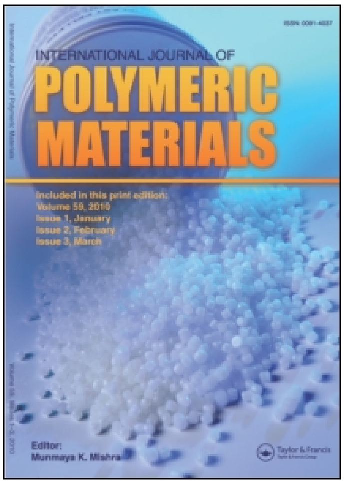

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Novel Terpolymers: Poly (Keto-Amine-Ureas)

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Thermally stable polymers containing keto-amine-urea groups have been prepared by condensation of keto-amino group containing diamine and various diisocyanates. The resulting polymer samples have been characterised by elemental analysis, IR spectra, Mn estimated by non-aqueous conductometric titration and thermogravimetry. Curing of commercial epoxy resin-DGEBA by employing these polymers scanned on Differential Scanning Colorimeter (DSC). The glass fibre reinforced composites (i.e. laminates) based on such terpolymer-epoxy resin system have also been prepared and characterised.

KEY WORDS Poly (keto-amines), diisocyanates, poly (ureas), poly (keto-amine-ureas), epoxy resin, glass fibre, glass fibre reinforced composites, mechanical properties.

INTRODUCTION

The poly(keto-amines) are reported as thermally stable polymers.[1,2] The introduction of urea group into these poly (keto-amines) chain may alter the properties of polymers up to certain extents. Hence it was thought interesting to study novel polymers containing ketone, amine and urea groups.

The present paper comprises synthesis, characterization and epoxy curing of thermally stable terpolymers shown in Scheme I. The glass reinforcement of such terpolymers-epoxy system has also been studied.

RESULTS AND DISCUSSION

All the (keto-amino-ureas) terpolymers (PKAU) samples are dark brown solids. They are insoluble in common organic solvents.

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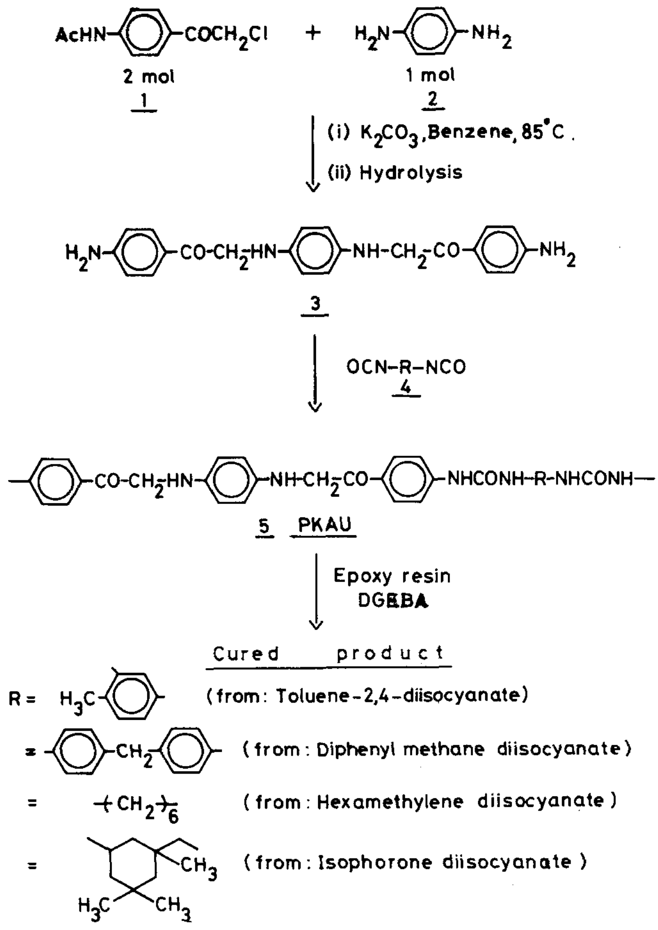

SCHEME I

The C, H and N content of all PKAU polymer samples agreed with the formula predicted on the basis of the structure of the respective unit.

The examination of the IR spectra (not shown) of all polymer samples reveals that each spectrum comprise a broad band with maximum around 3440 cm^{-1} belongs to the vibration of a secondary aryl-alkyl amino group. Weak bands around 2950 and 2890 cm^{-1} are characteristics for CH vibrations of $—CH_2—$ of $—CO—CH_2—$ groups. All spectra contain a strong band at 1680 cm^{-1} and 660 cm^{-1} attributed respectively to carbonyl of $—COCH_2NH—$ and urea linkages and strong bands around 1300 and 1220 cm^{-1} from C═N.

The DP values (Degree of polymerization) for all poly (keto-amine-ureas) samples (Table I) estimated by non-aqueous titration are in the range of 5 to 8. As The PKAUs are insoluble in common organic solvents, their viscometric properties have not been studied.

The TGA data (Table II) of all the polymers show that all the polymers degrade in one step. The degradation commences in the range of 280–300°C depending upon the nature of polymer, the rate is maximum around 500 and less is nearly com-

TABLE I

Synthesis and characterization of Poly (Keto-amine-ureas) (PKAU—1 to 4)

Polymer sample	Yield %	Elemental analysis						$\overline{\mathrm{Mn}}$	% wt. loss at °C from TGA				
		C %		H %		N %							
		Cald.	Found	Cald.	Found	Cald.	Found		300	350	400	500	600
PKAU-1	90	67.88	67.5	5.1	4.8	15.33	15.1	1650	10	37.5	59	69	93
PKAU-2	83	71.15	70.3	5.13	4.9	13.46	13.29	2400	12	43	66	73	94
PKAU-3	80	70.31	69.84	6.64	6.37	16.4	16.3	3000	14	40	63	73	95
PKAU-4	75	64.8	68.2	6.24	6.1	14.165	14.08	3600	16	39	61	78	95

TABLE II

Curing characteristics of PKAU-epoxy system

Resin system	Heating rate 10°C/min	PKAU to epoxy ratio	Kick off temp. T_i(°C)	Peak temp. T_p(°C)	Final temp. T_f(°C)	Activation energy(Ea) Kcal/mol	Order of reaction
PKAU-1	10	1:1	127	187	287	18.0	1.0
		1:1.2	125	160	275	17.0	1.1
PKAU-2	10	1:1	125	195	280	20.0	1.2
		1:1.2	115	160	250	18.0	1.2
PKAU-3	10	1:1	165	202	290	18.0	1.1
		1:1.2	155	195	270	18.0	1.2
PKAU-4	10	1:1	180	215	290	19.0	1.2
		1:1.2	175	205	275	18.0	1.3

TABLE III

TGA of unreinforced PKAU-epoxy cured materials

Resin system	PKAU to epoxy ratio	% wt. loss at °C from			
		300	400	500	600
PKAU-1	1:1	2	30	57	76
	1:1.2	3	32	60	72
PKAU-2	1:1	2	35	60	76
	1:1.2	3	42	72	90
PKAU-3	1:1	1	27	65	90
	1:1.2	1	26	66	90
PKAU-4	1:1	1	28	66	92
	1:1.2	2	25	70	96

plete around 600°C. The internal hydrogen bonding may play a significant role in the thermal stability of poly (keto-amino-ureas).

The cure reaction of PKAU-epoxy resin was studied for two different stoichiometric ratios of PKAU-epoxy namely 1:1 and 1:1.2. The data obtained from DSC scans are given in Table III. From the DSC thermograms (not shown) it was seen that all the PKAU-epoxy gave single exothermic peak in the range of 144–200°C. From the thermograms the kick off temperature (T_i), peak exotherm temperature (T_p) and temperature of completion of cure (T_f) were obtained.

The data (Table III) reveal that the curing temperature of the epoxy system is depending upon the nature of polymer. The higher temperature curing is probably due to the lower rate of diffusion of the high molecular weight polymer. The values of activitation energy (*Ea*) for such a system (Table III) have no wide variation and such study by increasing slight proportion of epoxy resin not giving any significant results. The kinetic parameters such as *Ea* (activation energy) and *n* (order of reaction) were calculated by assuming that the curing reaction obeys Arrhenius type kinetics and that the peak maximum represents a point of constant conversion at a heating rate of 10°C/min. To obtain information about the properties of unreinforced crosslinked materials, larger cured specimens were prepared by using the same proportions and temperature as stated in Table II. The unreinforced cured PKAU-epoxy samples prepared at 200°C for 8 hrs are dark brown in colour and are slightly hard materials that form powder under normal hand pressure. They are insoluble in all common organic solvents including formic acid. They are swelled little by 25% W/V NaOH and 25% V/V HCl. Thermogravimetric analysis (Table III) of all the unreinforced crosslinked materials reveals that they are degraded in a single step and start their decomposition above 300°C. Degradation becomes faster between 400°C and 550°C. The weight loss was almost 90% at 600°C in all cases.

IR spectra (not shown) of three unreinforced cured products clearly show disappearances of the oxirane group (910 cm^{-1}) (i.e. epoxy group). The inflections at 1170 cm^{-1} in the spectra of unreinforced product obtained by using a higher proportion of epoxy may be due to the linkage arises from the homopolymerization of the epoxy resin by formation of tertiary amine. However, the hompolymerization of epoxy resin is only possible in the presence of tertiary amine catalyst at elevated temperature.[5]

Glass reinforced PKAU epoxy composites prepared are in form of dark brown sheets. The specific gravity of all these composites is in the range 1.7–1.9 (Table IV). Results indicates that there is no appreciable change in the laminates specific gravity. Chemical resistance studies indicates that the glass fibre composites were not affected by immersion in organic solvents (DMF, ketones, alcohols, DMSO, 1,4-dioxane, THF). No change in weight or thickness was observed. It was also noted that concentrated hydrochloric acid (25% V/V) did not affect the composites. However, exposure to concentrated alkali (25% W/V, NaOH) resulted in change in thickness and weight (Table IV).

Since the film cast from the neat system is too brittle the hardness and other mechanical properties are not presented. The dielectric strength of all the composites is in the range 2.3–3.0 KV/mm. The values of the electrical strength of the present composites are low. This could result in the presence of a charred path, over which subsequent discharge could take place more and more readily. Additionally, a minute leakage of current may arise from surface contamination.

EXPERIMENTAL

Materials

4-Acetamidophenacyl chloride (1) was prepared according to the method reported earlier.[3] The diisocyanates (listed in Scheme I) used in the polymer synthesis were of Aldrich Chemicals, USA and used without purification. All other chemicals used were of laboratory grade. Commercial epoxy (i.e. Diglycidyl ether of bisphenol-A) (DGEBA) resin was obtained from Sympol Products Pvt. Ltd., Ahmedabad, India. Specification of epoxy resin are: epoxy eq. wt.: 190–210; viscosity at 25°C: 4–10 P; density at 25°C: 1.16–1.17 g/cm^3. E type fibre glass woven fabric (Epoxy compatible) of 0.25 mm thick (Unnati Chemicals, India) of arral weight 270 gm/m^2 was used for preparation of laminates.

Synthesis of Triblock Monomer-3

To a well stirred solution of 1 (0.2 mole) in dry benzene 0.2 mole of K_2CO_3 was added. Then the solution of phenylene diamine 2 was added (0.1 mole) and refluxed for 5 hours. Benzene was distilled out and resulted mass was washed with methanol and dried. The product is treated with 50% alcoholic HCl (5 hours) neutralised and precipitates were collected, washed with THF (50 ml) and dried. Thus triblock monomer 3 obtained in form of dark brown and did not melt up to 360°.

TABLE IV

Mechanical and electrical properties of glass reinforced composites based on PKAU-epoxy system

Resin system	PKAU to epoxy ratio	% change on exposure to 25 % (W/V) NaOH		Specific gravity	Flexure strength (mPa)	Compressive strength (mPa)	Impact strength (mPa)	Hardness Rockwell	Electrical strength (kV/mm)
		Thickness	Weight						
PKAU-1	1:1	1.2	1.3	1.9	205	230	220	195	2.5
	1:1.2	1.3	1.1	1.8	230	260	290	135	3.0
PKAU-2	1:1	1.3	1.3	1.9	200	222	220	118	2.4
	1:1.2	1.2	1.3	1.8	225	252	300	126	2.5
PKAU-3	1:1	1.1	1.3	1.8	192	210	157	110	2.4
	1:1.2	1.0	1.2	1.8	202	217	180	110	2.6
PKAU-4	1:1	0.9	1.1	1.7	175	200	150	110	2.3
	1:1.2	0.9	1.1	1.8	190	213	175	110	2.6

Analysis of 2

$(C_{22}H_{22}N_4O_2)$ (374)	% C	% H	% N
Cald.	70.58	5.88	14.97
Found.	69.80	5.82	14.90

Synthesis of Terpolymers (5): Poly (Keto-Amine-Ureas)

Terpolymers based on condensation of triblock monomer (3) with various diisocyanates (4) (Scheme I) were prepared under identical conditions. A typical procedure is given here.

To a well stirred solution of triblock monomer (3) (10 mmol) in 50 ml tetrahydrofuran was added gradually diisocyanate (10 mmol) and then heated (70°C) on water bath for 8 hours. The product was filtered off, washed with dry ether and air-dried. The dried product was Soxhlet extracted with 1,4-dioxane to remove unreacted monomers. The product is dark brown powder, insoluble in common organic solvents not melting up to 360°C. It was designated as terpolymer:PKAU. The details of all four terpolymers are shown in Table I.

MEASUREMENTS

Elemental Analysis

C, H, N content of each poly (keto-amine-urea) polymer samples were estimated by C, H, N elemental analyser Carlo Erba, Italy.

IR spectra of all the terpolymer samples were taken on a Perkin Elmer Spectrophotometer.

The number average molecular weight (*Mn*) of terpolymers were determined by non-aqueous conductometric titration method reported earlier.[1,4] A formic acid-acetic acid mixture† was used as the solvent and standard perchloric acid in acetic acid was used as a titrant. A digital conductivity meter (Tosniwal, India) was used for the titration.

Thermogrametry of all the polymer samples was carried out on a Linseis thermobalance at heating rate of 10°C/min.

Curing of DGEBA epoxy resin by each of terpolymer was carried out by Differential Scanning Calorimetry. A Dupont 900 DSC was used for this study. The instrument was calibrated using standard materials of known heat of fusion. Curing was carried out using single heating rate (10°C/min). The weight of the sample for this investigation was in the range of 4 to 5 mg and an empty cell was used as a reference.

All the chemical, mechanical and electrical tests of the prepared composites were conducted according to ASTM or IS methods.

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†Laboratory grade formic acid to which an appropriate amount of acetic anhydride was added which was used as solvent.

Composite Fabrication

A suspension mixture of terpolymer-epoxy resin in tetrahydroforan was prepared and was stirred well for 2 to 5 min. The suspension mixture was applied with a brush on to a 150 mm × 150 mm epoxy compatible fibre glass cloth and the solvent was allowed to evaporate. Once dried, the 10 plies of prepreg thus prepared were stacked one on top of another, pressed between steelplates coated with a Teflon film release and compressed in a flat plates press under about 70 psi pressure. The prepreg stack was cared by heating in the press to 160°C for 10 hrs. The composites so obtained was cooled to 45°C before the pressure was released. Test specimens were made by cutting the composite and machining them to final dimensions.

The carbon fibre composites were prepared by using 30 tows of (12″ each) carbon fibre wherein the fibres were allowed to pass through the suspension and then compression moulded under the similar moulding conditions as used in case of glass fibre composites.

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