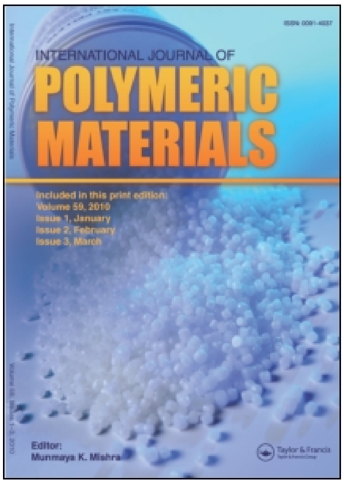

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Glass Reinforcement of Various Epoxy Resin (Dimethylolurea-Phenol Resin) Systems

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N,N′-dimethylolurea (DMU) was prepared and condensed with phenol (P) in the presence of an alcoholic alkali catalyst using 1:1 mole ratio of DMU:P. The resultant DMUP resin was characterized by elemental analysis, IR spectral studies and number average molecular weight ($\overline{Mn}$) estimates by nonaqueous conductometric titration. Further reaction of DMUP resin was carried out with the three epoxy resins DGEBA, DGEBC and DGEBF. The curing of the prepared resins was monitored by differential scanning calorimeter (DSC) and their kinetic parameters have been evaluated. Based on DSC thermograms, glass fiber-reinforced composites have been laminated and characterized by chemical, mechanical and electrical properties. The unreinforced cured resins were subjected to thermogravimetric analysis (TGA).

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

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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 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 process 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 coatings [9–15]. In the UF resin formation a mixture of monomethylol- and dimethylol-urea is formed. Here, the dimethylolurea (DMU) was prepared by following a reported method [16]. Methylol groups ($-CH_2OH$) of dimethylolurea can react with other active hydrogen compounds, like phenol. Glass reinforcement of dimethylolurea-phenol (DMUP) resin was also reported by us [17].

Epoxy resins are versatile resins having a wide range of properties such as adhesion to substrate, corrosion resistance and high tensile, flexural and compressive strengths. Because of the versatile properties exhibited by epoxy resin, it has found many applications [18,19]. Its crosslinking may, also, be done using low molecular weight phenolic (novolac) and urea resins, where the reactions may involve condensation of methylol groups with the secondary groups of the epoxy resin or epoxide ring opening through reaction with the phenolic hydroxyls or the amino groups of the urea resins. Due to the versatile properties of epoxy resins it was thought interesting to study the reaction between DMUP and epoxy resin (DGEBA, DGEBC and DGEBF) systems. Hence, in extension of our previous work [17], the present article comprises synthesis of DMUP-epoxy resin (DGEBA, DGEBC and DGEBF) systems. Based on DSC thermograms, glass-reinforced composites have been laminated and characterized by chemical, mechanical and electrical properties. The whole synthetic route is scanned in Scheme 1.

EXPERIMENTAL

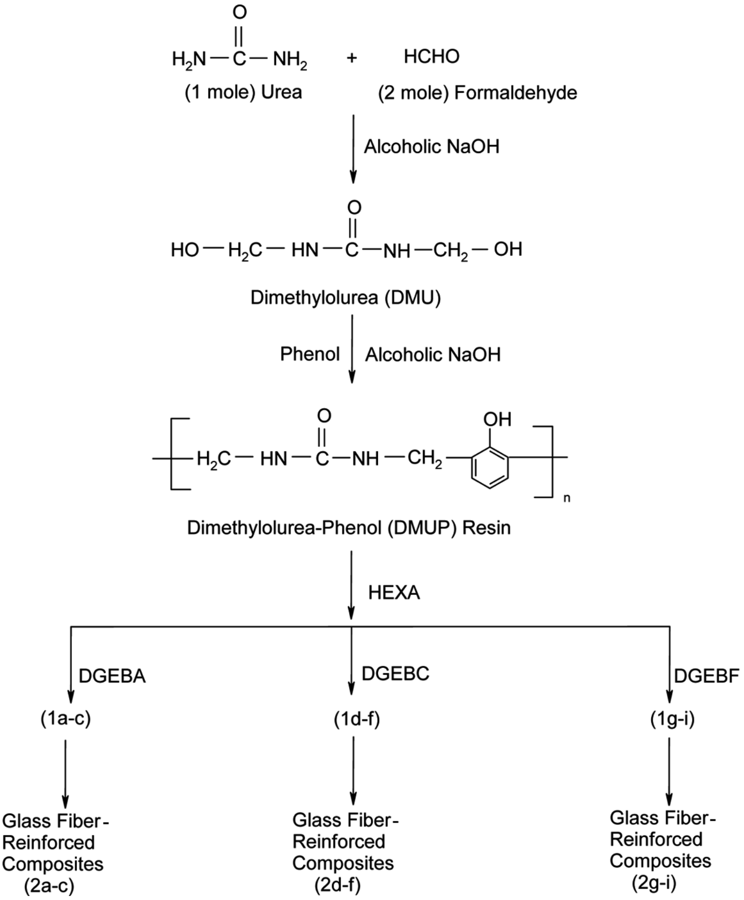
Materials

The specifications of the epoxy resins are:

Epoxy equivalent weight of Diglycidylether of bisphenol-A (DGEBA), 190

Epoxy equivalent weight of Diglycidylether of bisphenol-C (DGEBC), 210

Epoxy equivalent weight of Diglycidylether of bisphenol-F (DGEBF), 160



Scheme 1: Synthesis steps.

E-type glass-woven fabric (0.25 mm thick) was obtained from Unnati Chemicals, India. All other chemicals were of laboratory grade.

Synthesis of N,N′-dimethylolurea (DMU)

DMU was prepared by following a reported method [16]. The preliminary characterizations of DMU are given in Table 1.

Synthesis of N,N′-dimethylolurea-Phenol (DMUP) Resin

DMU and phenol in 1:1 mole ratio were refluxed in a methanolic solution of 3% NaOH of the total weight of the reactants for 2 h. The resulting solution was then poured immediately into distilled water to give a yellow thick resin,

Table 1: Preliminary characterization of DMU and DMUP resin.

Designation of product					
DMU	Molecular formula		$C_3H_8N_2O_3$		
	Elemental analysis		%C	%H	%N
		Calc.	30.00	6.71	23.32
		Found	29.83	6.62	23.20
	No. of –OH group		$2.1 \approx 2.0$		
	Melting point		123°C		
	Solubility	Soluble in water (1.5 g in 10 ml). Miscible with highly polar solvents like alcohols, DMF, THF			
DMUP Resin	Molecular formula		$C_9H_{10}N_2O_2$		
	Elemental analysis		%C	%H	%N
		Calc.	60.66	5.65	15.72
		Found	60.53	5.60	15.61
	Number average molecular weight ($\overline{Mn}$)		1645		
	Degree of polymerization (DP)		9.23		

and washed several times with distilled water to remove unreacted reactants. Preliminary characterizations of DMUP resin are given in Table 1.

Synthesis of DMUP-Epoxy Resin Systems

The DMUP-epoxy resin system has been prepared by mixing DMUP resin and epoxy resin (i.e., DGEBA) in different proportions (as shown in Table 2). To this mixture, the catalyst hexamethylenetetramine (HEXA), at 0.5% of the weight of the DMUP resin, was added under continuous stirring and stirred well for 15 min to form a homogeneous system.

Similarly, other DMUP-epoxy resin systems from the epoxy resins DGEBC and DGEBF were prepared by using the same method and conditions used for DGEBA.

Three different DMUP-epoxy resin systems were prepared by using different proportions of DMUP and DGEBA, DGEBC and DGEBF epoxy resins as shown in Table 2.

Composite Fabrication

Suspensions of DMUP-epoxy resin (DGEBA, DGEBC and DGEBF) systems were prepared in tetrahydrofuran (THF) and stirred well for 10 min. Each 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

Table 2: Curing characterization of DMUP-Epoxy resin systems.

Epoxy resins	Compositions		Designation	Kick-off temp. Ti (°C)	Peak temp. Tp (°C)	Final temp. Tf (°C)	Activation energy (Ea) KJ/mol	Order of reaction 'n'
	DMUP	Epoxy resin						
DGEBA	60	40	1a	111	139	151	196.3	1.8
	50	50	1b	119	141	160	195.6	1.8
	40	60	1c	126	148	168	194.7	1.9
DGEBC	60	40	1d	109	131	144	192.4	1.9
	50	50	1e	115	134	150	191.6	1.9
	40	60	1f	120	139	157	191.1	1.9
DGEBF	60	40	1g	106	129	141	189.6	2.0
	50	50	1h	113	131	146	188.8	2.0
	40	60	1i	119	135	151	188.1	2.1

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 150 ± 5°C for 4 h in an air-circulated oven. The composite so obtained was cooled to 50°C before the pressure was released.

ANALYSIS AND CURING STUDY

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 [20].

Curing

A Du Pont 900 DSC was used for the curing study of DMUP-epoxy resin systems. The instrument was calibrated using a standard indium metal with a 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 weights for this investigation were in the range of 4–5 mg, along with an empty reference cell.

Thermogravimetric analysis (TGA) of DMUP-epoxy resin systems have been carried out using a Du Pont 950 thermogravimetric analyzer at a heating rate of 10°C/min in air. The sample weights for this investigation were in the range of 4–5 mg.

Composite Characterization

The chemical, mechanical and electrical tests on composites were all conducted according to the ASTM methods listed below using five 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 (P). 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 (P), DMU under similar conditions remained rather unchanged.

The elemental analysis of the DMUP resins was found to be consistent with their predicted structure. The number average molecular weight ($\overline{Mn}$) of DMUP resins was estimated by nonaqueous conductometric titration [20]. The results of elemental analysis, number average molecular weight ($\overline{Mn}$) and degree of polymerization (DP) are given in Table 1. The IR spectra for DMUP resins was found to be consistent with the ones expected from the structure of resins.

The curing study of DMUP-epoxy cured product was carried out on DSC. The data obtained from DSC thermograms show that all the cured DMUP-epoxy resin systems give a single exothermic peak in the range 137 to 196°C. The values of activation energy (Ea) for such systems, furnished in Table 2, did not vary widely. The results of curing temperature with activation energy (Ea) and order of reaction (n) are given in Table 2.

The unreinforced cured DMUP-epoxy resin (DGEBA, DGEBC and DGEBF) samples were prepared at $150 \pm 5°C$ 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 3 for unreinforced cured resin samples

Table 3: TGA of unreinforced cured DMUP-Epoxy resin systems.

	% Weight loss at various temperature °C from TGA					
Designation	**200**	**300**	**400**	**500**	**600**	**700**
1a	2.0	9.3	17.3	28.1	53.9	56.1
1b	1.9	8.9	16.8	27.8	53.2	55.4
1c	1.7	8.4	15.7	27.6	52.4	54.3
1d	2.2	9.8	17.9	28.9	54.2	57.0
1e	2.1	9.4	17.3	28.6	53.8	56.8
1f	1.9	8.9	16.2	27.9	53.1	56.0
1g	2.4	9.8	18.4	29.1	55.1	57.7
1h	2.3	9.6	17.8	28.8	54.7	57.1
1i	2.2	9.1	9.1	28.3	54.0	56.2

Table 4: Chemical, mechanical and electrical properties of glass fiber-reinforced composites prepared from DMUP-Epoxy resin systems.

Glass fiber-reinforced composites	% Change on exposure to 25% (W/V) NaOH		Density g/cm^3	Flexural strength (MPa)	Compressive strength (MPa)	Impact strength (MPa)	Rockwell hardness (R)	Electrical strength (in air) (kV/mm)
	Thickness	Weight						
2a	1.16	1.18	1.33	316	318	316	132	18.3
2b	1.14	1.17	1.33	321	319	320	135	18.4
2c	1.11	1.14	1.34	326	322	324	139	18.5
2d	1.18	1.19	1.32	310	312	314	130	18.1
2e	1.17	1.18	1.32	317	314	318	133	18.1
2f	1.14	1.16	1.33	320	319	321	135	18.3
2g	1.19	1.21	1.31	307	306	310	128	17.8
2h	1.18	1.20	1.31	311	309	312	130	18.0
2i	1.16	1.18	1.32	315	314	317	131	18.2

and show that they all degrade in a single step and their decomposition starts around 200°C. The rate of decomposition becomes faster in the range of 300 to 600°C temperature. The glass-reinforced composites based on DMUP-epoxy resins were also prepared at 150 ± 5°C for 4 h. The density of all the composites was in the range of 1.31 to 1.34 g/cm^3 (shown in Table 4). Chemical resistance tests revealed that all composites had remarkable resistance properties towards organic solvents and concentrated acids (25% V/V). However, the concentrated alkali (25% W/V) caused changes in their thickness (1.11 to 1.19%) and a weight loss of about 1.14 to 1.21% was found. Electrical strength of all the composites was found in the range of 17.8 to 18.5 kV/mm. The results of composite characterizations suggest that the composites have good chemical, mechanical and electrical properties.

CONCLUSIONS

The DMUP and DMUP-epoxy resin (DGEBA, DGEBC and DGEBF) systems can be prepared easily. The glass-reinforced composites of DMUP-epoxy resin systems have good chemical, mechanical and electrical properties. There was not much variation in the mechanical properties with molar ratio. The improved properties of DMUP-epoxy resin-based 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 and, of course, due to the presence of epoxy resin. The properties of DMUP-epoxy resin systems are better than individual PF, UF, dimethylolurea-phenol (DMUP) and epoxy resins.

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