg range an empty cell was used as a reference.

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

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

CONCLUSION

The produced products have the following advantages:

i) Ease of preparation of AF as well as AF-MC resins.
ii) The resultant AF-MC-HMTA GRC product has better alkali resistance than those of commercial novolac/resol based GRC.
iii) Ease of glass reinforcement. The laminate have good mechanical properties.

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References

[1] Borodkina, N. I. and Frolov, S. S. (1963). *Zh. Prikl. Khim.*, **36**(2), 408–15.
[2] Sarnitskaya, S. Z. and Bronovitskii, V. E. (1973). VINITI (Rus.), 5732–73.
[3] Hayano, H. and Fujita, K. (1978). Japan Kanzei chuo Bunsekishoho, **18**, 89–100.
[4] Skoda, A., Mravec, D. and Ilavsky. (1989). *J. Chem. Prum.*, **39**(11), 575–85.
[5] VEB Farbenfabrik Wolfen. (1966). Belg. 657, 577; *Chem. Abst.*, **65**, 2128_f.
[6] Okay, O. and Schindlbauer, H. (1984). *Angew. Makromol. Chem.*, **127**, 203–9.
[7] Kuznetsova, E. P., Starkova, I. M., Vakulenko, V. A., Kurochkina, R. N. and Lyubimova, E. A. (1985). USSR SU **1**, 155, 605.

[8] Rasulov, A. A., Fazilov, T. I., Lem, R. A. and Salikhov, B. G. (1986). USSR SU **1**, 217, 872.

[9] Patel, H. S. and Dixit, B. C. (1997). *High. Perform. Polym.* (In press).

[10] Young, C. W., DuVall, R. B. and Wright, N. (1951). *Analyt. Chem.*, **23**, 709.

[11] Chatterji, S. K. and Agarwal, V. B. (1971). *J. Polym. Sci.*, **Part A-1** (9), 3225.

[12] Patel, H. S. and Patel, H. D. (1992). *High Perform. Polym.*, **4**, 35.