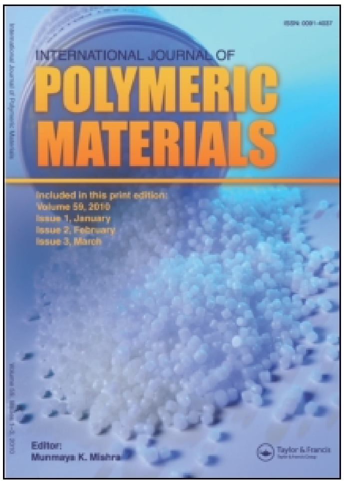

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Modified Urea-formaldehyde (UF) thermosetting resin, containing casein and p-amino phenol has been synthesized by polycondensation of urea, casein, and formaldehyde in the presence of varying proportion of p-aminophenol under alkaline condition. All the prepared resins were characterized by free-formaldehyde content, free-phenol content, viscosity measurements, and infrared spectroscopy (IR). Their curing kinetics were studied isothermally and also by Differential Scanning Calorimetry (DSC) on dynamic run. The resin samples were cured isothermally at 120°C using two different curing agents, that is p-toluene sulphonic acid (PTS) and hexamine, to understand the curing behavior of novel resin samples. The cured resins were characterized by IR and thermogravimetric analysis (TGA). The resin samples were employed for the fabrication of glass fiber and jute fiber reinforced composites respectively by maintaining 2:3 and 3:2 proportion of resin: reinforcement. The prepared composites were tested for their mechanical properties and resistance toward various chemicals.

Keywords: casein, composites, characterization, curing, mechanical properties

INTRODUCTION

Besides crosslinked rubber, phenol-formaldehyde, urea-formaldehyde, and melamine-formaldehyde are the most important members of the thermosetting resins. They differ fundamentally from most other

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resins, with few exceptions, by their ability to be rapidly cured. Curing involves the change of physical and chemical properties in the presence of catalyst, usually on the application of heat. An increase of molecular size by linear reaction and crosslinking leads to the formation of macromolecules and the hardened or cured product become insoluble and infusible. These resins are therefore called "Thermosetting" resins. One of the most commercially important thermosets is urea-formaldehyde resin [1], which is being studied here. The advantages of these resins stem from their initial water solubility and from the hardness, nonflammability, arc resistance, good thermal properties, and absence of color in the cured polymers. Today these resins enjoy outstanding importance as molding resins, adhesives, coating materials, and in treatment of paper and textiles [2–6].

The present work comprises the synthesis of modified urea-p-aminophenol-formaldehyde resin by incorporating natural polymer such as casein in it. The prepared resins were characterized by viscosity and other chemical methods and extensively studied for their curing behavior. The cured resins were characterized by IR and thermal analysis. Glass fiber and jute fiber reinforced composites were fabricated and tested for some mechanical properties and resistance toward various chemicals according to ASTM procedures.

EXPERIMENTAL

Materials

Urea was obtained from E. Merck (India) Limited, Bombay. The formaldehyde solution (37%) was obtained from Samir Tech. Chem. Pvt. Ltd. (India). The casein (alkali soluble) and p-amino phenol were obtained from Samir Tech. Chem. Pvt. Ltd. (India). E-type 10 mils plain-woven glass cloth of 0.25 mm thickness was purchased from Unnati Corporation (India) for composite preparation. Jute fabric used for composite preparation was purchased from a local market. All other chemicals used were of laboratory grade and were used without any further purification.

Synthesis of p-Amino Phenol-Urea-Formaldehyde-Casein (PAPUFC) Resins

The modified urea-p-aminophenol-casein-formaldehyde resin was synthesized by a two-stage reaction. The first stage involves refluxing of urea, p-aminophenol (up to 25% W/W of urea) and formaldehyde in the mole ratio of 1:2 in the presence of casein (25% casein was used on

TABLE 1 Percentage Free-Formaldehyde, Free-Phenol and Viscosity Results for the Prepared Resins

Resin code	Percentage of p-aminophenol to wt. of urea	% Free-formaldehyde content	% Free-phenol content	Intrinsic viscosity, η (dl $\cdot$ gm^{-1})
PAPUFC-5	5	4.27	1.12	0.205
PAPUFC-10	10	3.71	1.56	0.224
PAPUFC-15	15	1.90	1.78	0.285
PAPUFC-20	20	1.01	2.01	0.326
PAPUFC-25	25	0.87	2.38	0.384

the basis of urea required in the absence of p-aminophenol) for 30 min under mildly alkaline conditions ($pH = 8.5$). The product of the first stage was then refluxed for 15–20 min under acidic conditions ($pH = 5.5$). The resulting product from the second stage reaction was made slightly alkaline ($pH = 8.0$) and was vacuum distilled at 10 mm of Hg in the temperature range of 60–70°C. The final product was obtained as brownish syrup. Five different resin samples were prepared by varying the wt% of p-aminophenol from 5–25%. The prepared PAPUFC resins are coded by putting numbers as the suffix corresponding to amount of p-aminophenol in each and are listed in Table 1.

Composite Fabrication

The prepared resins were employed for the fabrication of glass fiber reinforced composites (GFRC) and jute fiber reinforced composites (JFRC) by maintaining resin: fabric ratio of be 40:60 and 60:40, respectively. The GFRC and JFRC were made by using dry lay-up prepreg technique by utilizing the prepared resins and PTS as curing agent. The resin composition containing curing agent (1% on wt. of resin) was dissolved in minimum quantity of methanol. The solution was then applied to fifteen pieces of glass fabric (150 mm × 150 mm) by hand lay-up technique and dried at room temperature for 30 min. The prepregs were then stacked between flat steel plates using teflon sheet as the mold-releasing agent at 120°C. After attaining the gel state it was compressed at a pressure of 70 psi. After completion of cure cycle (about 25–30 min), the mold was cooled in air to room temperature. The prepared sheets were cut into different required dimensions for the measurement of various mechanical properties and chemical resistance tests. Similarly, JFRC were prepared by following the same method but with 10 pieces of the jute fabric of the same size.

Characterization

The free-formaldehyde content of the prepared resins was determined by the sodium sulfite method [7] and presented in Table 1.

The free-phenol content of the prepared resins were determined by Koppeschaar method [8] and listed in Table 1.

The viscosity of all the resin samples was determined by a suspended level Ubbelohde viscometer using DMSO as the solvent at $30 \pm 0.1^\circ$C. The values of intrinsic viscosity $[\eta]$ for the prepared resins are shown in Table 1.

The FT-IR spectral analysis was carried out on a Nicolet Impact 400-D spectrophotometer by applying resin samples as thin films on KBr disks. The spectra of the cured resins were recorded by forming their pellets in spectroscopic grade KBr. Some important IR-characteristic bands of the representative samples are listed in Table 2.

The prepared resins were successfully crosslinked isothermally by using PTS (0.5% on wt. of resin) and hexamine (5% on wt. of resin) as the curing agents, at 120°C. The time required by the resin-curing agent system to attain gel state was recorded as the gel-time. These isothermal curing characteristics are furnished in Table 3.

Other useful thermal and kinetic parameters were determined by employing DSC on Dupont 9100 DSC module on the dynamic run

TABLE 2 Important IR-Characteristic Bands Observed for Resins

UF-Pure (cm^{-1})	CUF-Pure (cm^{-1})	PAPUFC-5 (cm^{-1})	CPAPUFC-5 (cm^{-1})	Probable assignment
3375	3368	3395	3361	υ N–H vibration in 2°-amine
2965	2938	2965	2968	υ sym. CH mode of CH_2 of ether, CH_2OH and $N-CH_2$
1669	1655	1669	1682	υ C=O vibration in $-CONH_2$ (amide-I).
1555	1555	1568	1535	NH-bending vibration (NH–CO) in 2°-amine (amide-II)
1387	1390	1400	1400	CH bending vibration in CH_2/CH_2OH
1145	1145	1140	1138	υ asy. Vibration in $N-CH_2-N$
—	1313	—	1313	$-OH$ deformation of CH_2OH
1279	1266	1280	1278	O–H bending mode of phenol
1024	1024	1017	1031	υ C–O vibration of ether
1460	1460	1467	1465	Twisting $-CH_2$ mode of the methylene ($-N-CH_2-N-$), $-CH$ mode in CH_2O; $N-CH_2-N$
—	—	789	769	$-CH$ bending vibrations, o-substituted benzene
—	—	836	809	p-substituted benzene

TABLE 3 Isothermal Curing of Resin Samples

Resin code	PTS gel-time (min)	Hexamine gel-time (min)
	120°C	120°C
PAPUFC-5	35	40
PAPUFC-10	27	34
PAPUFC-15	23	30
PAPUFC-20	17	24
PAPUFC-25	12	20

under nitrogen atmosphere at a heating rate of 10°C/min. The DSC parameters were determined by the Borchardt Daniels Method [9]. The DSC results of three selected representative resin samples are depicted in Tables 4 and 5.

The TGA of three selected representative, isothermally cured resin samples was carried out using universal V2.6D TA-instrument under nitrogen atmosphere at a heating rate of 10°C/min. The Broido method [10] was employed for TGA calculations. The usual thermal parameter obtained from TGA are presented in Tables 6 and 7. Integral procedural decomposition temperature (IPDT) was determined by using Doyle's method [11].

TABLE 4 Kinetic Parameters Evaluated from Single DSC Scan for Resin Samples

Resin code	Activation energy E (kJ mole^{-1})	Log Z (min^{-1})	Order of reaction, n	Heat of reaction ΔH (J · gm^{-1})
PAPUFC-5	649.5	66.66	1.04	13.9
PAPUFC-15	616.9	59.58	4.21	58.1
PAPUFC-25	821.2	79.79	5.88	35.9

TABLE 5 Thermal Parameters Evaluated from Single DSC Scan for Resin Samples

Resin code	Temp. at which curing started T_i°C	Peak exotherm temperature T_p°C	Temp. of complete curing T_f°C	Cure range $(T_f - T_i)$°C	Cure time (min)
PAPUFC-5	265.25	271.31	290.91	25.66	29.09
PAPUFC-15	256.42	269.41	300.00	43.58	30.00
PAPUFC-25	256.33	267.13	313.04	56.71	31.30

TABLE 6 Thermal Parameters of Cured PAPUFC Resins from TGA under Nitrogen Atmosphere

Resin code	T_i°C	T_{10}°C	T_{max}°C	T_f°C	IPDT°C	E kJ·Mole^{-1}
PAPUFC-5	163.0	190	311.1	786.3	427.1	47.51
PAPUFC-15	169.5	200	332.1	787.1	438.1	49.88
PAPUFC-25	207.8	210	347.2	800.0	494.0	51.96

T_i = Initial Decomposition Temperature; T_{max} = Temp. of Maximum Decomposition; T_f = Final Decompositon Temp.; T_{10} = Temp. at 10% wt. loss; E = Activation energy; IPDT = Integral Procedural Decomposition Temp.

TABLE 7 Percentage Weight Loss of Cured PAPUFC Resins at Different Temperatures from TGA

	Percentage (%) weight loss at							
Resin code	100°C	200°C	300°C	400°C	500°C	600°C	700°C	780°C
PAPUFC-5	1.49	10.13	47.66	64.14	71.75	75.95	83.15	91.14
PAPUFC-15	3.68	12.11	46.44	61.49	68.59	71.97	79.23	87.85
PAPUFC-25	2.25	11.01	39.93	52.41	62.01	65.89	71.57	78.40

The composites from a single batch were tested for their mechanical properties according to American Standards for Testing Materials (ASTM). Three test pieces of the required dimensions for each test were cut according to the ASTM. The average of three tests was recorded for each parameter.

- The measurement of flexural strength and interlaminar shear strength (ILSS), were carried out using Dutron's testing machine model number 13D according to ASTM D-790 and ASTM D-2344, respectively.
- The measurement of Izod impact strength of v-notched specimen was carried out according to ASTM D-256 using Zwick D-7900 impact machine.
- The rockwell hardness was measured according to ASTM D-785 on RAS/SL No. 4471 Rockwell hardness tester.

The results of the mechanical properties are furnished in Table 8.

The resistance to chemicals of the composite specimens was measured according to ASTM D-581. The composite specimens (10 mm × 10 mm) were immersed at room temperature for a week in

TABLE 8 Mechanical Properties of GFRC & JFRC Composites from UF and Various PAPUFC Resins

	Flexural strength 10^8 Pa.		Flexural modulus 10^{10} Pa.		Rockwell harness, R		Izod impact 10^2 Pa.		ILSS 10^7 Pa.	
Resin code	GFRC	JFRC	GFRC	JFRC	GFRC	JFRC	GFRC	JFRC	GFRC	JFRC
UF-PURE	1.881	0.959	0.813	0.827	175	167	21.3	5.9	0.516	0.480
PAPUFC-5	1.449	0.824	1.126	0.842	160	152	32.77	5.59	0.725	0.531
PAPUFC-10	1.291	0.735	1.085	0.747	155	147	52.21	6.83	0.689	0.469
PAPUFC-15	1.190	0.666	1.012	0.634	148	138	65.63	7.10	0.657	0.371
PAPUFC-20	1.166	0.620	0.996	0.625	139	130	66.82	11.80	0.514	0.336
PAPUFC-25	0.951	0.545	0.823	0.532	133	120	73.13	17.77	0.374	0.298

GFRC = Glass Fiber Reinforced Composites; JFRC = Jute Fiber Reinforced Composites.

various chemicals. The chemical resistance results are presented in Table 9.

RESULTS AND DISCUSSION

The preliminary characteristics of the samples are listed in Table 1. The decrease in percentage free-formaldehyde content with increase in the p-aminophenol percentage, that is, from 0% to 25% in the reaction mixture is very evident. This suggests that p-aminophenol also participates in the polycondensation reaction by utilizing formaldehyde for crosslinking. But this resin samples have casein as an extra molecule to be incorporated during synthesis. So, there is the other possibility that casein takes part in the reaction by utilizing formaldehyde for crosslinking and thereby consuming the excess formaldehyde to deplete the percentage of free formaldehyde in the resin. From Table 1, percentage free-phenol is found to increase as the p-aminophenol content increases from 0–25% in the reaction mixture. This increase in p-aminophenol content among the resin samples clearly suggests that crosslinking is not only due to p-aminophenol or urea, but casein also does take part in the reaction by utilizing formaldehyde for crosslinking and thereby depleting the percentage of free formaldehyde in the resin matrix.

The values of intrinsic viscosity were found to increase with increased percentage of p-aminophenol content in all the resins. Increase in viscosity reflects an enhanced resistance of the resin solution to flow. Similarly, this resin samples does have casein as an

TABLE 9 Chemical Resistance of the Composites from UF and Various PAPUFC Resins

Solvents		UF-Pure		PAPUFC-5		PAPUFC-10		PAPUFC-15		PAPUFC-20		PAPUFC-25	
		G	J	G	J	G	J	G	J	G	J	G	J
Acetone	A	0.912	4.104	0.203	0.373	0.194	0.342	0.173	0.321	0.152	0.237	0.109	0.261
	B	1.818	0.981	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Methnanol	A	0.924	6.432	0.196	0.293	0.193	0.276	0.176	0.251	0.157	0.234	0.123	0.211
	B	0.081	1.431	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
CCl_4	A	0.586	2.942	0.346	0.501	0.313	0.467	0.298	0.434	0.268	0.396	0.195	0.355
	B	0.719	1.103	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Methyl Ethyl Ketone	A	0.432	4.438	0.369	0.482	0.347	0.457	0.331	0.461	0.293	0.383	0.257	0.368
	B	0.041	0.098	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Toluene	A	0.489	2.412	0.567	0.737	0.481	0.610	0.503	0.567	0.392	0.434	0.371	0.357
	B	NA	0.084	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
25% Ethanol	A	5.501	6.872	0.463	0.807	0.443	0.769	0.421	0.642	0.388	0.531	0.376	0.424
	B	0.711	1.084	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
25% H_2SO_4	A	D	D	D	D	D	D	53.461	57.011	42.410	38.410	37.616	31.315
	B	D	D	D	D	D	D	12.170	9.023	7.714	6.415	4.311	4.310
15% HCl	A	D	D	D	D	9.363	11.751	8.686	8.886	8.432	7.942	5.942	5.455
	B	D	D	D	D	3.071	4.135	2.961	3.910	2.762	3.542	2.432	2.430
5% HNO_3	A	12.834	D	D	D	3.031	6.715	2.963	6.107	2.452	5.867	1.757	4.917
	B	13.143	D	D	D	1.960	2.253	1.432	2.017	1.238	1.913	0.955	1.410
5% NaOH	A	D	D	D	D	7.651	8.535	6.544	7.810	5.538	7.011	4.632	6.432
	B	D	D	D	D	3.071	4.107	2.856	3.003	2.071	2.716	1.857	2.109
25% CH_3COOH	A	21.413	11.432	1.961	2.331	1.436	2.001	1.296	1.848	1.067	1.236	0.846	1.036
	B	20.981	9.872	0.724	1.055	0.643	0.885	0.541	0.751	0.432	0.616	0.211	0.357
H_2O	A	8.411	14.734	1.136	2.067	0.998	1.432	0.735	0.810	0.513	0.417	0.369	0.263
	B	21.981	10.103	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA

A = %Change in weight; B = %Change in thickness; D = Destroyed; NA = Not Affected; G = Glass Fiber Reinforcered Composites; J = Jute Fiber Reinforcered Composites.

extra component. So, increased viscosity is also due to the incorporation of casein molecules in the resin matrix, which increases the average size/average molecular weight of resin samples.

The major absorptions of the IR spectra and their assignments are summarized in Table 2. Due to complexicity of structure in the polymer, the absorption peaks are broad. Broadening is probably due to the presence of byproducts in the resin, such as water and excess formaldehyde, which allow hydrogen bonding with reactive functional group such as $-CH_2OH$, NH_2 and $-NH$. However, the spectra of cured resins gave sharper characteristic absorption peaks. Additional details of the spectra are discussed in reference [12]. Some small peaks observed around $2750-2500\,cm^{-1}$ in the spectra of UFC resin may be due to S$-$H and S$-$S stretching vibrations of methionine and cystine present in casein.

The isothermal curing studies were performed with two different cure agents. The data are presented in Table 3. The study showed that gel-time decreased sharply with increase in the p-aminophenol content in the resins. This decrease in gel-time is due to the higher reactivity of p-aminophenol toward formaldehyde. So, as p-aminophenol percentage increases, more and more phenol is available for cross-linking, and hence the gel-time decreases toward higher p-aminophenol content in the resin samples.

The DSC scans obtained from the prepared resins were almost similar in general shape, giving an exotherm in some definite temperature range. This indicates that the exotherm was due to the curing reaction. From these DSC scans the temperatures at which reaction was initiated (T_i), had attained a maximum (T_p), and was completed (T_f) along with kinetic parameters, were evaluated by applying Borchardt Daniels method, and listed in Tables 4 and 5. The cure range ($T_f - T_i$) and cure-time were found to be in the range of 25–56°C and 29–31 min, respectively. These data imply the curing conditions to be employed during fabrication of fiber-reinforced composite from the resin samples covered in this study.

From TGA data (Tables 6 and 7), the temperature at which degradation started (T_i) suggests the temperature which can be withstood by the polymeric sample without undergoing degradation. The values of T_i are found in the range between 163–207°C, and it increases with increase in p-amino phenol content in the series. This indicates an increase in the temperature which can be withstood by the resins without undergoing any thermal degradation, resulting from the incorporation of p-aminophenol in the resin. The temperature at maximum weight loss, designated as (T_{max}), is observed to be around 311–347°C. It increases with increase in p-aminophenol content. This indicates an increase in thermal stability of the modified resins as p-aminophenol content increases. At 780–800°C about 8.83% residues was found for PAPUFC-5 resin sample, and residues for PAPUFC-15 and PAPUFC-25 were found to be 12.15% and 21.6%, respectively. This higher residual content of resin sample containing higher p-aminophenol percentage indicates an improvement of thermal stability as p-aminophenol percentage increases from 0–25% in the resin, as depicted in Table 7. The Integral Procedural Decomposition Temperature (IPDT) values remained in the range of 427–494°C for the resins. The values for activation energy (E) remained in the range of 47–52 kJ.mole^{-1}. The final decomposition temperatures (T_f) and temperature at 10% weight loss, designated as (T_{10}), were in the ranges of 780–800°C and 190–210°C. The TGA results thus suggest that incorporation of casein and p-aminophenol in the UF-resin favorably affect the thermal stability of the synthetic resin.

The mechanical properties of GFRC and JFRC follow similar trends (Table 8). As p-aminophenol content was increased, the flexural strength, flexural modulus, and rockwell hardness decreased. Izod impact strength was found to increase with increase in p-aminophenol content. This indicates an enhancement in toughness of the composite material with increase in the p-aminophenol concentration in the resin matrix.

The chemical resistance of the composite specimens was also found to be excellent, as shown in Table 9. All GFRC and JFRC samples showed excellent resistance toward common organic solvents, which was found to increase with increase in p-aminophenol content. GFRC and JFRC exhibited poor resistance toward mineral acids, especially 25% H_2SO_4, and alkali.

CONCLUSIONS

The decrease in percentage of free-formaldehyde and increase in percentage of free-phenol, with increase in p-aminophenol content in the resin confirms that casein molecules take part in the reaction by utilizing the excess formaldehyde for crosslinking. The IR-Spectral studies of resin samples strongly confirm the presence of secondary amine and methylene bridges together in the sample. This is an indication that the primary amino group has involved themselves in the reaction and are present randomly in the crosslinked structure. It also confirms p-substituted benzene due to bonding of the p-aminophenol moiety. Isothermal curing data show a decrease in the gel-time with increase in the percentage of p-aminophenol content, showing greater reactivity of p-aminophenol toward crosslinking reaction. Thermal parameters show increases in initial decomposition temperature (T_i) and maximum decomposition temperature (T_{max}), as the p-aminophenol content increases. This may be considered as the enhancement in thermal stability with the incorporation of p-aminophenol and casein in urea-formaldehyde resin. The lower percentage weight loss of resin sample containing the highest p-aminophenol percentage, indicates an increase in thermal stability by incorporation of p-aminophenol and casein. The mechanical properties of GFRC and JFRC follow a similar trend. Izod impact strength was found to increase with p-aminophenol content. This strength shows an enhancement in the toughness of the composite material with increasing p-aminophenol content in the resins. The chemical resistance of the composites was also found to be excellent toward common organic solvents.

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