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Synthesis, Characterization and Glass - Reinforced Composites of N,N'-Dimethylolthiourea – *m*-Aminophenol Resin

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Abstract: N,N'-Dimethylolthiourea (DMTU) resin having the methylol group ($-\text{CH}_2\text{OH}$) has been prepared and characterized. The condensation of DMTU resin with *m*-aminophenol was carried out in the presence of alcoholic alkali catalyst at varying ratios of DMTU: mAP, namely 1:1, 1:1.5 and 1:2. The resultant DMTUmAP resin was 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 DMTUmAP resin with hexamethylenetetramine (HMTA) was monitored by differential scanning calorimetry (DSC) and kinetic parameters were evaluated. Glass-reinforced composites based on the DMTUmAP-HMTA system have also been prepared and characterized.

Key words: N,N'-Dimethylolthiourea, *m*-aminophenol, hexamethylenetetramine, glass reinforced composites.

Introduction

The study of N,N'-Dimethylolthiourea (DMTU) resinification is well established¹⁻⁴. The DMTU resin, having two $-\text{CH}_2\text{OH}$ groups, have found many applications, for example in corrosion protection of building materials and metallic surfaces, polymerisation accelerators, decolouration of hair, flame resistant agent, coating, gelling agent, cross-linking agents, adhesives, binders, finishing agents⁵⁻⁹. Like resol (having $-\text{CH}_2\text{OH}$ self-curable groups) such resin (*i.e.* having $-\text{CH}_2\text{OH}$ groups) may afford condensation with *m*-aminophenol. Hence it was thought interesting to explore the field of DMTUmAP condensation.

The present communication comprises the synthesis, characterization of DMTU resin and its post-reaction with *m*-aminophenol. The resulting resin was studied for their curing characteristic with hexamethylenetetramine (HMTA) on DSC. Glass reinforcement of DMTUmAP-HMTA has also been studied. The whole process is shown in **Scheme 1**.

Scheme 1.

Experimental

All the chemicals used were of laboratory grade.

Synthesis of Dimethylol thiourea (DMTU) resin

These were prepared by method reported.¹ A mixture of thiourea (1 mole), formaldehyde (2 mole) and 2.5% alcoholic KOH was heated at 50⁰ C with constant stirring for 75 minutes. The resulting mixture was cooled at room temperature. The so-called resin obtained was in the form of colourless thick liquid. It was neutralized by acetic acid and dried azeotropically. The yield was 90%. Analysis of DMTU resin is given in **Table 1** and **Table 2**.

Synthesis of DMTU - m-Aminophenol (DMTUmAP) resin

The DMTU resin and m-aminophenol 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 two hours. The resin prepared, as method reported in¹⁰. The supernatant aqueous layer was decanted and the resultant resin was washed with large amount of distilled water to remove unreacted material. The water was removed by vacuum. All three resin obtained were thick reddish brown liquids. The yields were 85 to 90%. Details of all three resins are given in **Table 1** and **Table 2**.

Table 1. Elemental analysis of N,N'-Dimethylolthiourea – m-Cresol resin

S. No.	Resin sample	Nature of Resin	Elemental Analysis			
			Calculated		Found	
			%C	%H	%C	%H
1	DMTU	Colourless Viscous liquid	26.47	6.77	24.00	6.00
2	DMTUmC-1	Reddish brown thick liquid	64.39	6.34	64.18	5.89
3	DMTUmC-2	Reddish brown liquid	72.50	5.11	72.33	5.01
4	DMTUmC-3	Reddish brown liquid	73.54	5.22	73.22	5.03

Table 2. Physical parameters of N,N'-Dimethylolthiourea and N,N'-Dimethylolthiourea – m-Cresol resin

S.No.	1	2	3	4
Resin sample	DMTU	DMTUmC-1	DMTUmC-2	DMTUmC-3
Efflux [#] Viscosity	25	40	36	25
$\overline{D_p^*}$	---	14	12	8
$\overline{M_n}$	---	2660	2460	1640
Solubility	All resin samples were insoluble in water. Miscible in solvents like alcohols, acetone, pyridine etc.,			
Number of OH groups	Estimated by non- aqueous Conductometric titration and by – OH group determination for all resin samples were approximately equal to two.			

Time measured by flow cup 'B'5 (BS 1733) * Degree of polymerization.

Composite fabrication

A suspension of freshly prepared DMTUmAP resin (2) and HMTA in acetone was prepared and was stirred well for 3 minutes. The suspension mixture was applied with a brush to a 250mm x 250mm fibre-glass cloth and the solvent was allowed to evaporate. The 10 dried prepegs 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 prepeg stacks were cured by heating at 100°C for 4 hours and post-cured at $110 \pm 5^\circ\text{C}$ for 8 hours in air circulation oven. 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 and H contents were estimated by means of a Carlo Erba (Italy) elemental analyser. The IR spectra were taken in KBr pellets using Nicolet-400 DR FTIR spectrophotometer.

Non-aqueous conductometric titration of DMTU and DMTUmAP resin was carried out in pyridine against standard sodium methnolate in pyridine as titrant. The $\overline{M}_n$ value of each sample was calculated according to the methods reported¹¹. Curing of the DMTUmAP-HMTA system was carried out by differential scanning calorimetry. A Du Point 900 DSC was for this study. The instrument was calibrated using standard materials 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 4 to 5 mg range; an empty cell was used as a reference. Cured samples were subjected to thermogravimetric analysis (Universal V2.6D TA instruments) in air at a heating rate of 10^0 C min^{-1} .

All the chemical, mechanical and electrical tests of the prepared composites were conducted according to ASTM methods following the method reported¹².

Results and Discussion

DMTU condensation was performed by previous reported method¹. The resultant DMTU resin is a transparent viscous liquid. All the properties are given in **Table 1** and **Table 2**. The resin having active $-\text{CH}_2\text{OH}$ group is used for condensation with m-aminophenol, bearing in mind that (commercially base catalysed A-stage P-F condensate) resols are functioning in *situ* post-curing. DMTU condensates were obtained in the form of reddish brown thick liquids. They (freshly prepared) are soluble in most polar organic solvents and also water. On longer storage they harden. Efflux viscometry study of only the liquid resin of DMTUmAP has been attempted and the data are included in **Table 2**. It was observed that in the absence of m-aminophenol, DMTUmAP remains relatively intact under similar conditions. However, it will be cross-linked only at elevated temperature ($110\text{--}135^\circ\text{C}$). Elemental analysis of all the resin is consistent with the structure predicted (**Scheme 1**). A typical IR spectrum of self cured DMTUmAP resin was observed. The IR spectra of all three resin comprise important bands due to the DMTUmAP moiety and aromatic moiety. The broad bands appeared from 3390 to 2740 cm^{-1} with inflections at 3360 , 3030 and 3290 cm^{-1} is due to the polymeric groups. The first two inflections and the 1620 cm^{-1} may arise from the asymmetric and symmetric vibration of $-\text{NH}$ and $-\text{HN}-\text{CS}-\text{NH}-$ systems. substituted aromatic rings. The band at 1170 and 1180 cm^{-1} may be attributed to the group. The band at 2945 cm^{-1} may be attributed to $-\text{CH}_3$ stretching. Hence on the basis of these observations and the reactive site present in the monomer concerned (*i.e* The bands at 775 and 845 cm^{-1} may be attributed to adjacent H- atoms or 1,2- or 1,4-. DMTU and m-cresols) the most probable structure of such DMTUmAP resin may be shown in **Scheme 1**.

The $\overline{M}_n$ values of all three resin estimated by non- aqueous conductometric titration are shown in **Table 2**. The values indicate that decreases with increase in molar proportion of m-aminophenol.

As the DMTUmAP resin produced can react with curing agent like HMTA the cure reaction of DMTUmAP-HMTA was studied for DMTU: mAP : HMTA ratios of 1 : 1 : 1, 1: 1.5 : 1 and 1 : 2 : 1. The data obtained from DSC scans are given in **Table 3**. From the DSC thermogram, it is seen that all the DMTUmAP-HMTA curing systems gave a single exotherm peak in the range of 95 to 138°C . 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 a system (**Table 3**) do not vary widely, which indicates DMTUmAP is more reactive towards the HMTA. The kinetic parameter E_a (activation energy) was 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 10^0 C .

Table 3. Curing characteristics of the DMTUmC-HMTA systems at 10 K min^{-1}

S. No.	Resin sample	Kick-off Temp., T_i ($^\circ\text{C}$)	Peak Temp., T_p ($^\circ\text{C}$)	Final Temp., T_f ($^\circ\text{C}$)	Activation Energy (E_a) (KJ mol^{-1})
1	DMTUmC-1	100	130	165	90.76
2	DMTUmC-2	98	127	163	89.76
3	DMTUmC-3	96	125	160	87.44

To obtain information about the properties of unreinforced crosslinked materials, cured samples were prepared using the same proportions and temperatures as presented in **Table 3** and **Table 4**. The unreinforced cured DMTUmAP-HMTA samples were prepared at $110 \pm 5^\circ \text{C}$ for 8 hours, are dark brown in colour and are brittle materials that form powder under normal hand pressure. They are insoluble in all common organic solvents. IR spectra of all three cured products resemble in most aspects those of DMTUmAP resin, however the spectra comprise more intense bands due to the $-\text{CH}_2$ group and a weak band around 1940 cm^{-1} due to the 1,2,3,5- tetra substituted benzene ring system¹³⁻¹⁴. Typical TG curve of unreinforced crosslinked materials. The TG data are shown in **Table 4**. It shows that they all degrade in a single step, and their decomposition starts around 271°C . The degradation becomes faster between 200 and 300°C . The weight loss was about 74 - 78 % at 750°C in all cases. The degradation of all three systems in the range of 500 to 750°C indicates that the weight loss decreases with increase in the molar ratio of DMTUmAP systems. This may be due to *in situ* reaction of fragments degraded at an earlier stage.

Glass reinforced composites based on DMTUmAP-HMTA systems have also been prepared at $110 \pm 5^\circ \text{C}$, and are in the form of reddish brown sheets. The specific gravity of all composites is in the range 1.23 to 1.26 (**Table 5**). Chemical resistance tests reveal that all composites have remarkable resistance to organic solvents and concentrated acid (25% V/V). However, the concentrated alkali (25% W/V) causes changes in their thickness and weight of about 1.2 to 1.4%. The composites are found to have good mechanical properties (**Table 5**). The electrical resistivity of all the composites has been found to be in the range of 2.04×10^7 to $4.23 \times 10^7 \text{ Ohms.cm}^{-2}$.

Table 4. TGA of unreinforced DMTUmC : HMTA cured materials

S.No.	Resin sample	Percent weight loss at given temp. from TGA					
		200° C	300° C	400° C	500° C	600° C	750° C
1	DMTUmC-1	6.62	13.19	21.06	48.33	59.82	80.23
2	DMTUmC-2	7.37	13.82	20.68	47.05	58.89	81.43
3	DMTUmC-3	8.27	14.19	20.21	46.87	57.87	82.23

Table 5. Mechanical and chemical properties of glass-reinforced DMTUmC-HMTA composites

S. No.	Resin ^a sample	% change on exposure to 25% (W/V) NaOH ^b		Specific Gravity	Flexural strength	Impact strength	Rockwell hardness	Electrical Resistivity (Ohms/cm ²) x 10 ⁷
		Thickness	Wt		Kg/cm ²	Kg/cm ²		
1	DMTUmC-1	1.0	1.3	1.24	245	11.75	124	2.89
2	DMTUmC-2	1.1	1.3	1.28	250	12.66	130	4.76
3	DMTUmC-3	1.2	1.5	1.30	253	12.77	132	5.73

^a Reinforcement, E glass cloth, plain weave, 25 mm, 10 ply. Resin content: $40 \pm 2 \text{ wt\%}$. Molar ratio DMTUmC: HMTA = 1 : 1 (mol/mol). Curing temperature $130 \pm 5^\circ \text{C}$, time 8 h. Pressure 60-70 psi. Composite size 250 mm x 250 mm x 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).

It was also observed that the produced composites have better alkali resistivity than those of commercial novolac/resol based composites.

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