

Preparation, Characterization, and Composites from Low Formaldehyde Emission Urea–Formaldehyde–Casein Copolymer

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ABSTRACT: A modified urea–formaldehyde resin was synthesized by the condensation of urea and formaldehyde in the presence of varying proportions of casein up to 25% (w/w) of urea under alkaline conditions. All the prepared resins were characterized by free-formaldehyde content, viscosity measurements, and number-average molecular weight determination by vapor pressure osmometry and IR spectroscopy. Their curing kinetics were studied isothermally and by differential scanning calorimetry on dynamic runs. The resin samples were cured isothermally at 60, 80, and 100°C using ammonium chloride and hydroxylamine hydrochloride as curing agents. The isothermal curing study

was also performed with hexamine at 120°C. Cured resins were characterized by IR and thermogravimetric analysis. The resin samples were employed for the fabrication of glass fiber and jute fiber reinforced composites by maintaining 2 : 3 and 3 : 2 proportions of resin/reinforcement, respectively. The prepared composites were tested for their mechanical properties and resistance toward various chemicals. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 531–537, 2005

Key words: casein; composites; mechanical properties; modifications of urea–formaldehyde resins

INTRODUCTION

With growing economic competition and ecological pressure, there is an increasing need to develop more useful, low cost novel polymers and reinforcements. Thermosetting resin technology has advanced rapidly in terms of raw materials, basic chemistry, and applications in recent years.¹ The term amino plastics has been coined to cover a range of resinous polymers produced by the interaction of amines or amides with aldehydes.² Out of the various polymers of this type, there are two of current commercial importance in the field of plastics: urea–formaldehyde (UF) and melamine–formaldehyde resins.^{3,4} These resins are used extensively for molding materials, adhesives, textile materials, and paper finishing and in the production of surface coatings and wet strength papers.^{5–9} Melamine–formaldehyde is also used in decorative laminates.¹⁰

A perusal of the literature reveals that these resins are modified by collagen¹¹; casein, chitosan, polyacrylamide, and biuret¹²; casein and gelatin^{13,14}; soy pro-

tein¹⁵; and starch and cellulose.^{16–19} Such compositions showed improved storage stability, bonding strength, water resistance, and antiaging properties and lower free formaldehyde. Glass fiber reinforced composites (GFRCs) with improved thermal insulation properties were prepared from water dispersed Novolak phenolic resins blended with casein.¹⁴

Many reports are available for the blending of such modifiers in a resin composition prior to curing. However, incorporation of these modifiers during resin preparation has not been attempted much. In the present work we tried to synthesize a modified UF resin by polycondensation with casein. Prepared resins were characterized by viscosity and other chemical methods. The resins were extensively studied for their curing behavior. Cured resins were characterized by IR spectroscopy and thermogravimetric analysis (TGA). The GFRCs and jute fiber reinforced composites (JFRCs) were fabricated and tested for their mechanical properties and resistance toward various chemicals according to the American Society for Testing and Materials (ASTM).

EXPERIMENTAL

Materials

Urea was obtained from E. Merck Limited (Bombay, India). The formaldehyde solution (37%) was pro-

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TABLE I
Percentage of Free Formaldehyde, Intrinsic Viscosity (η), and M_n by VPO for Prepared Resins

Resin code	Ratio casein (%) / weight of urea	Free formaldehyde content (%)	η (dL g ⁻¹)	M_n
UF-pure	0	1.47	0.079	1488
UFC-5	5	1.35	0.088	1744
UFC-10	10	1.13	0.094	2047
UFC-15	15	1.05	0.135	2409
UFC-20	20	0.90	0.145	2660
UFC-25	25	0.75	0.162	2955

cured from Samir Tech. Chem. Pvt. Ltd. Casein (alkali soluble) was obtained from Loba Chemie Pvt. Ltd. For composite preparation, E-type 10-mill plain-woven glass cloth (0.25-mm thickness) was purchased from Unnati Corporation. The jute fabric used for composite preparation was purchased from a local market. All other chemicals were laboratory grade and used without any further purification.

Synthesis of UF-casein (UFC) resin

The modified UF resin was synthesized by a two-stage reaction. The first stage involves refluxing of urea and formaldehyde with a mole ratio of 1 : 2 in the presence of varying amounts of casein up to 25% (w/w) of urea 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 vacuum distilled in a temperature range of 60–70°C at 15 mmHg. The final product was obtained as a colorless to brownish syrup. The prepared UFC resins were coded by utiliz-

ing suffix numbers corresponding to the amount of casein in each.

Characterization

Free-formaldehyde content

The free-formaldehyde content of the prepared resins was determined by the sodium sulfite method,²⁰ and the results are presented in Table I.

Viscosity measurement

The viscosity of all resin samples was determined by a suspended level Ubbelohde viscometer using DMSO as the solvent at 30 ± 0.1°C. The values of the intrinsic viscosity [η] for the prepared resins are shown in Table I.

Molecular weight by vapor pressure osmometry (VPO)

The number-average molecular weight (M_n) of the prepared resins was determined by VPO on a Knauer vapor pressure osmometer using DMF as a solvent at 90°C. The M_n values for the prepared resins are listed in Table I.

IR spectroscopy

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

TABLE II
Important IR Characteristic Bands Observed for Resins

UF-pure (cm ⁻¹)	CUF-pure (cm ⁻¹)	UFC-5 (cm ⁻¹)	CUFC-5 (cm ⁻¹)	Probable assignment
3375	3368	3341	3375	ν N-H vibration in 2°-amine
		3502	3500	
2965	2938	2979	2958	ν sym. CH mode of CH ₂ of ether, CH ₂ OH and N-CH ₂
		2750–2500	2750–2500	S-H and S-S stretching vibrations of methionine and cystine present in casein
1669	1655	1669	1669	ν C=O vibration in -CONH ₂ (amide I)
1555	1555	1568	1555	NH-bending vibration (NH-CO) in 2°-amine (amide II)
1387	1390	1394	1394	CH bending vibration in CH ₂ /CH ₂ OH
1145	1145	1145	1145	ν asym. vibration in N-CH ₂ -N
1300	1313	1300	1306	-OH deformation of CH ₂ OH
1279	1266	1273	1269	ν C-N vibration in amines
1024	1024	1014	1017	ν C-O vibration of ether
1460	1460	1460	1460	Twisting -CH ₂ mode of methylene (-N-CH ₂ -N-), -CH mode in CH ₂ O; N-CH ₂ -N

TABLE III
Isothermal Curing of Resin Samples

Resin code	Gel time (min)						
	Hydroxylamine hydrochloride (1%)			Ammonium chloride (1%)			Hexamine (5%)
	60°C	80°C	100°C	60°C	80°C	100°C	120°C
UF-pure	13	11	8	10	6	3	45–50
UFC-5	22	16	13	14	22	12	68–70
UFC-10	52	20	18	30	40	18	69–76
UFC-15	80	26	29	62	50	23	95–97
UFC-20	110	31	36	90	54	27	100–105
UFC-25	145	38	44	128	61	31	120–125

Curing study

The prepared resins were successfully crosslinked isothermally by using ammonium chloride and hydroxylamine hydrochloride as the curing agents with 1% (w/w) of resin at 60, 80, and 100°C. The curing study was also performed employing hexamine at 120°C and 5% (w/w) of resin. The time required by the resin-curing agent system to attain the gel state was recorded as the gel time. These isothermal curing characteristics are furnished in Table III.

The other useful thermal and kinetic parameters were determined by employing differential scanning calorimetry (DSC) on a Dupont 9100 DSC module on dynamic runs under a nitrogen atmosphere at a heating rate of 10°C/min. The DSC parameters were determined by the Borchardt–Daniels method.²¹ The DSC results are depicted in Tables IV and V.

The TGA of isothermally cured resin samples was carried out using a universal V2.6D TA instrument under a nitrogen atmosphere at a heating rate of 10°C/min. The Broido²² method was employed for TGA calculations. The usual thermal parameters obtained from the TGA are presented in Tables VI and Table VII. The integral procedural decomposition temperatures (IPDTs) were determined by using the Doyle method.²³

Composite fabrication

The prepared resins were employed for the fabrication of GFRCs and JFRCs by maintaining resin/fabric ra-

tios of 40 : 60 and 60 : 40, respectively. The GFRCs and JFRCs were made by using E-type 10-mill plain-woven glass cloth and jute fabric cloth, respectively, using a resin/curing agent system. In the present investigation a dry lay-up prepreg technique was employed by utilizing the prepared resins and NH₄Cl as the curing agent. The resin composition containing the curing agent (1% vs. weight of resin) was dissolved in a minimum quantity of methanol. The solution was then applied to 15 pieces of glass fabric (150 × 150 mm) by a hand lay-up technique and dried at room temperature for 30 min. The prepregs were then stacked between flat steel plates using teflon sheets 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 the 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 the chemical resistance test. JFRCs were also prepared by following the same method but using 10 pieces of the jute fabric of the same size.

Testing of composites

The composites from a single batch were tested for their mechanical properties according to ASTM standards. Three test pieces of required dimensions for each test were cut according to ASTM. The average of three tests was recorded for each parameter. In the first test, the measurements of the flexural strength

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

Resin code	T_i (°C)	T_p (°C)	T_f (°C)	$T_f - T_i$ (°C)	Cure time (min)
UF-pure	264.0	278.8	293.3	29.3	29.3
UFC-5	281.9	291.7	295.8	13.9	29.6
UFC-10	270.0	275.7	283.3	13.3	28.3
UFC-15	286.9	290.4	294.4	7.6	29.4
UFC-20	274.3	279.7	290.0	15.7	29.0
UFC-25	272.3	278.1	286.1	13.8	28.6

T_i , temperature at which curing started; T_p , peak exotherm temperature; T_f , temperature of complete curing; $T_f - T_i$, Cure range.

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

Resin code	E (kJ mol ⁻¹)	Log Z (min ⁻¹)	n	ΔH (J g ⁻¹)
UF-pure	215.0	28.5	4.36	761.6
UFC-5	328.3	42.4	3.05	684.0
UFC-10	202.7	37.8	4.82	349.4
UFC-15	381.8	50.1	5.21	1448.0
UFC-20	148.3	17.9	0.50	220.6
UFC-25	410.1	39.1	0.96	364.4

E , activation energy; n , order of reaction; ΔH , heat of reaction.

and interlaminar shear strength were carried out using a Dutron testing machine (model 13D) according to ASTM D 790 and D 2344, respectively. In the second test, the measurement of the Izod impact strength of a V-notched specimen was carried out according to ASTM D 256 using a Zwick D-7900 impact machine. In the third test, the Rockwell hardness was measured according to ASTM D 785 on a RAS/SL No. 4471 Rockwell hardness tester. The results of the mechanical properties are provided in Table VIII.

The resistance to chemicals of the composite specimen was measured according to ASTM D 581. The laminate specimens (10 × 10 mm) were immersed at room temperature for 1 week in various chemicals. The chemical resistance results are presented in Table IX.

RESULTS AND DISCUSSION

In order to achieve the target of producing low formaldehyde emitting resin compositions, we opted for casein, which is very well known to undergo reactions with aldehydes.^{24,25} The preliminary characteristics of the samples are listed in Table I. The decrease in the percentage of free-formaldehyde content with the increase in the casein percentage (from 0 to 25%) in the reaction mixture suggests that casein actively participates in the reaction by utilizing formaldehyde for crosslinking, thereby consuming the excess formalde-

hyde to deplete the percentage of free formaldehyde in the resin samples. The optimum level for casein to be incorporated in the resin remained 25% on the weight basis of urea. Above this level, in the second stage of resin preparation some amount of casein tended to precipitate out in the reaction mixture near its isoelectric point.

The intrinsic viscosity values were found to increase with an increase in the percentage of casein content. An increase in viscosity also suggests the enhanced resistance of the resin solution to flow. The M_n studies on VPO also showed an increase in the M_n value with an increase in the casein content in the resins. The values are depicted in Table I. This is clear-cut evidence of the incorporation of casein molecules in the resin matrix to increase the average size and average molecular weight of the resin samples.

The details revealed by the examination of the IR spectra are summarized in Table II. Because of the complexity of the structure in the polymer, the absorption frequencies are broad in the case of the resin spectra. Broadening is observed that is due to the presence of by-products in the resin, such as water and excess formaldehyde, which allow hydrogen bonding with reactive functional groups such as —CH₂OH, NH₂, and —NH. However, the spectra of cured resins gave sharper characteristic absorption peaks in this region. The resin samples showed absorption in the region of 3500–3310 cm⁻¹. In the UF-pure resin, a medium absorption peak is observed at 3375 cm⁻¹, which is the characteristic absorption of the NH stretching mode for the H-bonded —NH₂ group. Similar absorption bands for cured UF (CUF-pure), UFC-5, and cured UFC-5 (CUFC-5) were recorded in the same region. A medium absorption band in all resin spectra appears in the range of 2970–2850 cm⁻¹, which is ascribed to the symmetrical C—H stretching mode of the CH₂ of ether, CH₂OH, and N—CH₂. A very strong absorption band is observed at around ~1670 cm⁻¹ in all spectra, which may be assigned to the C=O stretching (amide I) in the —CONH₂ group. The strong absorption bands around 1560 cm⁻¹ may be attributable to the —NH bending

TABLE VI
Thermal Parameters of Cured UF and UFC Resin from TGA Under Nitrogen Atmosphere

Resin code	T_i (°C)	T_{10} (°C)	T_{max} (°C)	T_f (°C)	IPDT (°C)	E (kJ mol ⁻¹)
UF-pure	141.4	200	338.9	787.4	433.3	73.4
UFC-5	148.2	180	340.5	785.0	443.3	59.4
UFC-10	170.4	220	349.8	786.5	472.3	64.7
UFC-15	178.6	225	357.1	783.5	457.7	66.3
UFC-20	180.8	200	366.7	786.9	468.0	62.4
UFC-25	185.2	180	383.4	786.0	430.9	55.9

T_i , initial decomposition temperature; T_{max} , temperature of maximum decomposition; T_f , final decomposition temperature; T_{10} , temperature at 10% weight loss; E , activation energy; IPDT, integral procedural decomposition temperature.

TABLE VII
Percentage Weight Loss of Cured UF and UFC Resins at Different Temperatures from TGA

Resin code	Percentage weight loss							
	100°C	200°C	300°C	400°C	500°C	600°C	700°C	780°C
UF-pure	3.88	10.24	56.10	76.69	80.28	84.14	88.92	92.97
UFC-5	3.02	15.39	49.09	74.16	77.89	80.48	83.85	86.43
UFC-10	3.97	7.96	56.67	69.59	74.97	78.50	84.87	90.89
UFC-15	3.87	7.96	56.15	72.68	77.56	80.98	86.26	91.91
UFC-20	4.43	10.90	50.15	69.35	73.02	76.26	79.96	83.42
UFC-25	5.82	14.49	55.01	74.75	79.12	82.73	86.44	89.85

mode in the 2°-amine (amide II). The 1°-amino group of casein first forms methylol derivatives with formaldehyde. The crosslinking between two such methylol groups provides ether linkage ($-\text{CH}_2-\text{O}-\text{CH}_2-$) to which $-\text{NH}$ is attached on both sides.²⁶ Crosslinking may also occur between methylol casein and monomethylolurea. Thus, the hydroxymethylation of the primary amino group of casein followed by crosslinking forms 2°-amine in the resin along with such linkages between dimethylol urea and formaldehyde. A weak absorption band at 1470–1460 cm^{-1} may be due to the $-\text{CH}$ mode in $-\text{CH}_2\text{O}$ and $\text{N}-\text{CH}_2-\text{N}$. The weak absorption bands around 1400–1390 cm^{-1} for all polymer samples may be ascribed to the C–H bending mode in $-\text{CH}_2/\text{CH}_2\text{OH}$. The medium absorption band appearing between 1150 and 1130 cm^{-1} may be generally assigned to the asymmetric stretching vibration of $-\text{N}-\text{CH}_2-\text{N}-$. The medium bands in the range of 1340–1250 cm^{-1} are attributed to the C–N stretching for all of the polymer samples. The medium band at $\sim 1300 \text{ cm}^{-1}$ appears to be mainly due to the $-\text{OH}$ deformation in $-\text{CH}_2\text{OH}$. The strong absorption peaks at $\sim 1024 \text{ cm}^{-1}$ in the spectra of all polymers are assigned to C–O stretching. The band indicates the presence of ether linkage ($\text{CH}_2-\text{O}-\text{CH}_2$) that is due to a crosslinking reaction during condensation. The small peaks observed around 2750–2500 cm^{-1} in the spectra of the UFC-5 resin may be due to S–H and S–S stretching vibrations of methionine and cystine that are present in casein.

The isothermal curing studies were performed with three different cure agents. The data are presented in Table III. The study showed that the gel time was found to increase sharply with an increase in the casein content in the resins. The time required by hexamine as the curing agent for the gel formation to occur (i.e., gel time) ranged between ~ 45 and 125 min, whereas the gel time for ammonium chloride and hydroxylamine hydrochloride at various temperatures ranged between 3–128 and 8–145 min, respectively. As is evident from Table III, pure UF resin crosslinks in 45–50 min using 5% hexamine at 120°C. This duration is found to increase with an enhancement in the amount of casein in the resin. The resin with 5% casein had a gel time of ~ 70 min, which reached a maximum of 125 min at 25% casein content. Nearly a 2.5-fold increase is observed in the gel-time values with increasing casein percentages from 0 to 25% in the resin samples. This could be viewed as the lesser reactivity of resins toward the crosslinking reaction at higher casein concentration. The gel time observed by using ammonium chloride as the curing agent was less than the other two curing agents (hexamine and hydroxylamine hydrochloride).

The DSC scans obtained for the prepared resins were almost similar in general shape, giving an exotherm in some definite temperature ranges. This indicates that the exotherm obtained in the resin systems were attributable to the curing reaction. From these DSC scans the temperatures at which the reaction was initiated (T_i), attained a maximum (T_p), and was com-

TABLE VIII
Mechanical Properties of GFRCs and JFRCs from UF and Various UFC Resins

Resin code	Flexural strength 10^8 Pa		Flexural modulus 10^{10} Pa		Rockwell hardness		Izod impact 10^2 Pa		ILSS 10^7 Pa	
	GFRC	JFRC	GFRC	JFRC	GFRC	JFRC	GFRC	JFRC	GFRC	JFRC
UF-pure	1.88	0.96	0.81	0.83	175	167	21.31	5.88	0.52	0.48
UFC-5	1.67	0.70	0.66	0.80	162	155	39.27	4.58	0.50	0.44
UFC-10	1.59	0.62	0.61	0.57	158	148	22.97	4.40	0.44	0.38
UFC-15	1.46	0.55	0.57	0.48	152	140	52.49	6.63	0.40	0.28
UFC-20	1.29	0.48	0.50	0.39	142	132	33.64	4.86	0.37	0.27
UFC-25	1.19	0.43	0.45	0.27	138	126	42.37	6.27	0.32	0.25

TABLE IX
Chemical Resistancy of Composites from UF and Various UFC Resins

Solvents	UF-pure		UFC-5		UFC-10		UFC-15		UFC-20		UFC-25	
	G	J	G	J	G	J	G	J	G	J	G	J
Acetone												
A	0.91	4.10	0.58	1.61	0.49	1.34	0.38	0.98	0.33	0.61	0.29	0.49
B	1.82	0.98	1.71	0.23	NA	0.08	NA	NA	NA	NA	NA	NA
Methanol												
A	0.92	6.43	0.62	3.87	0.58	3.57	0.49	3.37	0.39	2.79	0.38	2.38
B	0.08	1.43	NA	0.95	NA	0.18	NA	NA	NA	NA	NA	NA
CCl ₄												
A	0.59	2.94	0.40	1.20	0.39	1.15	0.28	1.11	0.21	1.08	0.19	0.96
B	0.72	1.10	0.68	0.74	1.12	0.65	0.23	0.56	NA	NA	NA	NA
Methyl ethyl ketone												
A	0.43	4.44	0.17	1.98	0.42	1.97	0.12	1.91	0.09	1.85	0.08	0.88
B	0.04	0.09	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Toluene												
A	0.49	2.41	0.38	1.89	0.34	1.54	0.29	1.38	0.27	1.10	0.25	0.97
B	NA	0.08	NA	NA	NA	NA	NA	14.50	NA	NA	NA	NA
25% Ethanol												
A	5.50	6.87	3.70	4.23	3.48	4.20	3.11	4.13	2.98	3.12	2.87	3.01
B	0.71	1.08	0.67	NA	0.57	NA	0.12	NA	NA	NA	NA	NA
25% H ₂ SO ₄												
A	D	D	D	D	D	D	27.35	29.11	20.31	18.24	17.36	13.94
B	D	D	D	D	D	D	36.76	38.42	29.53	30.61	16.86	14.51
15% HCl												
A	D	D	15.22	D	14.33	D	10.32	D	9.13	D	8.93	10.96
B	D	D	11.11	D	10.07	D	8.71	D	6.12	D	5.49	7.21
5% HNO ₃												
A	12.83	D	10.94	D	9.72	D	7.86	D	7.10	D	6.34	D
B	13.14	D	10.53	D	8.18	D	6.43	D	4.80	D	4.60	D
5% NaOH												
A	D	D	D	D	D	D	19.48	21.79	17.93	19.83	14.51	16.63
B	D	D	D	D	D	D	30.52	35.86	28.42	28.61	20.43	20.54
25% CH ₃ COOH												
A	21.41	11.43	15.07	7.56	9.88	6.11	8.43	5.36	6.85	4.98	6.55	3.23
B	20.98	9.87	18.06	3.93	14.61	2.12	10.41	1.39	6.47	0.89	4.03	0.82
H ₂ O												
A	8.41	14.73	3.35	6.01	3.10	5.41	3.05	4.04	3.04	2.46	3.03	2.23
B	21.98	10.10	14.84	7.06	12.54	6.98	10.41	6.09	9.57	4.25	9.50	4.17

A, change in weight (%); B, change in thickness (%); NA, not affected; G, glass fiber reinforced composites; J, jute fiber reinforced composites; D, destroyed.

pleted (T_f) along with the kinetic parameters were evaluated by applying the Borchardt–Daniels method. These important parameters are listed in Table IV. The cure range ($T_f - T_i$) for the resins decreased with the incorporation of casein, and the cure time was in the range of 28.3–29.6 min. These data are invaluable because they imply the curing conditions to be maintained during fabrication of FRCs from the resin samples covered under the study. The useful kinetic parameters evaluated from the DSC scans are presented in Table V.

From the TGA data (Table VI), the temperature at which degradation started (T_i) suggests the temperature value that can be withstood by the polymeric sample without undergoing any type of degradation. The T_i values are in the range between 140 and 190°C, and they increase with an increase in casein content. This indicates a considerable increase in the thermal

stability of the resins with enhanced incorporation of casein in the resins. The temperature at maximum weight loss (T_{max}) was quite high (around 338–385°C) and increased with casein content. This is also an indication of the enhancement of the thermal stability with an increased casein percentage in the resin samples. At 780–800°C about 7.0% residue was found for UF-pure, and residues for other resins were in the range of 8–16%. This higher residual content indicates slightly higher thermal stability of modified resin than the pure resin even at elevated temperatures of around 800°C. The IPDT values remained in the range of 430–470°C for all resins and it was found to be higher than the pure resin sample. The values for the activation energy (E) remained in the range of 50–70 kJ mol⁻¹. The final decomposition temperatures (T_f) and temperature at 10% weight loss (T_{10}) were found at 780–790 and 180–230°C, respectively. The percent-

age weight loss of the pure resin sample was higher than that of all other samples, indicating higher thermal stability of all modified resins as depicted in Table VII. The results from TGA thus suggest that incorporation of casein in the UF resin does affect the thermal stability of the synthetic resin and enhances it to some extent.

The mechanical properties of GFRCs and JFRCs follow a somewhat similar trend. As the casein content was increased, the flexural strength, flexural modulus, and Rockwell hardness were decreased. Izod impact strength was found to increase with an increase in casein content. This strength shows the enhancement in the toughness of the composite material when increasing the casein content in the resin matrix.

The chemical resistance of the specimen was also excellent as shown in Table IX. All GFRC and JFRC samples showed excellent resistance toward common organic solvents that was found to increase with an increase in casein content. GFRCs and JFRCs exhibited somewhat poor resistance toward mineral acids, especially 25% H₂SO₄ and alkali.

CONCLUSIONS

The decrease in the percentage of free formaldehyde with increasing casein content confirms that casein molecules do take part in the reaction by utilizing the excess formaldehyde for crosslinking. The increasing values of the intrinsic viscosity with an increase in the casein percentage may be explained by considering the greater involvement of casein molecules in the resin structure.

The IR spectral study of the resin samples strongly confirms the presence of secondary amine and methylene bridges together in the sample. This is an indication that the primary amino groups of casein have involved themselves in the reaction and have been set randomly in the crosslinked structure.

Curing data show enhancement in the gel time with an increase in the percentage of casein content, demonstrating involvement of casein in the reaction, which has a slight retarding effect on the crosslinking reaction.

The thermal parameters show increases in the initial decomposition temperature and maximum decomposition temperature as the casein content increases. This may be considered as the enhancement in thermal stability with the incorporation of casein. The higher

percentage weight loss of the pure resin sample than all other modified resins indicates an increase in the thermal stability by the incorporation of casein.

The mechanical properties of GFRCs and JFRCs follow a nearly similar trend. The Izod impact strength was increased with the casein content. This strength shows the enhancement in the toughness of the composite material with increasing the casein content. The chemical resistance of the composites was also excellent toward common organic solvents and improved toward the mineral acids as the casein content increases.

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