A Study on Composites from Phenol-Formaldehyde-Casein Resin

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ABSTRACT: A modified phenol-formaldehyde (PF) resin was synthesized under alkaline condition in varying proportion of casein up to 20% (w/w) of phenol. All the prepared resins were characterized by free phenol content, free formaldehyde content, viscosity measurements, number average molecular weight determination by conductometry and Infrared Spectroscopy (IR). Their curing kinetics was studied isothermally and by differential scanning calorimetry (DSC) on dynamic runs. The resin samples were cured using concentrated hydrochloric acid and hexamine individually. Cured resins were characterized by IR and Thermogravimetry (TGA). Glass fabric reinforced composites (GFRC) were fabricated by maintaining 40 : 60 proportion of resin to reinforcement material. The laminates thus formed were characterized for their mechanical properties and chemical resistance. Enhancements in thermal stability of the resin as well as toughness of composite with increase in casein content were observed for the resins studied. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 2838–2846, 2010

Key words: casein; composites; mechanical properties; modification of phenol-formaldehyde resin

INTRODUCTION

With growing economic competition and ecological pressure, there is an increasing need to develop more useful, low cost novel polymers and reinforcements. Among the thermosetting resins, the phenolic resins are by far the most important polymers in terms of industrial output and applications. They are widely used because of their low cost, versatility, and numerous invaluable applications such as adhesives, casting and molds, composites, nanocomposites, hollow particles, foams[1–6] etc.

A perusal of the literature reveals that these resins were modified by sulfonated phenol-formaldehyde (PF) resin,[7] organic acid esters,[8] lignins,[9,10] nitrogen, phosphorous,[11] pyrolitic oil,[12] and vapor-grown carbon-fibers.[13] High-performance, cost-effective, lightweight hybrid composites were developed by combining high-modulus glass-fibers with banana fiber in phenolic resin.[14] Glass fabric reinforced composites (GFRCs) with improved thermal insulation properties were prepared from water dispersed novolac phenolic resins blended with casein.[15] From the perusal of the literature, it soundly effervesces that nobody has yet reported the incorporation of casein in the resin during the preparative stage. Recently, incorporation of casein in urea-formaldehyde and melamine-formaldehyde resins is reported from our laboratory.[16–18] The composites fabricated from these resins showed enhancement in toughness with increase in casein content. The resultant composites also exhibited good chemical resistancy. Incorporation of biomaterials into synthetic resin is advantageous because of their lower cost, renewable alternate for the petroleum based monomers, best utilization of the abundant material to preserve industrial ecology and environment. The present work deals with the incorporation of casein in PF resin during the preparation, to study the curing behavior of resins and the fabrication of GFRCs therefrom.

EXPERIMENTAL

Materials

Phenol and formaldehyde solution (37%) were purchased from Samir Tech Chem. Casein (alkali soluble) was obtained from Loba Chemie. For composite preparation E-type 10-mill plain-woven glass-cloth (0.25 mm thickness) was obtained from Unnati Corporation. All other chemicals were of laboratory grade and used without any further purification.

Synthesis of PF-casein (PFC) resin

The synthesis of PFC resin was performed by following the polycondensation method for the preparation of resol type resin. In a 500 mL round-

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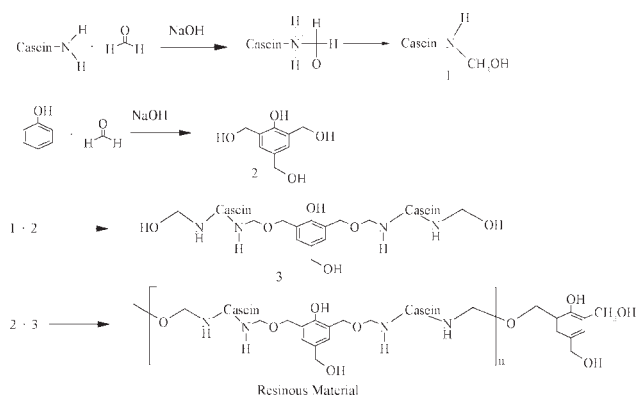
Scheme 1 Plausible reaction scheme.

bottomed flask, fitted with the standard taper joints, equipped with a reflux condenser and mechanical stirrer, the required amount (1 mol) of phenol monomer and 50 mL 5% w/w sodium hydroxide solution were placed. The reaction flask was kept in an oil bath maintained initially at 70°C. The required amount (0–20%, on the basis of weight of phenol) of casein was added with continuous stirring. After the addition of casein was completed, the reaction mixture was allowed to stir for further 10–15 min at 80°C. The required amount (1.4 mol) of formaldehyde monomer was then added and the temperature was raised up to 120°C and heated for 1–2 h. After the completion of the reaction, the reaction mixture was cooled to room temperature and neutralized with 1% aqueous oxalic acid solution. The liquor was then vacuum distilled at 5 mm of Hg at 80°C to remove unreacted phenol, formaldehyde, and produced water. The resultant resinous product was highly vis-

cous and light brown to dark brown in color in all the cases. The resins thus obtained were found soluble in common organic solvents such as acetone, methanol, butanol, etc. They are coded as PFC-0, PFC-4, PFC-8, PFC-12, PFC-16, and PFC-20 based on the percentage of casein incorporated in the resin. The plausible reaction scheme is depicted in Scheme 1.

CHARACTERIZATION

Free phenol content

The percentage of free phenol was determined by using Koppeschaar method[19] and the results are presented in Table I. Accurately weighed about 2 gm of resin sample was taken in 250 mL round-bottomed flask. To that 10% acetic acid was added and steam distilled until the negative test for phenol with bromine water. The distillate was diluted to 500 mL with double distilled water. An aliquot of 25 mL was taken in Erlenmeyer flask and 25 mL of 0.1N bromate-bromide solution and 10 mL concentrated HCl was added. The flask was then closed and kept in dark for 20 min. Finally, 10 mL of 20% potassium iodide solution was added and titrated with 0.1N sodium thiosulphate solution using starch as indicator. The free phenol was calculated by following formula

$$\% \text{ Phenol content (by weight)} = \frac{1.567(V_1 - V_2) \times 0.1}{W \times N}$$

Where, V_1 and V_2 are the volumes of 0.1N sodium thiosulphate solution required for blank and sample

TABLE I
Percentage of Free Phenol, Free Formaldehyde, Intrinsic Viscosity (η) and Molecular Weight (M_n)
by Conductometry for Prepared Resins

Resin code	Ratio casein (%)/weight of phenol	Reaction time (min)	Resin yield (%)	% Free phenol	% Free formaldehyde	η (dL g^{-1})	$\overline{M}_n$
PFC-0	0	60	31.3	1.581	1.281	0.056	1051.80
		90	45.0	1.345	0.897	0.090	1728.34
		120	85.0	1.028	0.720	0.124	3801.60
PFC-4	4	60	34.0	0.692	1.890	0.055	1319.00
		90	46.8	1.326	1.390	0.091	1998.00
		120	90.0	1.208	1.269	0.130	4455.00
PFC-8	8	60	39.4	1.862	1.341	0.061	1320.00
		90	51.6	1.601	1.102	0.100	1980.00
		120	89.0	1.421	0.891	0.151	3956.00
PFC-12	12	60	40.3	2.013	0.705	0.061	1165.24
		90	53.4	1.792	0.525	0.102	2376.00
		120	89.0	1.612	0.372	0.186	4360.00
PFC-16	16	60	39.5	2.163	1.055	0.085	1386.00
		90	51.6	1.923	0.810	0.110	3148.62
		120	90.0	1.791	0.434	0.207	4291.00
PFC-20	20	60	40.0	2.464	1.026	0.095	1480.00
		90	52.8	2.301	0.721	0.121	3090.00
		120	90.0	2.012	0.321	0.225	4680.93

respectively. W is the weight of sample in gm and N is the exact normality of sodium thiosulphate solution.

Free formaldehyde content

The free formaldehyde content of the prepared resins was determined by the sodium sulphite method,[20] and the results are presented in Table I. Accurately weighed about 2 gm of resin sample was transferred into conical flask and dissolved in R-spirit. Simultaneously, neutralized sodium sulphite solution was prepared by titrating saturated sodium sulphite solution against 0.5N sodium hydroxide solution using thymolphthalein as indicator. 25 mL of this neutralized solution and 10 mL of 0.5N HCl solution were mixed well in a beaker and cooled in ice-bath. Then 50 mL of water and cooled sodium sulphite–HCl mixture were added to the conical flask containing resin solution and titrated with standard 0.5N sodium hydroxide solution. Free formaldehyde content was calculated by using following formula

$$\% \text{ Free formaldehyde} = \frac{(S - B) \times N \times 3.002}{W}$$

where, 'S and B' are volumes of 0.5N sodium hydroxide solution required in the titration for sample and blank respectively. 'N' is the exact normality of sodium hydroxide solution. 'W' is weight of sample in gm.

Viscosity measurements

Viscosity of the resin samples was determined by suspended level Ubbelohde Viscometer.[21] Methanol was used as the solvent at $30 \pm 0.1°C$. The results are presented in Table I. A clean and dry suspended type Ubbelohde viscometer was placed in a water bath thermostatically controlled at $30 \pm 0.1°C$. Solvent (4 mL) was carefully introduced into the viscometer. The viscometer containing solvent was allowed to attain the bath temperature. Three independent readings were noted and the average flow time (t_0) was evaluated. The process was repeated in the same viscometer with given polymer solution (4 ml of 5.0%) to measure the efflux time (t). Then 2 mL of the solvent was introduced into the viscometer. The efflux time of the diluted solution was measured after 20 min, in the mean time, the solution in the viscometer had attained the bath temperature. Subsequent dilutions were made by successive addition of 2 mL of solvent. The efflux time of all these solutions were measured. The quantities measured in the viscometric study were the viscosity functions, η_{sp}, η_{red} and η_{inh} were evaluated for all solutions of different concentrations.

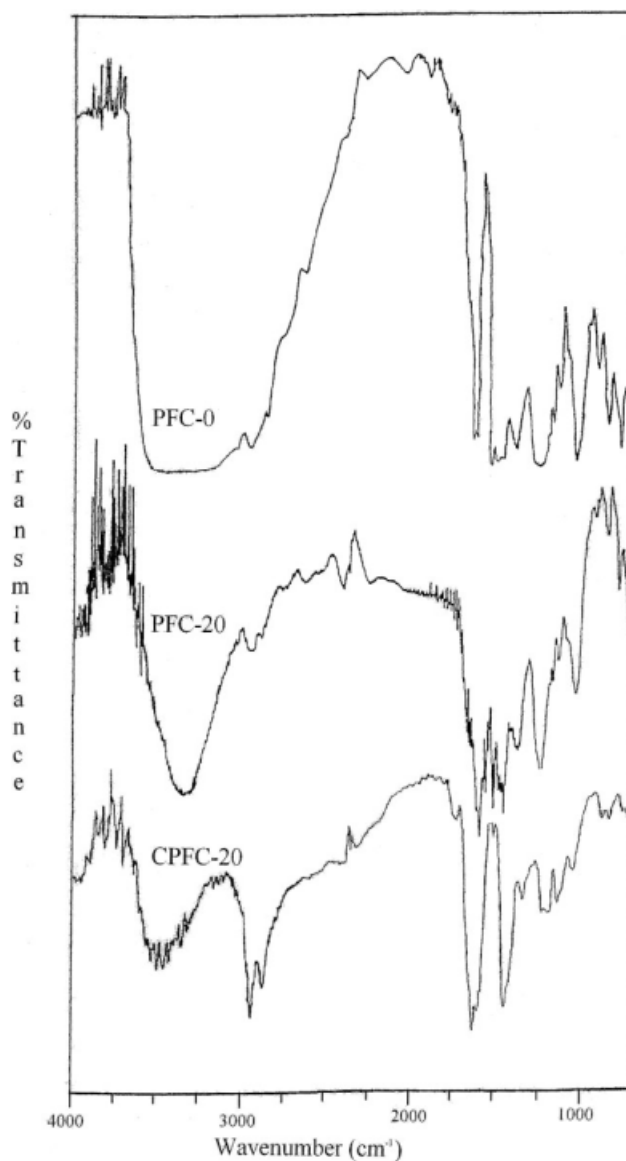Where, $\eta_{sp} = (\eta - \eta_0)/\eta_0 = (t - t_0)/t_0$ and $\eta_{inh} = \ln \eta_r/C$.

Figure 1 FTIR spectra of representative resin samples.

The plots of ln η_r/C vs. C and ln η_{sp}/C vs. C were made. They were found to be linear and intrinsic viscosity [η] were evaluated from the plots.

Molecular weight by conductometry

The number average molecular weight ($\overline{M}_n$) of the prepared resin was determined by the nonaqueous conductometric titration[22] using anhydrous pyridine as the solvent. The results are shown in Table I.

IR spectroscopy

A Nicolet Impact 400D FTIR Spectrophotometer was employed for the measurements. All the spectra were obtained by applying resin samples on KBr cell covering the range of frequency from 4000–
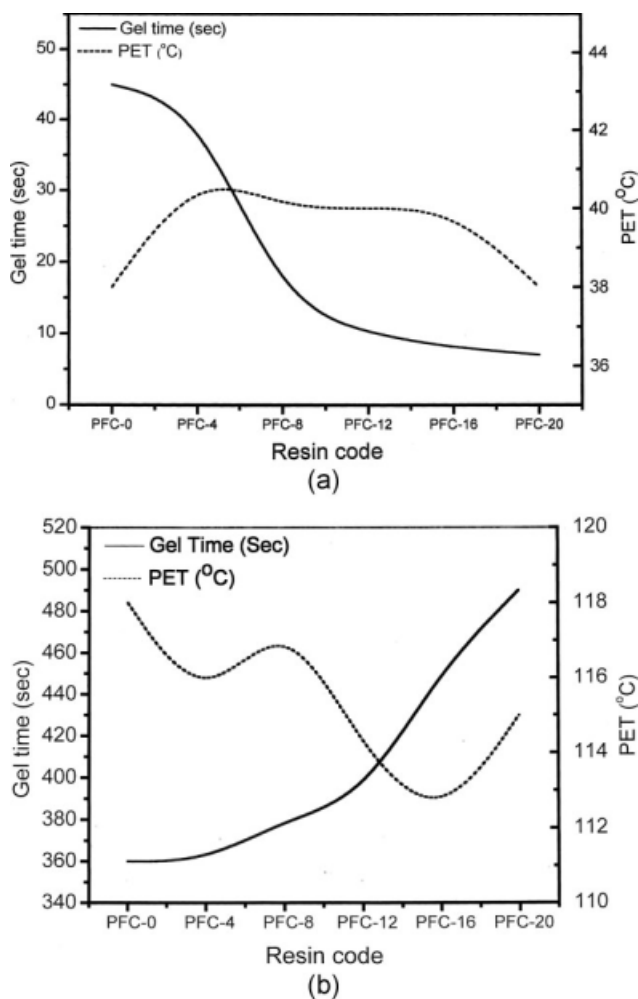
Figure 2 (a) Isothermal curing of resin samples using concentrated HCl at room temperature, (b) isothermal curing of resin samples using hexamine at 150°C.

400 cm^{-1}. The spectra of cured resins were also recorded. IR spectra of representative resins are shown in Figure 1.

Curing study

The prepared resins were successfully cross-linked isothermally by using hexamethylenetetramine (HMTA) and concentrated hydrochloric acid (HCl) as curing agents with stoichiometric amount of resin at 150°C and room temperature respectively. The time required by resin-curing agent system to attain the gel state was recorded as the gel time, and concomitantly the temperature of the gelled mass was recorded as peak exotherm temperature (PET). These isothermal curing characteristics are depicted in Figure 2(a,b), respectively, for HCl at room temperature and HMTA at 150°C. The other useful thermal and kinetic parameters were determined by employing differential scanning calorimetry (DSC) on a DuPont 9100 DSC module connected to DuPont 9900

TABLE II
Thermal Parameters Obtained from Single DSC Scan for PFC Resins

Resin	T_i (°C)	T_p (°C)	T_f (°C)	Cure range $(T_f - T_i)$ (°C)	Cure time (min)
PFC-0	109.96	160.48	166.66	56.70	16.39
PFC-12	135.83	152.75	189.16	53.32	18.54
PFC-20	134.52	146.75	163.09	28.57	16.18

thermal analyzer on dynamic runs under nitrogen atmosphere at a heating rate of 10°C/min. The DSC parameters were determined by the Borchardt-Daniels method.[23] Following equation was used for the calculation of the parameters and the DSC results are depicted in Table II and Table III.

$$K_{(T)} = Z \times e^{-E/RT}$$

Where, Z is pre-exponential factor (sec^{-1}), R is gas constant (8.314 J mol^{-1} K^{-1}), E is the activation energy (J mol^{-1}) and T is absolute temperature (K).

The TGA of selected cured resins (obtained by isothermal process of curing) was carried out on the Mettler Toledo star system, IICT, Hyderabad at a heating rate of 10°C/min under static air atmosphere. The Broido[24] method was employed for TGA calculation. The formula used for calculation is

$$\int_y^1 dy/y^n = A/u \times \int_y^1 e^{-E/RT} dT$$

Where, 'A' is pre-exponential factor, 'y' is number of initial molecules not yet decomposed, 'n' is order of reaction, 'u' is variable, E is activation energy, 'R' is gas constant and 'T' is absolute temperature.

The usual thermal parameters obtained from the TGA are furnished in Tables IV and Figure 3. The integral procedural decomposition temperatures (IPDTs) were determined by using Doyle method.[25]

Composite fabrication

The prepared resins were employed for the fabrication of GFRCs by maintaining ratio of resin:

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

Resin	$E \pm 2$ (kJ mol^{-1})	Log $Z + 2$ (min^{-1})	Order of reaction	Heat of reaction ΔH (J g^{-1})
PFC-0	154.20	19.30	2.44	114.0
PFC-12	322.70	39.38	5.48	28.7
PFC-20	342.90	42.84	4.26	339.8

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TABLE IV
Thermal Parameters of Cured PFC Resins from TGA Under Static Air Atmosphere

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Resin	T_i (°C)	T_{10} (°C)	T_{max} (°C)	T_f (°C)	IPDT (°C)	E kJ mol^{-1}
CPFC-0	110.00	360.29	449.00	814.24	734.59	56.280
CPFC-12	109.07	364.70	483.00	816.81	741.68	33.520
CPFC-20	109.28	332.35	522.00	820.00	727.66	29.009

reinforcement to be 40 : 60. The GFRCs were made by using plain-woven glass cloth and a resin/curing agent system. In the present work, dry lay-up pre-prag technique was employed and the curing agent used was hexamine. The resin containing cross linking agent was dissolved in the minimum quantity of methanol. This solution was applied to ten pieces of glass fabric (18 × 18 cm^2) using hand lay-up technique. The preprag were than stacked between flat steel plates using Teflon sheets as the mold releasing agent at 150°C. When gel point was reached, it was compressed at a pressure of 90–100 psi. After completion of mold cycle the mold was cooled in air to room temperature. The prepared sheets were cut into different required dimensions for the measurements of various mechanical properties and various chemical tests according to ASTM standards.

Testing of laminates

The prepared laminates were tested for their mechanical properties according to ASTM standards. Three test pieces of required dimensions for each test were cut. The average of three tests was recorded for each parameter. The measurement of the flexural strength and flexural modulus were carried out using a Dutron testing machine (model 13D) according to ASTM D790. Measurement of Izod impact strength of a V-notched specimen was carried out according to ASTM D256 using a Zwick D-7900 impact machine. The Brinell hardness was measured on KM/02/AS – III, Budapest Hardness tester. In determining the number of measurements and the method of evaluation the relating standards MSZ 1421/DIN 53456 were considered. The Rock well hardness was measured according to ASTM D785 on a RAS/SL No.4471 Rockwell Hardness tester. The results of the mechanical properties are provided in Figure 4. The laminate samples (10 × 10 mm^2) were immersed at room temperature for one week in various chemicals. Resistance to various chemicals was measured according to ASTM D581. The data comprising the results of chemical resistance are included in Figure 5(a,b), respectively, describing % change in weight and % change in thickness in a variety of solvents including acetone, methanol, carbon-tetrachloride, methyl ethyl ketone, toluene, ethanol, 15% hydrochloric acid, 5% nitric

acid, 5% sodium hydroxide, 5% acetic acid, and water.

RESULTS AND DISCUSSION

To produce low formaldehyde emitting composition we opted for casein, which is very well known to undergo reactions with aldehyde.[26,27] All the polymers were obtained in good yields and were in the form of brownish colored resins. The increased content of casein (0–20%), increases the percentage of free phenol content, whereas decreases the percentage of free formaldehyde content (Table I). This suggests that casein consumes formaldehyde to give methylol derivatives, and participates actively in the reaction by utilizing formaldehyde for crosslinking, thereby consuming the excess formaldehyde to deplete the percentage of free formaldehyde in the resin samples. The optimum level of casein to be incorporated with the resin remained 20% on the weight basis of phenol. 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. It also suggests the enhanced resistance of the resin solution to flow. The $\overline{M}_n$ studies by conductometry also showed an increase in the $\overline{M}_n$ value with casein content in the resins. The values are
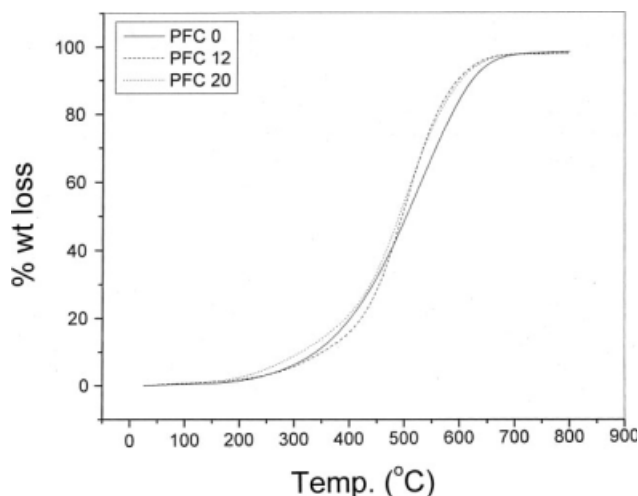

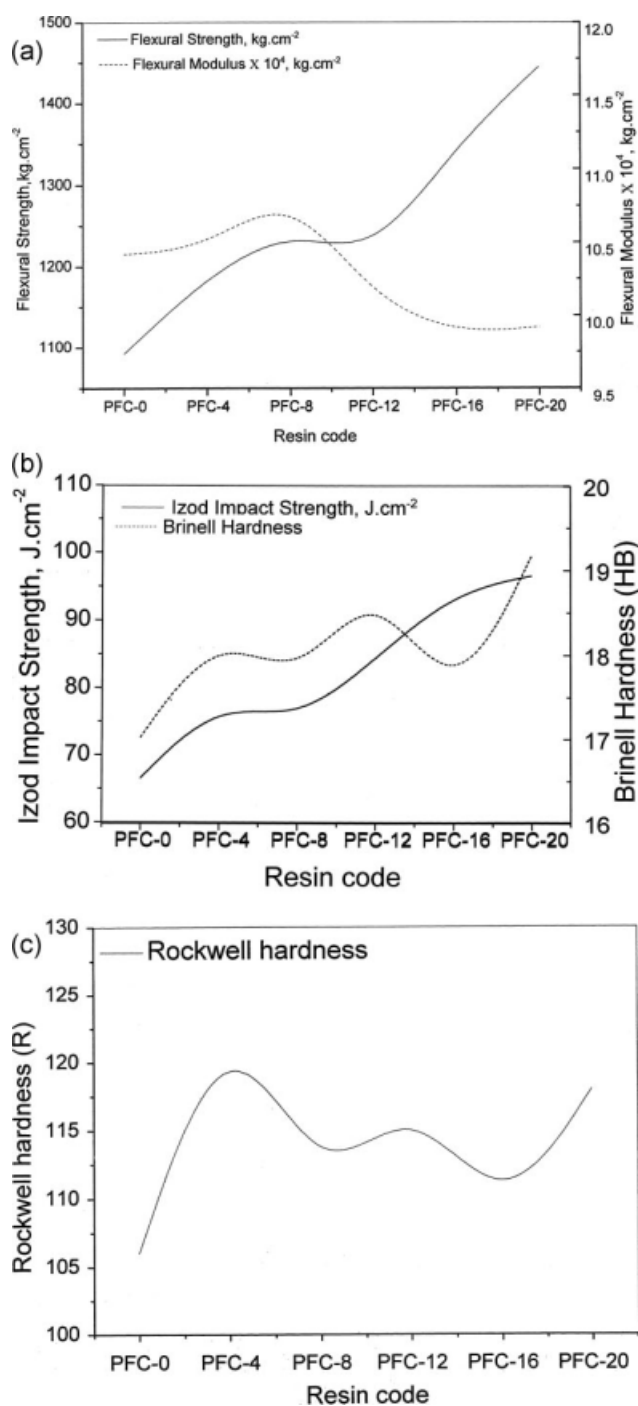**Figure 3**   % Weight loss at various decomposition temperatures from TGA under static air atmosphere.

Figure 4 (a) Mechanical properties of glass fiber reinforced composite; Flexural strength, kg cm^{-2} and Flexural modulus $\times 10^4$, kg cm^{-2}, (b) mechanical properties of glass fiber reinforced composite; Izod impact strength, J cm^{-2} and Brinell Hardness (HB) and (c) mechanical properties of glass fiber reinforced composite; Rockwell Hardness.

listed in Table I. It proves the incorporation of casein molecules in the resin matrix to increase the average size and average molecular weight of the resin samples.

The IR Spectra of representative samples PFC-0, PFC-20, and cured PFC-20 (CPFC-20) are depicted in

Figure 1. 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 because of the presence of by-products in the resin, such as water and excess formaldehyde, which allows hydrogen bonding with reactive functional groups such as —CH$_2$OH, —NH$_2$ and —NH. However, the spectra of cured resins gave sharper characteristic absorption peaks in this region.

The resin samples showed absorption peak in the region of 3450–3350 cm^{-1}. In the PF resin, this broad band appearing at 3462 cm^{-1} is perfectly assigned to —OH stretching vibrations. The hydroxyl group originated from phenolic moieties, methylol groups as the end group in the resol type resin and some trace amount of water molecules trapped in the resin. The similar absorption bands in PFC-20 and CPFC-20 were recorded in the same region. These resin samples have casein as the extra component incorporated during the synthesis. The lowering in the frequency values may be ascribed to the greater chances for hydrogen bonding as casein has also a variety of polar groups like —NH$_2$, —CONH$_2$, —O—Ph etc. The separation of bands because of —O—H and —N—H stretching becomes rather impossible because they resonate in the same region.

The additional bands observed, only in the IR spectra of PFC-20 and CPFC-20, at $\sim$ 1680 and $\sim$ 1575 cm^{-1} confirm the presence of —NH— and —CONH— group in the resin. Medium absorption bands in all resin spectra appear at $\sim$ 2950 and 2850 cm^{-1}, which may be ascribed to C—H stretching in —CH$_2$ of ether, —CH$_2$OH, and N—CH$_2$. A very strong absorption band is observed at around $\sim$ 1670 cm^{-1} in all spectra except PFC-0. It may be assigned to the C=O stretching in the —CONH$_2$ group (amide-I). The band at $\sim$ 1575 cm^{-1} may be attributed to —NH bending in 2° amine (amide-II). The 1° amino groups of casein first form methylol derivatives with formaldehyde. The crosslinking between two such methylol group provides ether linkage (—CH$_2$—O—CH$_2$—) to which —NH is attached on both the sides.[28] Crosslinking may also occur between methylol casein and monomethylolphenol. Thus the hydroxymethylation of primary amino group of casein followed by crosslinking forms 2° amine in the resin along with such linkages between methylol phenol and formaldehyde.

The —C=C— stretching vibrations present in the aromatic ring resonate at $\sim$ 1610 and 1515 cm^{-1} in the spectra of all resin samples. A weak absorption band at $\sim$ 1380 cm^{-1} for all resin samples may be ascribed to the C—OH in 1° alcohol. The band at 1240–1250 cm^{-1} in the spectra of all the resins may be ascribed to C—O stretching and O—H bending modes present in phenol. The band at $\sim$ 1025 cm^{-1} observed in all of the samples is a straight forward
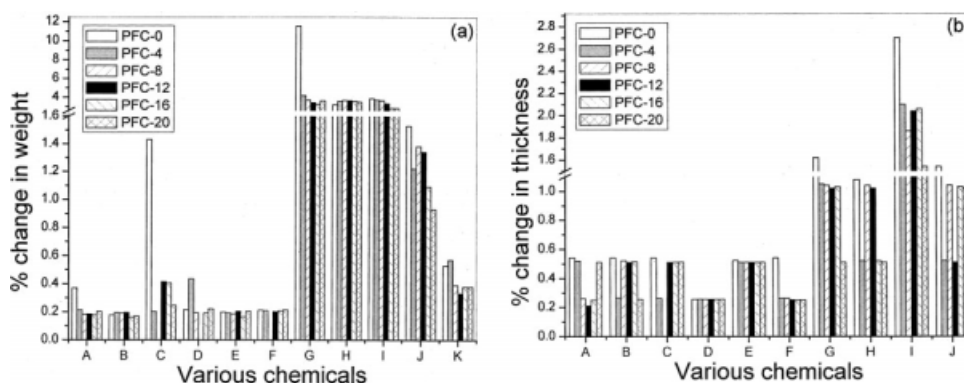
Figure 5 Effect of various chemicals on (a) % change in weight and (b) % change in thickness of prepared laminates; where, A = acetone, B = methanol, C = carbontetrachloride, D = methyl ethyl ketone, E = toluene, F = 25% ethanol, G = 15% hydrochloric acid, H = 5% nitric acid, I = 5% sodium hydroxide, J = 5% acetic acid, and K = water.

indication of the C—O—C linkages formed because of crosslinking reaction during condensation. The band at around ~ 1130–1150 cm^{-1} observed in all spectra may be ascribed for stretching vibration in 1° alcohol. The bands observed around ~ 900 cm^{-1}, 830 cm^{-1}, and 760 cm^{-1} in all the spectra may be clearly assigned to tetrasubstituted, trisubstituted, and disubstituted benzene, respectively.

The isothermal curing studies were performed with concentrated HCl and Hexamine at room temperature and at 150°C, respectively. The results are shown in Figure 2. The curing studies by concentrated HCl showed the decrease in gel time values with the increase in the casein content in the resin matrix. This may be because of active involvement of casein moiety in the curing reaction. The PET found to range between 38–44°C. In case of Hexamine as curing agent, the time required for the gel formation to occur (i.e. gel time), ranged between 360–490 sec. The gel time found to increase with increase in casein content. In the resin-hexamine system, the PET could not be observed because the elimination of water and ammonia which might have decreased the temperature.

From the DSC study, it was observed that the resin samples gave exothermic peaks in the range of 146–161°C. 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 completed (T_f) along with the kinetic parameters were evaluated by applying the Borchardt-Daniels method.[23] The parameters are listed in Table II. The cure range ($T_f - T_i$) for the resins decrease with incorporation of casein, and the cure time remained in the range of 16.18 to 18.54 min. The depicted data are invaluable because they imply the curing condition to be maintained during fabrication of GFRCs from the resin samples covered under the study. The useful kinetic

parameters evaluated from DSC scans are presented in Table III.

The TGA data are included in Table IV. The temperature at which degradation started (T_i) suggests the temperature value that can be withstood by the resin samples without undergoing any type of degradation. The T_i values are almost constant ($\sim$ 110°C) for all resin samples. The temperature at maximum weight loss (T_{max}) was quite high (around 449–522°C) and found to increase with casein content. This is an indication of the enhancement of the thermal stability with increased casein percentage in the resin samples. At around 800°C the percentage of residue ranged between 1.8 to 2.5%. The IPDT values remained in the range of 727–742°C for all resin samples. The values for the activation energy (E) remained in the range of 29–57 KJ mol^{-1}. The final decomposition temperature (T_f) and temperature at 10% weight loss (T_{10}) were found at 814–820°C and 332–365°C, respectively. Figure 3 shows the decomposition pattern of cured PFC resin from TGA under static air atmosphere. The results from TGA thus suggest that incorporation of casein in the PF resin affects the thermal stability of the synthetic resin and enhances it to some extent.

Ultimately, most interesting properties are afterall those of finished composites. The most relevant property for structural composites is the mechanical one. The tests include measurement of flexural strength, flexural modulus [Fig. 4(a)], izod impact strength, brinell hardness [Fig. 4(b)], and rockwell hardness [Fig. 4(c)] of the composites. Flexural strength is the measure of maximum stress in the outer fibers at the moment of break. It is found to increase with increase in casein content. The results ranged in between 1092.34 and 1444.34 (kg cm^{-2}). The flexural modulus is the measure of stiffness during the first part of the bending process. The flexural modulus ranges between 9.87×10^{-4} and 10.87×10^{-4} (kg cm^{-2}) for all the samples. As the casein

content increase in resin matrix, good flexural properties are found. Impact resistance is the ability of the material to resist breaking under a shock loading or the ability to resist the fracture under stress applied at high speed. Impact test indicates the energy to break standard test specimen of specified size under the stipulated conditions of specimen mounting and pendulum velocity at impact. The data covers the range of 66.50–96.55 (J cm^{-2}) for izod impact strength with increment in casein content in resin matrix and is found to be maximum for PFC-20. A steel ball of known diameter is pressed at a known pressure against the specimen for a predetermined period of time. The brinell hardness is given by the area of the spherical collate formed by the loading, this being in ratio with the depth of penetration. In present study, the measurement was carried out by using the penetrating ball having diameter of 5 mm and the load applied was 50 kg. The results are found in the range of 17.02–19.16. The rockwell hardness test measures the net increase in depth impression as the load on an indenter is increased from a fixed minor to a major load and then returned to minor load. In the present study, load of 60 kg was applied for each measurement. Generally, rockwell hardness numbers derived are just the numbers without unit and the results obtained ranges between 106 and 125.

Chemical resistance of the prepared GFRCs to the series of standard reagents shown in Figure 5 has been studied quantitatively. The specimen of each GFRC (10 × 10 mm^2) were put in 100 mL of standard reagents, individually, as stated in Figure 5 for seven days. The physical parameters such as % change in weight (a) and in thickness (b) were measured and are represented in Figure 5(a,b). It was observed that each of the GFRC samples was mostly found to be stable in almost all standard reagents. However, change in color of the specimen resulting into scarce patches on the surface, very slight loss in gloss and negligible changes in thickness and weight were observed in some of the standard chemical reagents. Whereas, major losses were observed in sulphuric acid, hydrochloric acid, nitric acid, and sodium hydroxide solutions.

CONCLUSIONS

- The decrease in the percentage of free formaldehyde and increase in the percentage of free phenol and values of intrinsic viscosity with an increase in the casein percentage may be explained by considering the involvement of casein molecules in the resin structure.

- The IR spectral study also shows the involvement of primary amino group of casein into the reaction. The results from IR spectroscopy of the resin samples strongly confirm the presence of secondary and tertiary aromatic amine, and methylene bridge together in the samples. This is an indication that the primary amino groups present in casein have taken part in the reaction and set randomly in between two phenolic rings.

- Curing data shows decrease in the gel time with an increase in the percentage of casein content when conc. HCl was used as the cure agent and increase in gel time when hexamine was used as the cure agent. These data also demonstrate the involvement of casein in the reaction.

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

- The mechanical properties of GFRCs showed the enhancement in the toughness of the composite materials with increasing the casein content in the resin matrix. The resistance of the composite was also excellent toward organic solvents, and improved toward the mineral acids as the casein content increases.

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