Synthesis, Characterization and Glass - Reinforced Composites of Thiourea - Formaldehyde - Phenol Resin

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Abstract N,N'-Dimethylol thiourea-formaldehyde (DMTUF) resin having the methylol group (CH_2OH) has been prepared and characterized. The condensation of DMTUF resin with Phenol (P) was carried out in the presence of alcoholic alkali catalyst at varying ratios of DMTUF : P, namely 1:1, 1:1.5 and 1:2. The resultant DMTUFP resin was characterized by elemental analysis, IR spectral studies, number average molecular weight (M_n) estimated by non-aqueous conductometric titration, and thermo gravimetry. The curing study of DMTUFP resin with hexamethylene tetramine (HMTA) was monitored by differential scanning calorimetry (DSC) and kinetic parameters were evaluated. Glass-reinforced composites based on the DMTUFP-HMTA system have also been prepared and characterized.

Key words N,N'-Dimethylol thiourea-formaldehyde, dimethylol thiourea-formaldehyde phenol, number average molecular weight, glass reinforced composites..

Introduction

The study of N,N'-Dimethylol thiourea-formaldehyde (DMTUF) resinification is well established.¹⁻⁷ The DMTUF resin, having two CH_2OH groups, have found many applications, for example in corrosion protection of building materials and metallic surfaces, polymerisation accelerators, decolourating hair, flame resistant agent, coating, gelling agent, cross-linking agents, adhesives, binders, finishing agents, insect proofing in textiles.⁸⁻²⁰ Like resol (having CH_2OH self-curable groups) such resin (i.e. having CH_2OH groups) may afford condensation with phenolic derivatives. Hence it was thought interesting to explore the field of DMTUFP condensation.

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

Experiment

All the chemicals used were of laboratory grade.

Synthesis of Dimethylol thiourea-formaldehyde (DMTUF) resin

These were prepared by slight modification of the method reported.¹ A mixture of Thiourea (1 mole), formaldehyde (2 mole) and 2.5% alcoholic KOH was heated at 50°C with constant stirring for 75 min.

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 DMTUF resin is given in Table 1 and Table 2.

Synthesis of DMTUF- Phenol (DMTUF) resin

The DMTUF resin and phenol 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, was with a slight modification reported [21]. 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 yellowish liquids. The yields were 85 to 90%. Details of all three resin are given Tables 1 and 2.

Composite fabrication

A typical method of fabrication for composites is given below.

A suspension of freshly prepared DMTUF 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 $135 \pm 5^\circ \text{C}$ 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. 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 DMTUF and DMTUF resin was carried out in pyridine against standard sodium methanolate in pyridine as titrant. The M_n value of each sample was calculated according to the method reported.^{22, 23, 24}

Curing of the DMTUF-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 $10^\circ \text{C min}^{-1}$.

All the chemical, mechanical and electrical tests of the prepared composites were conducted according to ASTM methods following the method reported.²⁵

DMTUF condensation was performed by slight modification of previous reported method.¹ The resultant DMTUF 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 phenol, bearing in mind that (commercially base catalysed A-stage P-F condensate) resols are functioning *in situ* post-curing. DMTUF condensates were obtained in the form of yellowish semisolids to thick liquids. They (freshly prepared) are soluble in most polar organic solvents. On longer storage they harden. Efflux viscometry study of only the liquid resin of DMTUF has been attempted and the data are included in table 2. It was observed that in the absence of phenol, DMTUF remains relatively intact under similar conditions. However, it will be cross-linked only at elevated temperature ($135\text{--}160^\circ\text{C}$). Elemental analysis of all the resin is consistent with the structure predicted (scheme 1). The IR spectra of all three resin comprise important bands due to the DMTUF moiety and aromatic moiety. The broad bands appeared from 3360 to 3800 cm^{-1} with inflections at 3355 and 2650 cm^{-1} . This is due to the polymeric groups. The first two inflections may arise from the asymmetric and symmetric vibration of $-\text{NH}$ and $-\text{HN}-\text{CS}-\text{NH}-$ systems. The bands at 755 and 823 cm^{-1} may be attributed to adjacent H- atoms or 1,2- or 1,4- substituted aromatic rings. The band at 1105 cm^{-1} may be attributed to the group. Hence on the basis of these observations and the reactive site present in the monomer concerned (i.e. DMTUF and phenols) the most probable structure of such an DMTUF resin may be shown in scheme 1.

Cured Product

Scheme 1. Thiourea-formaldehyde-phenol resin

DMTUF condensation was performed by slight modification of previous reported method.¹ The resultant DMTUF 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 phenol, bearing in mind that (commercially base catalysed A-stage P-F condensate) resols are functioning *in situ* post-curing. DMTUF condensates were obtained in the form of yellowish semisolids to thick liquids. They (freshly prepared) are soluble in most polar organic solvents. On longer storage they harden. Efflux viscometry study of only the liquid resin of DMTUFP has been attempted and the data are included in table 2. It was observed that in the absence of phenol, DMTUFP remains relatively intact under similar conditions.

However, it will be cross-linked only at elevated temperature (135–160°C). Elemental analysis of all the resin is consistent with the structure predicted (scheme 1). The IR spectra of all three resin comprise important bands due to the DMTUFP moiety and aromatic moiety. The broad bands appeared from 3360 to 3800 cm^{-1} with inflections at 3355 and 2650 cm^{-1} . This is due to the polymeric groups. The first two inflections may arise from the asymmetric and symmetric vibration of $-\text{NH}$ and $-\text{HN}-\text{C}-\text{NH}-$ systems. The bands at 755 and 823 cm^{-1} may be attributed to adjacent H- atoms or 1,2- or 1,4- substituted aromatic rings. The band at 1105 cm^{-1} may be attributed to the group. Hence on the basis of these observations and the reactive site present in the monomer concerned (i.e. DMTUF and phenols) the most probable structure of such an DMTUFP 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 the Table 2. The values indicate that decreases with increase in molar proportion of phenol.

As the DMTUFP resin produced can react with curing agent like HMTA the cure reaction of DMTUFP-HMTA was studied for DMTUF: P : 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 thermograms, it is seen that all the DMTUFP-HMTA curing systems gave a single exotherm peak in the range of 92 to 160°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 DMTUFP 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°C.

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 DMTUFP-HMTA samples were prepared at $135 \pm 5^\circ\text{C}$ 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 DMTUFP 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 system^{26,27}. The TG data are shown in Table 4.

Table 1 Elemental analysis of Dimethylol thiourea-formaldehyde-phenol resin

Sr. No.	Sample Code	Nature of Resin	Elemental Analysis			
			Calculated		Found	
			%C	%H	%C	%H
1.	DMTUF	Colourless Viscous liquid	26.47	6.77	24.89	6.33
2.	DMTUFP1	Yellow semi-solid	65.06	6.02	64.78	5.69
3.	DMTUFP2	Yellow thick liquid	73.56	5.21	73.23	5.10
4.	DMTUFP3	Yellow thick liquid	74.00	5.337	73.77	5.23

It shows that they all degrade in a single step, and their decomposition starts around 292 °C. The degradation becomes faster between 550 and 650 °C. The weight loss was about 85-92% 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 DMTUFP systems. This may due to *in situ* reaction of fragments degraded at an earlier stage.

Glass reinforced composites based on DMTUFP - HMTA systems have also been prepared at $135 \pm 5^\circ\text{C}$, and are in the form of reddish brown sheets. The specific gravity of all composites is in the range 1.22 to 1.31 (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 1.0 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 2.86×10^7 to $5.72 \times 10^7 \text{ Ohms.cm}^{-2}$.

Table 2 Physical parameters of Dimethylol thiourea-formaldehyde and Dimethylol thiourea- formaldehyde-phenol resin

Sr. No. of Resin	1	2	3	4
Sample code of resin	DMTUF	DMTUF1	DMTUF2	DMTUF3
Efflux Viscosity (s)	Time measured by flow cup 'B'5 (BS 1733)			
	25	45	34	17
Dp	-----	14	12	8
$\overline{M}_n$	-----	1272	1060	848
Solubility	All sample code resins 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 sample codes were approximately equal to two.			

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

Sr. No.	Sample Code	Kick-off Temp., T_i (°C)	Peak Temp., T_p (°C)	Final Temp., T_f (°C)	Activation Energy (E_a) (KJ mol ⁻¹)
1	DMTUF1	95	135	160	180.4
2	DMTUF2	94	133	158	178.2
3	DMTUF3	92	131	155	175.6

Table 4. TGA of unreinforced DMTUF : HMTA cured materials.

Sr. No.	Sample Code	Percent weight loss at given temp. from TGA					
		200° C	300° C	400° C	500° C	600° C	750° C
1	DMTUF1	6.43	12.23	21.19	28.40	45.28	91.54
2	DMTUF2	7.33	13.12	20.66	33.55	46.89	90.67
3	DMTUF3	8.21	14.09	20.34	32.87	44.87	86.22

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

Sr. No.	Sample Code	% change on exposure to 25% (W/V) NaOH ^b		Specific Gravity	Flexural strength Kg/cm ²	Impact strength Kg/cm ²	Rockwell hardness	Resistivity (Ohms/cm ²)
		Thickness	Weight					
1	DMTUFP1	1.0	1.3	1.22	243	12.75	125	18.22
2	DMTUFP2	1.2	1.35	1.26	249	13.66	131	19.16
3	DMTUFP3	1.4	1.4	1.31	255	13.77	133	20.2

^a Reinforcement, E glass cloth, plain weave, 25mm, 10 ply, Resin content: 40 ± 2 wt%.

Molar ratio DMTUFP : HMTA = 1 : 1 (mol/mol). Curing temperature 135 ± 5 °C, time 8 h.

Pressure 60-70 psi. Composite size 250 mm x 250mm 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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