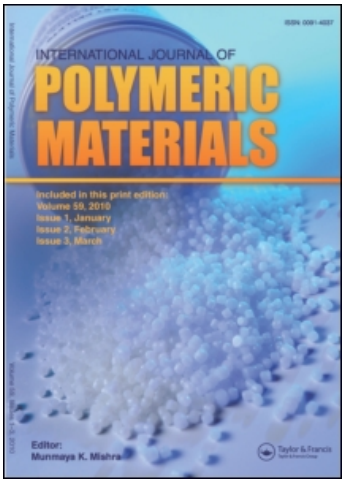

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Hasmukh S. Patel[a]; Bhavdeep K. Patel[a]; Manish M. Morekar[b]; Bharat C. Dixit[b]
[a] Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, Gujarat, India [b] V.P. and R.P.T.P. Science College, Sardar Patel University, Vallabh Vidyanagar, Gujarat, India

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Synthesis, Characterization and Glass Reinforcement of Urea-Formaldehyde-Phenol Resins

Hasmukh S. Patel,[1] Bhavdeep K. Patel,[1] Manish M. Morekar,[2] and Bharat C. Dixit[2]
[1]Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, Gujarat, India
[2]V.P. and R.P.T.P. Science College, Sardar Patel University, Vallabh Vidyanagar, Gujarat, India

N,N′-dimethylolurea (DMU) was prepared and condensed with phenol (P) in the presence of alcoholic alkali catalyst at varying mole ratios of DMU: P, namely 1:1, 1:1.5 and 1:2. The resultant DMUP resins were characterized by elemental analysis, IR spectral studies, number average molecular weight ($\overline{Mn}$) estimated by nonaqueous conductometric titration and thermogravimetry. The curing study of DMUP resins with hexamethylenetetramine (HEXA) was monitored by differential scanning calorimeter (DSC) and kinetic parameters were evaluated. Glass-reinforced composites based on DMUP-HEXA systems have also been prepared and characterized for chemical, mechanical and electrical properties.

Keywords: differential scanning calorimeter (DSC), hexamethylenetetramine (HEXA), infrared spectra (IR), N,N′-dimethylolurea (DMU), N,N′-dimethylolurea-phenol (DMUP) resin, number average molecular weight ($\overline{Mn}$), phenol (P), thermogravimetric analysis (TGA)

INTRODUCTION

The adhesives often used in furniture industries are formaldehyde-condensation resins. These are urea-formaldehyde (UF), phenol-formaldehyde (PF), malemine-formaldehyde (MF) and phenol-resorcinol-formaldehyde (PRF) resins. UF resins are preferred by the

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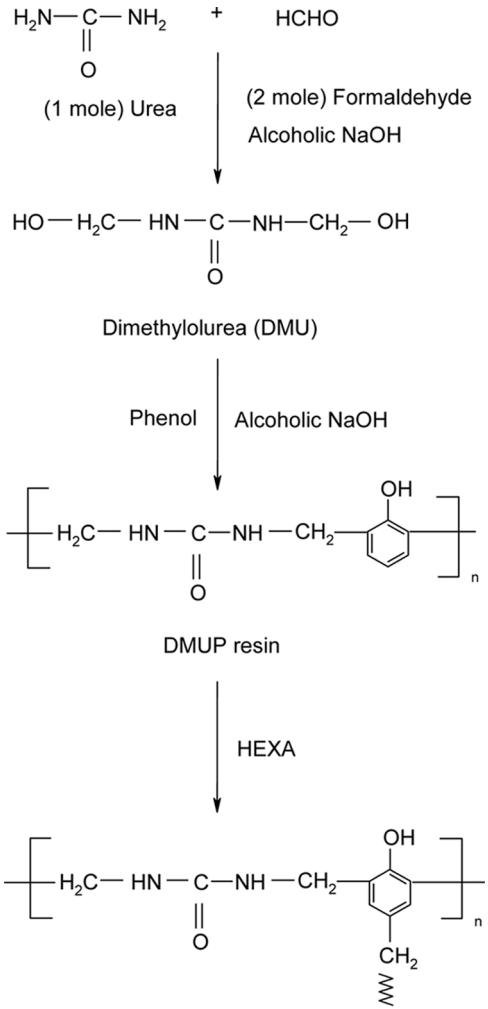
Address correspondence to Dr. Hasmukh S. Patel, Chemistry Department, Sardar Patel University, Vallabh Vidyanagar–388120, Gujarat, India. E-mail: drhspatel786@yahoo.com

wood-based panels industry due to their high reactivity and cost efficiency. Bonding with UF adhesive is cheaper than with PF adhesive and it permits the formation of strong bonds under a wide variety of conditions. The study of urea-formaldehyde resinification and characterizations are well established [1–8]. UF resins offer technical advantages in many applications such as adhesives, binders, resin glue and anticorrosive coatings [9–15]. In the UF resin formation a mixture of monomethylol- and dimethylol- urea is formed [16].



SCHEME 1 DMUP-HEXA cured product.

Methylol groups (–CH_2OH) of dimethylolurea (DMU) may also react with other active hydrogen compounds, like phenol. However, the terpolymers of PUF contain a mixture of all three comonomers [17,18]. Hence it was thought to explore the DMU: P condensation reaction.

The present article comprises synthesis, characterization and glass reinforcement of DMUP resin. The resulting resins were studied for their curing characteristic with HEXA, on DSC. Glass-reinforced composites of DMUP-HEXA have been also prepared and characterized. The synthetic route is shown in Scheme 1.

EXPERIMENTAL

Materials

All the chemicals used were of laboratory grade.

Synthesis of N,N′-Dimethylolurea (DMU)

DMU was synthesized [16]. The yield was 90%. The preliminary characterization of DMU is shown in Table 1.

Synthesis of N,N′-Dimethylolurea-Phenol (DMUP) Resins

DMU and phenol in molar rations of 1:1, 1:1.5 and 1:2, respectively, were refluxed in a methanolic solution of 3% NaOH of the total weight of the reactant for 2 h. The resulting solution was then poured immediately into distilled water to give a yellow thick resin which was washed several times with distilled water to remove unreacted reactants. The yields of resins were 87 to 94%. The details of the three resins are furnished in Table 2.

TABLE 1 Preliminary Characterization of N,N′-Dimethylolurea (DMU)

Elemental analysis		%C	%H	%N
($C_3H_8N_2O_3$)	Calc.	30.00	6.71	23.32
	Found	29.83	6.62	23.20
Solubility	Soluble in water (1.5 g in 10 ml). Miscible with highly polar solvents like alcohols, DMF, THF etc.			
Number of –OH group	$2.1 \approx 2.0$			
Melting Point	123°C			

TABLE 2 Characterization of DMUP Resins

Molar ratio of DMU: P resins	Color and state	*Efflux time (sec.)	Elemental analysis calc./(found)			Nonaqueous conductometric titration	
			%C	%H	%N	**DP	$\overline{Mn}$
1:1	Yellow Semisolid	—	60.66 (60.53)	5.65 (5.60)	15.72 (15.61)	9.23	1645
1:1.5	Yellow Thick liquid	44	60.66 (60.40)	5.65 (5.51)	15.72 (15.59)	6.15	1096
1:2	Yellow Thick liquid	21	60.66 (60.43)	5.65 (5.53)	15.72 (15.63)	4.61	823

*Efflux time measured by using flow cup type "B" 5 (BS 1733) (at 30°C).
**DP = Degree of Polymerization.

Composite Fabrication

A suspension of DMUP resin and HEXA (1:1 mol) in tetrahydrofuran was prepared and stirred well for 5 min. The suspension was applied with a brush to 250 mm × 250 mm phenolic-compatible fiberglass cloth and the solvent was allowed to evaporate. The dried ten prepregs so prepared were stacked one over another and pressed between steel plates coated with a Teflon release sheet and compressed in a flat platen press under 70 psi pressure. The prepregs stacks were cured by heating at 100 ± 3°C for 4 h in an air-circulated oven. The composite so obtained was cooled to 50°C before the pressure was released. The composites were machined to final dimensions.

MEASUREMENTS

Elemental Analysis

The C, H, N contents were estimated by means of a Carlo Earba elemental analyzer (Italy). The IR spectra of all the samples were taken in KBr pellets on a NICOLET 760 D spectrophotometer. The number average molecular weight was estimated by using nonaqueous conductometric titration method [19].

Curing

DMUP resin samples were mixed with the curing agent HEXA. A Du Pont 900 DSC was used for this study. The instrument was calibrated using standard indium metal with known heat of fusion

($\Delta H = 28.45\,J/g$). Curing was carried out using a single heating rate of 10°C /min in air. The sample weight for this investigation was in the range of 5–8 mg along with an empty reference cell.

Thermogravimetric analysis (TGA) of DMUP: HEXA systems have been carried out using a Du Pont 950 thermogravimetric analyzer at a heating rate of 10°C/min in air. The sample weight for this investigation was in the range of 5–8 mg.

COMPOSITE CHARACTERIZATION

All the chemical, mechanical and electrical tests on composites were conducted according to the ASTM methods listed below, using three specimens for each test.

Chemical Resistance Test

ASTM D 543-67 was used to measure the chemical resistance of the composites towards sodium hydroxide, organic solvents and mineral acids.

Mechanical and Electrical Testing

1. The flexural strength was measured according to ASTM D 790.
2. The compressive strength was measured according to ASTM D 695.
3. The impact strength was measured according to ASTM D 256.
4. The rockwell hardness was measured according to ASTM D 785.
5. The electrical strength was measured according to ASTM D 149.

RESULTS AND DISCUSSION

The DMU having two active $-CH_2OH$ groups per molecule was used for further condensation with phenol. The DMUP condensation product was a yellow, thick liquid. The freshly prepared products were soluble in most organic solvents, but on longer storage they harden slightly. It was observed that in the absence of phenol, DMU under similar conditions remained relatively unchanged.

The elemental analysis of all the DMUP resins was found consistent with their predicted structures. The number average molecular weight ($\overline{Mn}$) values of the three resins were estimated by nonaqueous conductometric titration [19]. The results indicate that $\overline{Mn}$ decreases with increasing molar proportion of phenol. Naturally, the efflux viscosity time decreases with decreases in $\overline{Mn}$. The results of elemental

TABLE 3 Curing Characterization of DMU: P: HEXA Resin Systems

Molar ratio of DMU: P: HEXA resin systems	Kickoff Temp. Ti(°C)	Peak Temp. Tp(°C)	Final Temp. Tf (°C)	Activation energy (Ea) KJ/mol	Order of reaction 'n'
1:1:1	103	124	142	186	1.9
1:1.5:1	99	120	140	184	2.1
1:2:1	96	118	136	183	2.1

analysis, $\overline{Mn}$, DP and efflux viscosity time are furnished in Table 2. IR spectra for both DMUP and DMUP-HEXA resins were consistent with the ones expected from the structures of resins.

The DMUP resin produced can react with a curing agent such as HEXA. The cure reaction of DMUP: HEXA was studied for DMU: P: HEXA molar ratios of 1:1:1, 1:1.5:1 and 1:2:1, respectively. The data obtained from DSC thermograms show that all the cured DMU: P: HEXA systems give a single exothermic peak in the ranged 96 to 142°C. The activation energy (Ea) values for such systems, shown in Table 3, did not vary widely, which indicates that DMUP was reactive towards the HEXA. The curing temperature, activation energy (Ea) and order of reaction (n) results are furnished in Table 3.

The unreinforced cured DMU: P: HEXA samples were prepared at 100 ± 3°C for 4 h. They formed a powder under normal hand pressure, and were insoluble in all common organic solvents. TG data are shown in Table 4 for unreinforced cured resin samples and show that they all degrade in a single step and their decomposition starts at around 200°C. The rate of decomposition becomes faster in the range of 300 to 600°C. The glass-reinforced composites based on DMU: P: HEXA systems were prepared at 100 ± 3°C for 4 h. The density of all the composites was in the range of 1.29 to 1.36 g/cm^3 (shown in Table 5). Chemical resistance tests revealed that all composites had remarkable resistance to organic solvents and concentrated acids

TABLE 4 TGA of Unreinforced Cured DMU: P: HEXA Resin Systems

Molar ratio of DMU: P: HEXA resin systems	% Weight loss at various temperature (°C)						
	200	300	400	500	600	700	800
1:1:1	2.6	10.0	18.9	30.0	51.5	55.9	58.2
1:1.5:1	3.0	9.8	18.0	31.0	50.4	56.0	57.2
1:2:1	3.3	10.4	17.2	29.5	50.1	55.3	56.6

TABLE 5 Chemical, Mechanical and Electrical Properties of Glass-Reinforced Composites of DMU: P: HEXA Resin Systems

Composites molar ratio of DMU: P: HEXA resins	% Change on exposure to 25% (W/V) NaOH[a]		Density g/cm^3	Flexural strength (MPa)	Compressive strength (MPa)	Impact strength (MPa)	Rockwell hardness (R)	Electrical strength (in air) (kV/mm)
	Thickness	Weight						
1:1:1	1.1	1.4	1.29	298	293	309	117	17.3
1:1.5:1	1.2	1.4	1.33	303	301	307	120	17.9
1:2:1	1.0	1.2	1.36	305	306	312	126	18.2

[a]Chemical resistance to alkali (25%W/V NaOH); composites are unaffected by organic solvents such as acetone, concentrated mineral acid such as sulphuric acid, nitric acid, and hydrochloric acid (25%V/V).

(25% V/V). However, the concentrated alkali (25% W/V) caused changes in their thickness and a weight loss of about 1.0 to 1.4%. The result shows that the composites have good properties.

CONCLUSION

The DMUP resin can be prepared easily. The glass-reinforced composites of DMUP have good chemical, mechanical and electrical properties. There was not much variation in the mechanical properties with molar ratio. The improved properties of DMUP base composites might be due to the presence of aliphatic ketonic segments and strong H- bonds between the phenolic –OH and keto (C=O) groups of neighboring polymeric chains. The properties of DMUP system are better than individual PF and UF resins.

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