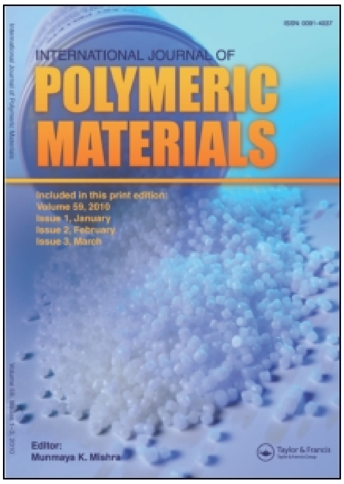

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Synthesis, Characterization and Glass-reinforced Composites of Trimethylolmelamine-phenol Resins

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Trimethylolmelamine (TMM) has been prepared and characterized. The TMM condensed with phenol in the presence of alkali catalyst at the varying ratios of TMM: Phenol, *viz.* 1 : 1, 1 : 1.5 and 1 : 2. The resultant triazine ring containing resins (TMMP) were characterized by elemental analyses, IR spectral studies and thermogravimetry. The isothermal curing study of TMMP resin with hexamethylenetetramine (HMTA) was also carried out. Finally, the glass-reinforced composites based on TMMP-HMTA system have also been prepared and characterized for synergetic property combination of both MF and PF.

Keywords: Trimethylolmelamine synthesis; Trimethylolmelamine-phenol resins; Glass-reinforced composites

INTRODUCTION

The number of patents (nearly 400) available on use of Trimethylolmelamine (TMM) reflects the commercial importance and interest of the molecule. The TMM have found many applications, for example, in crease proofing and improving durability of cotton, silk, nylon and polyester fabrics, for improving heat resistance of fabrics, as fire proofing agents *etc.* [1–4]. Since the MF resin is well known polymeric material for industrial applications [5]. The merging of MF and PF

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type structure has not been developed so far. Hitherto only once instance blending of MF and PF has been reported technically [6]. It is also reported that melamine act as selective catalyst in the reaction of phenol with formaldehyde [7]. Like resol (having —CH_2OH self-curable group), the TMM may afford condensation with phenolic derivatives through —CH_2OH group. Hence, it was thought interesting to explore the field of TMMP condensation in order to get synergetic combinations of both melamine-formaldehyde and phenol-formaldehyde.

The present paper comprises the synthesis and characterization of TMM and subsequent reaction with phenol. The resulting resin was

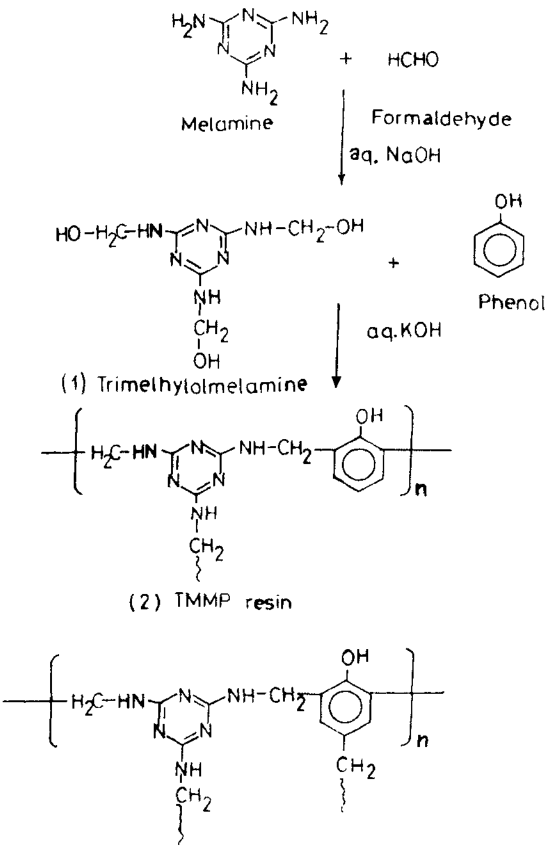

FIGURE 1 Trimethylolmelamine-phenol resin.

cured by hexamethylenetetramine with isothermal curing of resin [8]. Finally, the glass reinforcement of MFP-HMTA has also been studied, the reaction is shown in Figure 1.

EXPERIMENTAL

All the chemicals were used of laboratory grade.

Synthesis of Trimethylolmelamine

This was prepared by slight modification of method reported [9]. About 267 part of 37% aqueous formaldehyde (3.3 mole) is charged into a three necked flask and its pH was adjusted to about 8 with 1N sodium hydroxide. 126 part of melamine (1 mole) is then added, the mixture is heated with agitation until all the melamine is dissolved. It requires temperature around 75°C. The resulting syrup is discharged into tray and immediately cooled after solidified it is broken into lumps and dried at about 50°C for approximately 10 hrs to moisture content of 2–3%. The water soluble TMM was obtained by spray drying of resultant syrup [10]. Analysis of compound is shown in Table I.

TABLE I Analysis of Trimethylolmelamine (TMM)

Molecular formula: $C_6H_{12}N_6O_3$			
Elemental analysis:	%C	%H	%N
Calc.	33.33	5.55	38.88
Found	32.30	5.40	38.80
Solubility:		Soluble in water (spray dried product)	
Number of Methylol group:			$3.1 \approx 3$
Storage Capacity:			Stable for several months
IR Features:			
vCH$_2$ of —CH$_2$—OH:	2959 cm^{-1}		
vOH:	3335 cm^{-1}		
vC—O of —CH$_2$OH:	991.0 cm^{-1}		
Melamine characteristic peak:	1602, 816 cm^{-1}		
vNH (sec):	3247 cm^{-1}		

TABLE II Characterization of TMMP resins

Molar ratio of TMM : P resin system	*Nature of resin*	*Elemental analysis*						*Efflux viscosity (S)*[a]	*DP*[b]	$\overline{M}_n$
		% C		*% H*		*% N*				
		Calc.	*Found*	*Calc.*	*Found*	*Calc.*	*Found*			
1 : 1	Yellowish semisolid	56.03	55.7	5.06	4.93	32.68	32.27	–	9	2313
1 : 1.5	Yellowish thick liquid	56.03	55.90	5.06	4.97	32.68	32.34	52	6	1542
1 : 2	Reddish yellow thick liquid	56.03	55.72	5.06	5.13	32.68	32.14	22	3	771

[a] Efflux viscosity measured using floe cup type B-5 (Bs 1733).
[b] Measured using non-aqueous conductometric titration.

TABLE III Isothermal curing study* of the TMMP-HMTA system

Molar ratio of TMM:P:HMTA resin system	*Gel time*		*Peak exotherm temperature (°C)*
	Min	*Sec*	
1:1:0.5	6	10	158
1:1.5:0.5	6	30	153
1:2:0.5	6	50	152
1:1:0.25	7	10	155

*Performed in constant temperature bath at 145 ± 2°C.

TABLE IV TGA of unreinforced TMMP:HMTA cured system

Molar ratio of MF:P:HMTA resin system	*Percentage weight loss at given temperature (°C)*				
	300	400	500	600	700
1:1:0.5	4.2	10.6	33.2	67.1	97.2
1:1.5:0.5	4.9	9.7	28.8	64.5	96
1:2:0.5	5.7	11.8	31.3	62.5	93.0

Synthesis of Trimethylolmelamine-phenol Resin

The trimethylolmelamine (1) and phenol in a molar ratio of 1 : 1, 1 : 1.5 and 1 : 2 were refluxed in the aqueous solution of 3% KOH of total weight for 2.5 hrs at 110°C. The reaction mass was allowed to cool to the room temperature. The upper water layer was decanted followed by washing of resultant resin by large amount of distilled water to remove unreacted material. The water was removed by vacuum distillation. All three resins obtained (2) were thick yellowish to reddish yellow clear liquid. The yield was 85% to 91%. All details about resin were furnished in Tables II and III.

COMPOSITE FABRICATION

A typical method of fabrication is given below:

Suspension of freshly prepared TMMP resin and HMTA in tetrahydrofuran was stirred well for 5 min the mixture was applied with a brush to a 200 × 200 mm fiber glass cloth and the solvent was allowed to evaporate. The ten dried prepregs prepared in a similar way were stacked one over top of another and pressed between steel plates using Teflon sheet as mold releasing agent. It was then kept in an oven maintained at 130°C. Initially normal contact pressure was applied and at the gel point the plates were clamped to develop a pressure of about 100 psi and after 1 hrs temperature of oven increased to 155 ± 5°C for post curing about three more hours. The composite so obtained was cooled to 50°C before the pressure was released. Test specimens were made by cutting the composites and machining them to final dimensions.

MEASUREMENTS

The C, H and N contents of all the resins were estimated by means of a Carlo Erba elemental analyzer (Italy). The IR spectra were taken using Nicolate-400D FTIR spectrophotometer with KBr as reference.

Non-aqueous conductometric titration of MFP resin was carried out in pyridine against standard sodium methnolate in pyridine as titrant. The $\overline{M}_n$ of each sample was calculated according to the method reported in [11, 12].

Cured sample was subjected to thermogravimetric analysis (Du pont 950 thermogravimetric analyzer) in air at a heating rate of 10 K/min^{-1}.

Chemical resistance of composite sample having dimension 25 mm × 1 mm was measured according to ASTM and give D543. The data are included in Table V.

The measurements of flexural strength, compressive strength, impact strength and hardness were carried out according to method of ASTM D770, ASTM D675, ASTM D256 and ASTM D785 respectively. The dielectric strength was measured on high voltage tester machine-oil test set.

All the mechanical and electrical properties of composites are furnished in Table V.

TABLE V Mechanical and electrical properties of glass-reinforced TMMP : HMTA composites

Composites[a] *molar ratio of*	*Chemical resistance*[b] *% change in*		*Density*	*Flexural strength*	*Compressive strength*	*Impact strength*	*Rockwell hardness*	*Electrical strength in air*
TMM : P : HMTA	*Thickness*	*Weight*	*(gm/cm^3)*	*(MPa)*	*(MPa)*	*(MPa)*	*(R)*	*(kV/mm)*
1 : 1 : 0.5	0.7	1.1	1.43	300	294	312	118	19.4
1 : 1.5 : 0.5	0.5	1.3	1.46	304	306	311	115	20.1
1 : 2 : 0.5	0.8	1.2	1.40	305	306	313	119	20.3

[a] Reinforcement: 'E' type glass cloth, plain weave, 7 mil, ten layers; resin content: 40 ± 2 wt.%; curing temperature: 155 ± 5°C; curing time 6 hrs; curing pressure 100 Psi; composite size: 200 mm × 200 mm × 1.87 mm.

[b] Chemical resistance to 25% w/v NaOH; composites are unaffected by organic solvents and 25% v/v HCl.

RESULTS AND DISCUSSION

Trimethylolmelamine was prepared by slight modification of previously reported method [9] the resultant compound is white crystalline powder. All the properties are given in Table I. Bearing

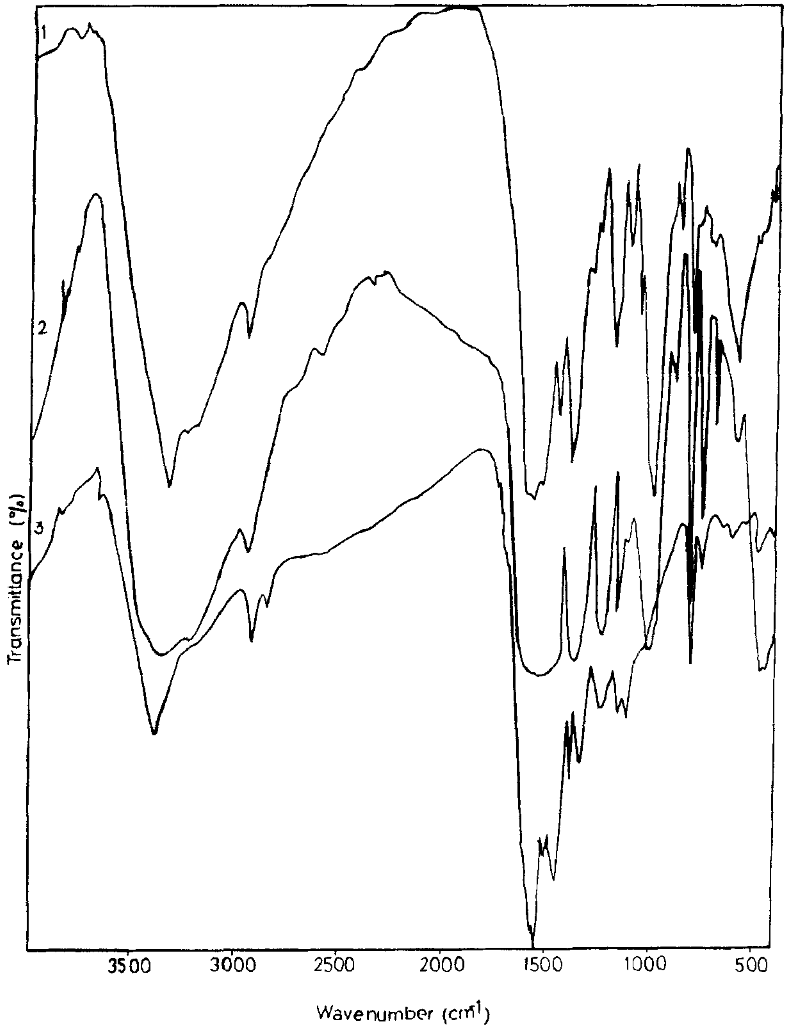

FIGURE 2 IR spectra of 1. TMM, 2. TMMP resin, 3. TMMP-H.

in mind that resol (commercially base catalyzed A-stage PF condensates) are functioning *in-situ* post curing through —CH_2OH group. The produced TMM was condensed with varying ratio phenol.

TMMP condensates were obtained in the form of clear yellowish semisolids to thick liquids. They (freshly prepared) are soluble in most of polar organic solvents. On longer storage they harden in air and also in vacuum. Efflux viscosity study of only liquid resin of TMMP has been included in Table II. It was observed that in the absence of phenol TMM remains relatively intact under similar conditions. However, it cross-linked only at elevated temperature (155 ± 5°C). Elemental analyses of all the resins is consistent with the structure predicted (Fig. 1). A typical IR spectrum of TMMP resin is shown in Figure 2. The IR spectra depicted in figure comprises the melamine characteristic bands. The shoulder appears at around 1590 cm^{-1} and sharp band at 823 cm^{-1} appears due to N-substituted melamine moiety. The spectrum of TMM shows sharp peaks at 3335 cm^{-1}, 3247 cm^{-1} and 2959 cm^{-1} due to alcoholic —OH, secondary amine and —CH_2— respectively. It also shows very strong sharp peak at 1001 cm^{-1} due to C—O stretching of —CH_2OH group. In the spectrum of TMMP resin, broad band appeared from 3150 to 3450 cm^{-1} with inflections at 3368 cm^{-1} and 3234 cm^{-1} due to phenolic group and secondary —NH respectively. The slight inflection at 2885 cm^{-1} and 2700 cm^{-1} is due to CH stretching indicates presence of very little free formaldehyde in the uncured TMMP resin. The band at 756 cm^{-1} and 832 cm^{-1} may be attributed to adjacent H atoms or 1,2 or 1,4- substituted aromatic ring. The absent of very strong band around 1000 to 1050 cm^{-1} in the spectrum of cured TMMP resin indicates absence of any free —CH_2OH group. Hence on the basis these observation and the reactive site present in the monomers concerned (*i.e.*, TMM and Phenol), the most probable structure of such TMMP resin shown in Figure 1.

The $\overline{M}_n$ value of all three resins estimated by non-aqueous conductometric titration are shown in Table II. The value indicates decrease in $\overline{M}_n$ with increase in molar proportion of phenol.

As the TMMP resin produced can react with curing agent HMTA, the isothermal curing study of all three resin shows peak exotherm temperature in the range 155 ± 3°C. To obtain information about the properties of unreinforced cross-linked materials, cured sample were prepared using the same proportions and temps as presented in Table III. The unreinforced cured TMMP-HMTA samples were prepared at 155 ± 3°C for 4 hrs, are reddish yellow in color and are brittle materials. They are insoluble in all common organic solvents. The typical TG curves of unreinforced cross-linked materials are shown in Figure 3. The TG data shown in Table IV. It shows that they all degrade in single steps up to 250°C, the polymer remains almost intact degradation becomes faster between 550 to 650°C. The weight loss was about 93 to 98% at 700°C in all cases. The %wt loss decreases with increasing molar ratio of TMM : P. The specific gravity of all composite is in the range of 1.4 – 1.46 g/cm^3 and indicates no appreciable change in specific gravity. Examination of chemical resistance test reveals that all composites have remarkable resistance to organic solvents and concentrated HCl (25% v/v). However the concentrated alkali (25% w/v) causes changes in their thickness and weight of about 1%. The composites have found good mechanical properties (Tab. V). The dielectric strength of all the composites has been found to be in the range of 19.4 – 20.3 Kvmm^{-1}. It was also observed

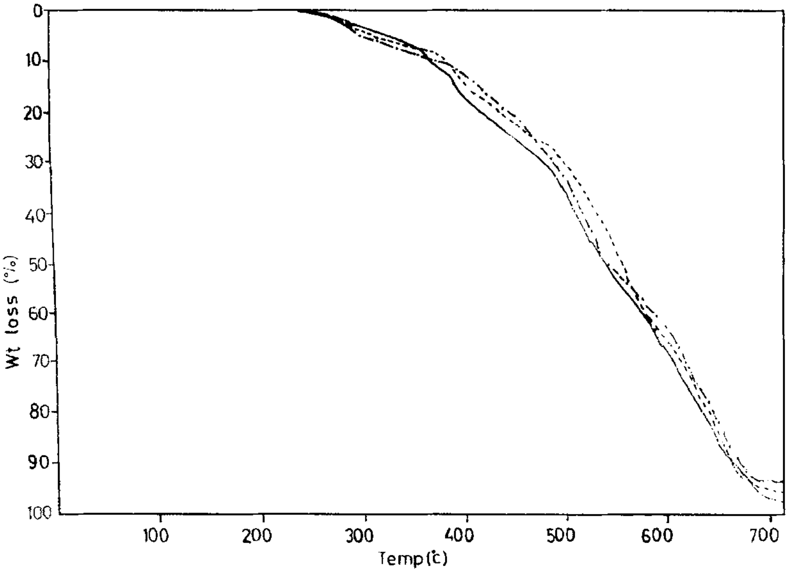

FIGURE 3 TG thermograms of TMMP H System, 1 : 1 : 0.5 (——), 1 : 1.5 : 0.5 (- - - -), 1 : 2 : 0.5 (–·–·).

that the produced composites have better resistivity than those of commercial novolak/resol based composites.

CONCLUSION

The overall advantages of glass-reinforced composites of TMMP resin are as follows:

1. Resistance to deformation and degradation at temperature of the order of 250°C.
2. Composites with better mechanical properties, chemical resistance and good dielectric strength than commercially available PF resin.

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