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Der Chemica Sinica, 2011, 2 (2):98-117

ISSN: 0976-8505
CODEN (USA) CSHIA5

Studies on [(tetrahydrophthalated cyclohexanone-formaldehyde resin)-(epoxy resin)] condensates

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ABSTRACT

Cyclohexanone – formaldehyde (CHF) resins with different hydroxyl value were treated with tetrahydrophthalic anhydride (THPA) stoichiometrically. The resultant carboxy unsaturated CHF resins were then polycondensated with various epoxy resins (i.e. diglycidylether of various bisphenols) in the presence of pyridine. The unsaturated CHF resins thus obtained and unsaturated polyesters (UPE's) were characterized by unsaturation, spectral studies, and by number average molecular weight ($\overline{Mn}$ *) estimated by vapor pressure osmommetry (VPO). The curing of UPE's was carried out by using benzoyl peroxide (BPO) as catalyst and monitored on differential scanning calorimeter (DSC). Based on DSC data, glass fiber reinforced composites (i.e. laminates) of these UPE's were fabricated, maintaining 40/60 proportion of resin to glass fiber. The laminates thus formed were tested for chemical, mechanical, and electrical properties. The unreinforced cured samples of UPE's resins were also analyzed thermogravimetrically.*

Keywords: Epoxy resins; Cyclohexanone –formaldehyde resin; Thermal properties; Mechanical properties; Glass fiber reinforced composites.

INTRODUCTION

Tetrahydrophthalic anhydride is one of the important anhydride which is manufactured industrially [1-3].It offers very attractive properties as an intermediate and starting material [4], and employed as epoxy resin curing agent [5-10], modifier for unsaturated polyester [11-14] and in the formation of high performance polyimides [15-19]. Due to unsaturated group and cyclohexane ring, the end products have better properties, in term of physical and mechanical properties [20-23]. Recently we have sent a research paper regarding the unsaturated polyesters based on maleated cyclohexanone formaldehyde resin and epoxy resin. In continuous of this

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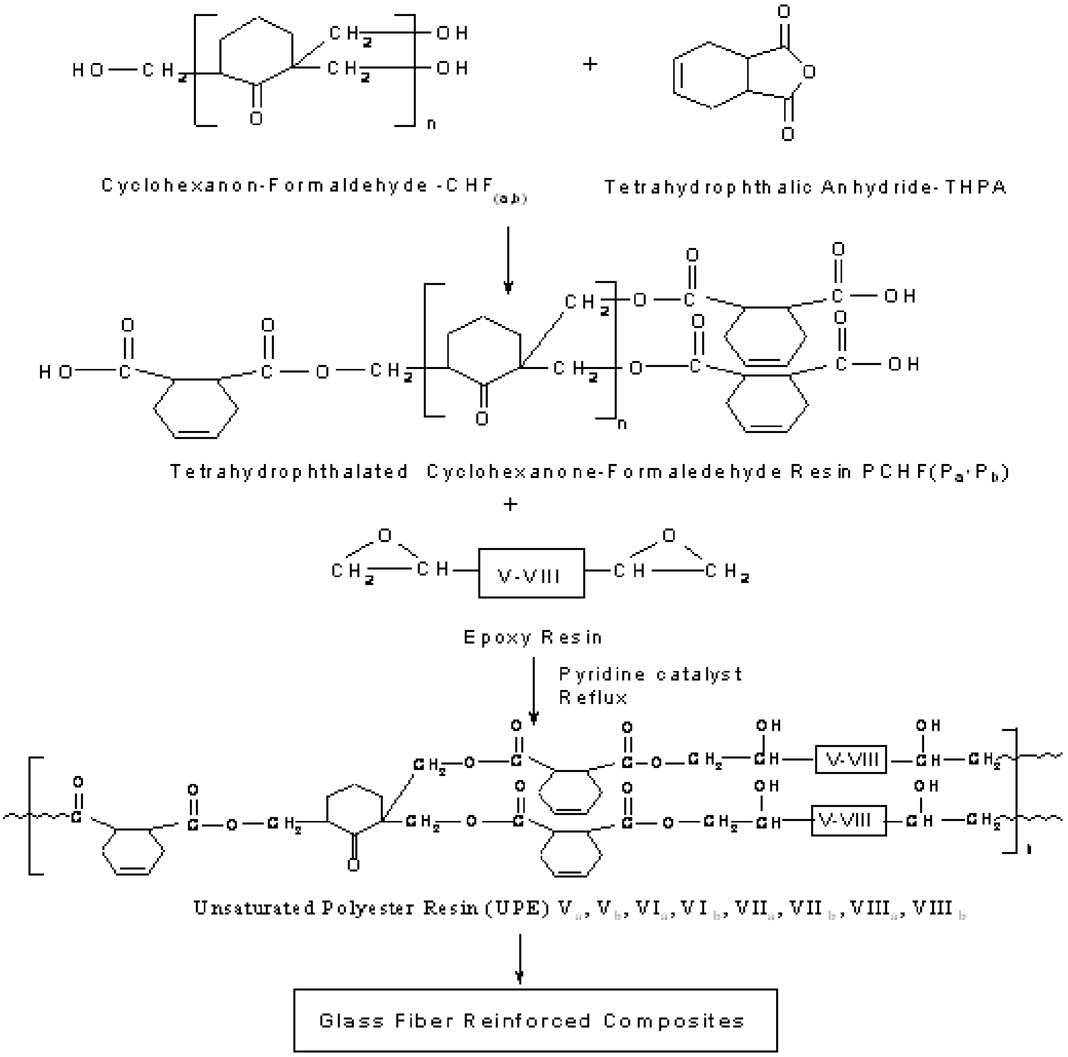
work the present communication comprises the formation of unsaturated (i.e. tetrahydrophthalated) cyclohexanone formaldehyde resins through the modification of cyclohexanone formaldehyde resin(CHF) of different hydroxyl values with tetrahydrophthalic anhydride , then their post polymerization with varying epoxy resins and studies on such end products. The synthetic steps are shown in Scheme 1.



Where:

a = CHF resin of 300mg KOH/gm resin *b = CHF resin of 235mg KOH/gm resin*

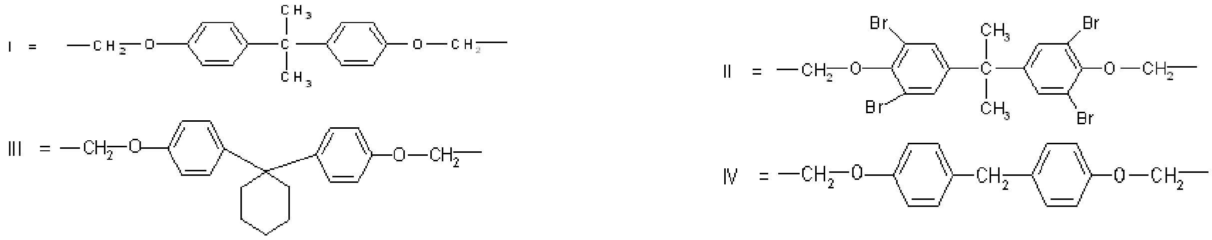
P_a = PCHF resin based on (a) *P_b = PCHF resin based on (b)*

V_a = UPE resin based on DGEBA and (a) *V_b = UPE resin based on DGEBA and (b)*

II_a = UPE resin based on brominated DGEBA and (a) *I_b = UPE resin based on brominated DGEBA and (b)*

III_a = UPE resin based on DGEBC and (a) *III_b = UPE resin based on DGEBC and (b)*

IV_a = UPE resin based on DGEBF and (a) *IV_b = UPE resin based on DGEBF and (b)*



Scheme 1. Synthetic route of unsaturated polyester based on (tetrahydrophthaleated CHF – epoxy resin) condensates and their glass reinforcement

MATERIALS AND METHODS

2.1. Materials

Cyclohexanon-formaldehyde (CHF) resins of different hydroxyl value (OHV) (300 and 235 mg KOH / gm resin) were obtained from Polyols and Polymers Vapi, Gujarat, India.

Epoxy resins used for the preparation of the unsaturated polyester resins were:

a. Diglycidylether of bisphenol A (DGEBA) obtained from Synpole Product Pvt. Ltd., Ahmadabad, India. Epoxy equivalent weight (EEW) 190 g/mole, viscosity 400- 1000 cp at 25 °C).
b. Diglycidylether of bisphenol F (DGEBF),EEW 160 g/mole, viscosity 7000 cp at 25°C, and brominated diglycidylether of bisphenol A (BER) EEW 225-280 g/mole were obtained from Atul Ltd., India.
c. Diglycidylether of bisphenol C (DGEBC) was prepared in laboratory according to a known method [24]. EEW 220-225 g/mole, viscosity 5500 cp at 25°C.
d. E-type fiber glass (epoxy compatible) woven fabric of 0.25 mm thickness (Unnati Chemicals, Ahmadabad, India) of areal weight 270 g/m^2 was used for laminate preparation. All other chemicals used were of laboratory pure grade.

2.2. Synthesis of tetrahydrophthalated cyclohexanone – formaldehyde resins

Equal molar of each of the two CHF resins and tetrahydrophthalic anhydride (THPA) in pyridine (Py) was refluxed at (~120 °C) for three hours, the ratio of THPA to Py was kept at 1:3.The mixture was cooled and poured in cold water. Then precipitate was dissolved again in methanol and re precipitated by adding water. The precipitate was dried at 105 °C in a vacuum oven. The modified CHF resins which are based on CHF resin of 300 and 235 OHV are designated as P_a and P_b respectively as shown in Scheme - 1.Their details are given in Table 1.

2.3. Synthesis of unsaturated polyester resins (UPE's)

Stiochiometric amount of epoxy resin (DGEBA, BER, DGEBC and DGEBF) was added to a well stirred solution of tetrahydrophthalated CHF resins (0.5 mole) i.e. P_a or P_b respectively in THF and mixed well by vigorous agitation. Then pyridine (8 %of total weight) was added as a catalyst. The resulting mixture was heated to 85 °C with continuous stirring. Sample was taken at regular intervals to check the acid value. The reaction was continued until the acid value fell below 55mg KOH/gm. All the eight resins were obtained in the form of solid mass. The designation of all the UPE resins is shown in Scheme- 1. Their details are furnished in Table 1.

2.4. Composite Fabrication

UPE resins were dissolved in small amount of tetrahydrofuran, using 0.1 % of benzoyl peroxide as a hardener and the mixture was stirred well for 5 to 10 minutes. The mixture was applied with a brush on to a 150 mm x 150 mm fiber glass cloth and the solvent was allowed to evaporate. The 10 dried prepregs so prepared were stacked one on top of another and pressed between steel plates coated with a Teflon film release sheet and compressed in a flat platen press under about 70 psi pressure . The prepregs were cured by heating the press to 110-130 ^{0}C for three hours in an air circulated oven. The composite so obtained was cooled to 50 ^{0}C before the pressure was released. Test specimens were made by cutting the composite and machining them to final dimensions. All the chemical, mechanical and electrical tests were conducted according to ASTM method using three test specimens for each test.

2.5. Measurements

The number average molecular weight ($\overline{Mn}$) in P_a, P_b and all samples of UPE was estimated by VPO in DMF solvent at 90 ^{o}C. The acid value and number of double bonds were measured following the methods already reported [25, 26]. Number of hydroxyl group present in per repeating unit of all UPE resins was obtained by employing acetylating method [27]. FT-IR spectra were recorded with a Perkin-Elmer, Spectrum GX, USA, by using KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Avance 400MHz spectrometer using DMSO-d_6 as a solvent at 25 ^{o}C.

Curing studies were carried out by a differential scanning calorimeter DSC 2920. The calorimeter was previously calibrated according to ASTM 3417. Dynamic –heating experiments were carried out under a nitrogen flow of 40 ml min^{-1}.The UPE's samples were dissolved in small amount of THF and mixed homogenously with 0. I % w/w with benzoyl peroxide and left until all solvent evaporated. Samples in the range of (2.53-3.10) mg of the mixture were weighed accurately into an aluminum DSC sample pan and sealed with an aluminum lid. The entire operation was carried out in a dry chamber. Curing was carried out from 30 to 300 ^{o}C at 10 ^{o}C min^{-1} heating rate and an empty pan was used as a reference. The exothermic transition associated with curing was characterized by determining, $T_{i=}$ temperature of onset of exotherm, $T_{p=}$ temperature of peak position of exotherm, $T_{f\,=}$ temperature of end of exotherm. $\Delta H=$ heat of curing reaction. Ea = activation energy. The themogravemetric analysis (TGA) of the unreinforced cured UPE's samples was carried out on Perkin –Elmer pyres 1 TGA in air at a heating rate of 10 ^{o}C min^{-1}. For this the samples were dissolved in small amount of THF in a glass crucible, mixed homogenously with 0.I % w/w with benzoyl peroxide and heated at their DSC temperatures for three hours. The materials were then crushed by pestle pressure and (5.52-6.66) mg of the cured resins was used.

2.6. Characterization of composite samples

The chemical resistance of the glass reinforced composites was measured according to ASTM D543. The sample size was approximately 20mm x 20mm. The chemicals used for the study were H_2SO_4 (25% v/v),HCl (25% v/v), NaOH (25% w/v), ethanol , acetone, DMF and THF. The tests were performed by dipping the composite samples in 100 ml each of the reagents for 7 days at room temperatures. After 7 days the specimens were taken out from the reagents and after drying they were examined for the percentage changes in thickness and weight.

All the mechanical and electrical tests were performed using three test specimens and average results have been documented. The compressive strength was measured according to ASTM D 695. The sample size was 12.5 mm x 12.5 mm x12.5mm. Impact strength was measured using Izod type impact tester at room temperature, according to the method of ASTM D 256.The Rockwell hardness strength was measured according to ASTM D 785. The sample size was 25 mm x 25mm x3 mm. The flexural strength was measured according to ASTM D 790 at room temperature .The electrical strength was measured according to ASTM D 149.

RESULTS AND DISCUSSION

3.1. Synthesis and characterization of unsaturated polyester (UPE) resins

Two tetrahydrophthalated cyclohexanone-formaldehyde (PCHF) resins were obtained as amorphous colored powders .The number of carboxyl groups per polymer chain was found to be three and are quite consistent with the original hydroxyl value. The number of double bonds also matches the hydroxyl values. The resultant PCHF resins were reacted with four different epoxy resins [28-29] as mentioned in the experimental part .The powder unsaturated polyesters thus obtained are designated as UPE (I_a–IV_a) and (I_b–IV_b).

All the UPE samples are soluble in DMF, DMSO, $(CH_2)_5CO$, $CHCl_3$, THF, and pyridine, sparingly soluble in ethanol and insoluble in carbon tetrachloride, methanol and ether. The number of double bonds and hydroxyl groups in UPE samples are furnished in Table 1.The values are quite consistent with the predicted structure. The ($\overline{Mn}$) values listed in Table 1 show that 5 to 6 epoxy resin molecules are connected with PCHF resin.

FT-IR spectra of P_a and P_b resins (Figure 1) are quite identical and show the peaks due to CHF resin and THPA segments. The absorptions in the range (1750-1749) cm^{-1} are due to carbonyl of the ester group, broad band at (3450-3448) cm^{-1} is attributed to carboxylic groups. The bands at (1295-1296) $cm^{-1}$and 3027 cm^{-1} are traced to the asymmetric stretching vibration of C-O-C of ester groups and the stretching of the double bond of cyclohexenyl ring respectively.

The FT-IR spectra of UPE's (Figure 1) comprise the important spectral bands of epoxy and CHF resin segments [30-33]. Only discernible differences are observed in terms of presence of unsaturation and –COO ester groups. The bands at (3034-3026) cm^{-1} and a band at (1750-1749) cm^{-1} are observed as additional bands, these are responsible respectively to the double bond of cyclohexenyl ring and ester group. The band appeared at 915 cm^{-1} in the spectrum of epoxy resin due to epoxy group is almost vanished in the spectrum of UPE's. Also the FT-IR spectra of UPE's showed abroad band at (3424-3404) cm^{-1} due to the secondary –OH groups. This is supported by the bands at the range (1111-1127) cm^{-1} which are due to the secondary –OH bending vibration. And also the disappearance of the free carboxylic acid group which appeared in the spectrum of tetrahydrophthalated CHF resins and the presence of the peak at (1243-1251) cm^{-1} which corresponds to the ether linkage formed during epoxide ring opening.

NMR spectra of terahydrophthalated CHF and UPE resins are shown in Figures 2 and 3. The assignment of the proton and ^{13}C signals (Tables 2-5) agrees well with the proposed structure of resins. (P_a and P_b) The ^{13}C signals at (176.31) ppm and at (64.50-64.53) ppm are attributed to the carbon of carboxylic acid and ester group respectively, the resonance at (124.32 – 125.76) ppm is traced to the double bonded carbon of cyclohexenyl ring. The proton NMR signals at (12.442 - 12.303) ppm and at (4.071-4.077) ppm are due to the proton of the free carboxylic acid group and ester group situated in α position in cyclohexanone ring respectively. The hydrogen connected to double bonded carbon of cyclohexenyl ring show proton NMR signal at (5.584-5. 616) ppm.

In UPE'S the proton NMR signals at (5.505-5.616) ppm are attributed to the hydrogen of the double bond of cyclohexenyl ring .The signal specific to the proton of OOC-CH_2 appears at (4.206-4.303) ppm. In ^{1}H NMR spectra of UPE's the three ^{1}H NMR signals due to epoxy ring protons at 2.64, 2.84 and 3.24 ppm disappeared. Also disappearance of ^{13}C peaks at 54.0 and 54.3 of C-O-C group of epoxy ring suggest the formation of UPE.

Qualitative and quantitative analysis of functional oxirane ring [34, 35] also confirmed the results obtained by ^{1}H NMR, ^{13}C NMR and FT-IR. All these facts confirm the chemical structure of the UPE's.

3.2. Thermal properties of UPE resins

It is well known that processing of thermoset resins is complicated because of the involvement of chemical reaction. Understanding of curing is therefore of fundamental importance in the design and processing of materials.

The cross- linking of UPE resins (I_a - IV_a) and (I_b – IV_b), was initiated through an exothermic reaction by using benzoyl peroxide as a catalyst and their curing study was monitored on a differential scanning calorimeter. The kinetic data were derived from DSC thermograms (Figures 4-7) of UPE-benzoyl peroxide system, obtained at 10 °C /min heating rate. During the curing reaction of the thermosetting resins, the heat of reaction at any time is proportional to the number of moles at that time, namely, the released heat is proportional to the extent of the reaction, then the reaction rate $d\alpha/dt$ is proportional to the heat flow dH/dt, that is:

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_o}$$

The curing kinetics were studied and the kinetic data obtained [36].

The curing reactions for all systems were found to be different in respect of total heat of reaction and the temperature at which the reaction were initiated, peaked and terminated. The initial curing temperature T_i , peak exotherm temperature T_p ,and temperature of completion of cure T_f, values of total exothermic heat of curing and the activation energy (kj/mole)were obtained from the characteristics DSC traces and are shown in Table 6.

Arrhenius plots (Figures 8 - 11) for all systems are linear, hence it is reasonable to assume that any change in the curing mechanism with curing temperature does not affect the overall reaction rate. The DSC thermograms of all UPE-benzoyl peroxide systems gave a single exothermic peak meaning there by that the rate of reaction of all polymerizable reactive groups in UPE resin with the benzoyl peroxide catalyst occur simultaneously .It has also been found that the UPE resins based on tetrahydrophthalated CHF resin of 300 OHV gave higher values of total exothermic heat of curing than UPE resins based on tetrahydrophthalated CHF resin of 235 OHV, implying the reactivity of the former is higher than the later.

Thermal stability of a polymeric material is one of the most important properties for both processing and applications. The thermogravemetric analysis (TGA) is the most favored technique for rapid evaluation in comparing and ranking the thermal stability of various polymers. TGA thermograms of all UPE resins (I_a -IV_a) and (I_b–IV_b) are shown in

Figures 12-15. The weight loss at various temperatures, the onset temperature of decomposition T_o, the temperature of final decomposition $T_{f,}$ 50% weight loss temperature and the chare yield % at 750 ^oC were noted and summarized in Table 7. As can be seen , the cured samples start degradation at about 200 ^oC and their initial weight loss was about (0.48-2.09) % .This weight loss may be due to either insufficient curing of components used or due to catalyst used .A weight loss of about (4.08-10.36) % was found at 300 ^oC. As the temperature rose to (267.55-356.01) ^oC the TGA curves of UPE resins exhibited a dramatic decreasing .However , it was found that the UPE II_a and II_b resins exhibited a relative slow weight loss in comparison with (I_a, I_b, III_a, III_b ,IV_a and IV_b) resins which suggested that the former have better thermal stability than the latter . The improved thermal stability of IIa and II_b resins might be attributed to the presence of the bromine in the epoxy moiety .The C-Br linkages are weak points, which degrade to form free radicals that may further undergo recombination to form new compounds which would degrade at elevated temperature. Also it was noted that UPE (I_a -IV_a) resins , were more thermally stable than UPE(I_b–IV_b) resins . The increment in the resin functionality provides a very high cross-linking density as well as improvements in the mechanical, chemical and electrical properties [37] .Above 700 ^oC, a stable residue is formed that corresponds to carbon black.

Comparison of the thermal stability of all samples based on char yield % at 750 ^oC suggests the following order of stability:

$$\mathbf{II_a > II_b > IV_a > IV_b > I_a > I_b > III_a > III_b}$$

3.3. Characterization of glass fiber reinforced composites of UPE resins

Glass fiber- reinforced composites of all UPE (I_a -IV_a) and (I_b –IV_b) resins were cured at temperatures based on DSC data using benzoyl peroxide. The composites were characterized for their chemical resistance; the details are furnished in Table 8. Results reveal that all the composites are very negligibly affected by the common organic solvents like ethanol, acetone etc. However, considerable percentage change in thickness and weight is observed in DMF, H_2SO_4 ,HCl and NaOH for all the composites. The glass fiber-reinforced composites of all UPE resins were also characterized for their mechanical and electrical resistance properties, the details are furnished in Table 9. All the UPE based composites have good mechanical properties. The electrical strength of the UPE based composites is in the range of 18.1 to 26.8 KV/mm. The values of the electrical strength of the composite samples are rather low. This could result in a charred path, over which subsequent discharge could take place a minute leakage of current may arise from surface contamination.

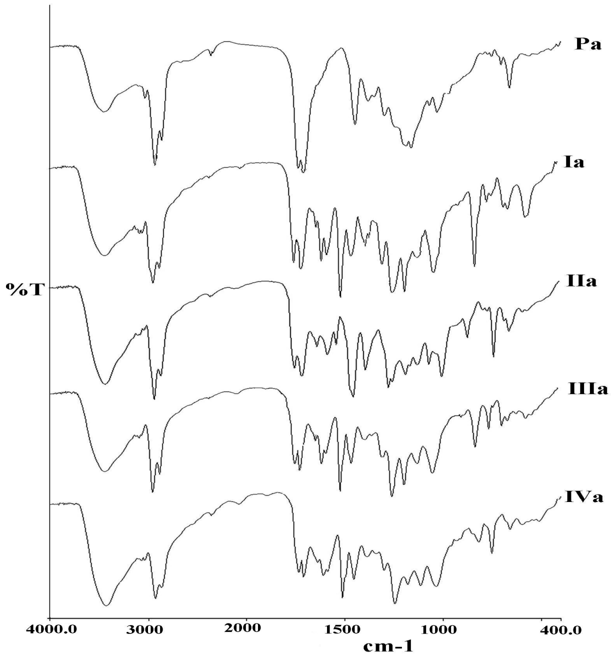


Figure 1 FT-IR spectra of P_a and UPE's (I_a-IV_a)

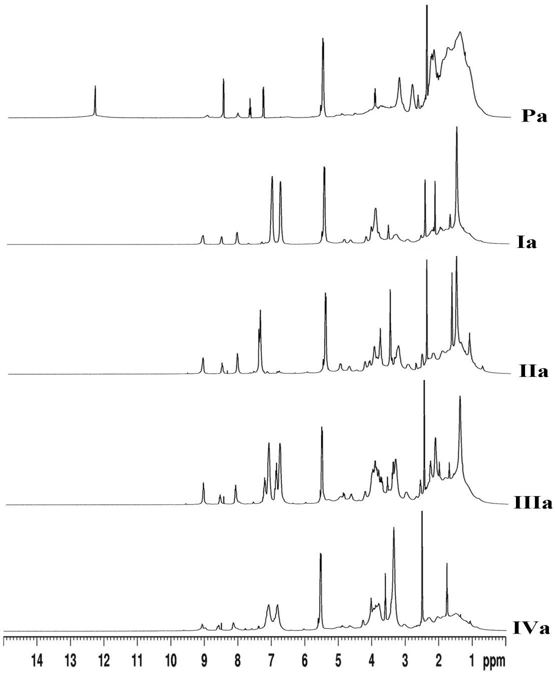


Figure 2 .^{1}H NMR spectra of P_a and UPE's (I_a-IV_a)

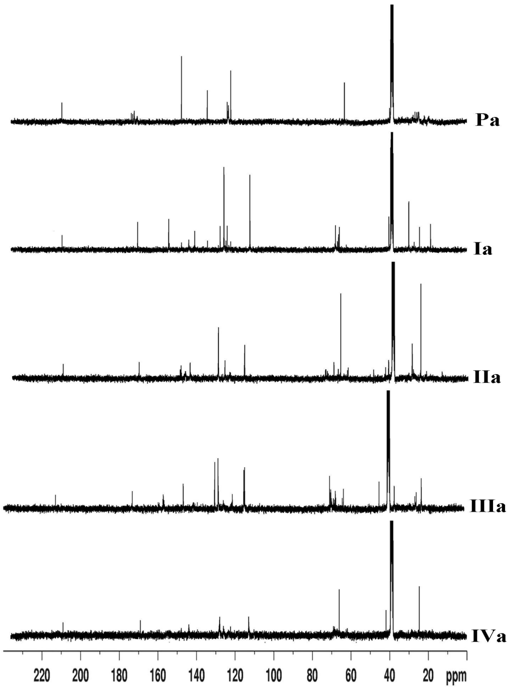


Figure 3 .^{13}C NMR spectra of P_a and UPE's (I_a-IV_a)

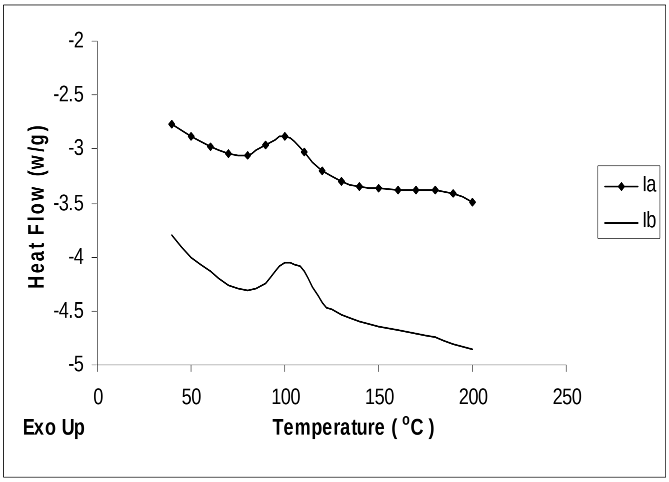


Figure 4. DSC Thermograms of UPE I_a and I_b resins

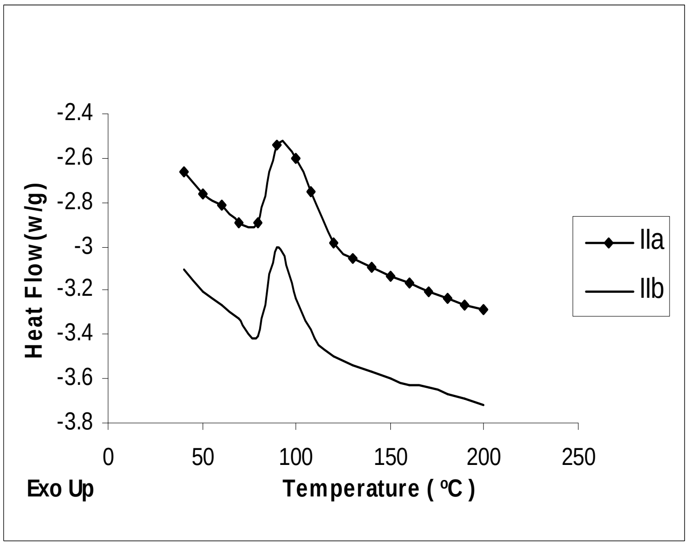


Figure 5. DSC Thermograms of UPE II_a and II_b resins

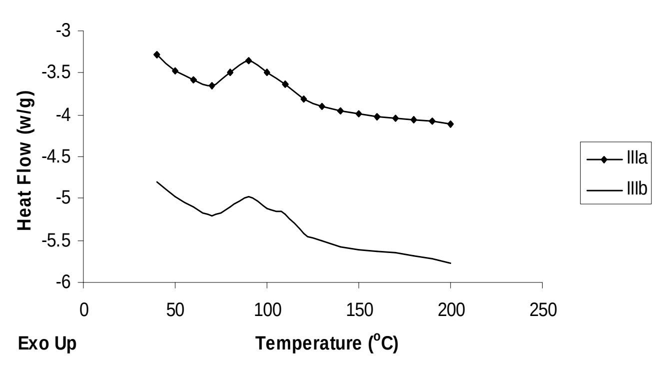


Figure 6. DSC Thermograms of UPE III_a and III_b resins

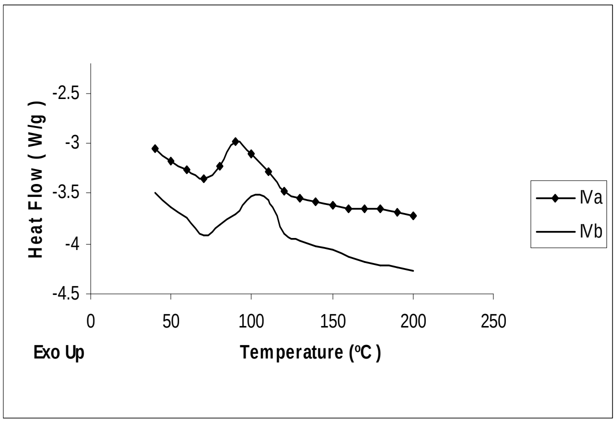


Figure 7. DSC Thermograms of UPE IV_a and IV_b resins

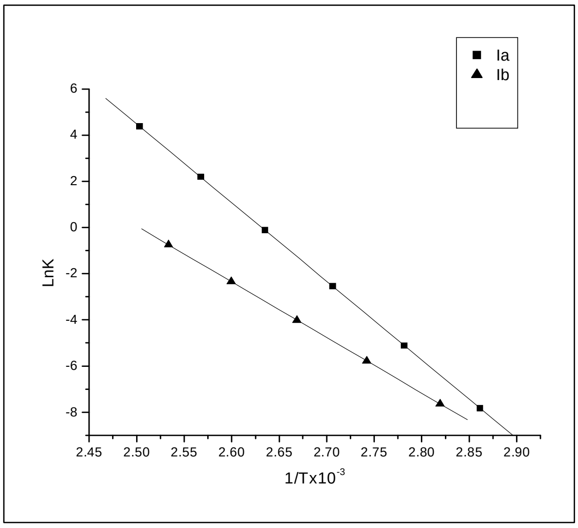


Figure 8. Arrhenius Plot for UPE I_a and I_b resins

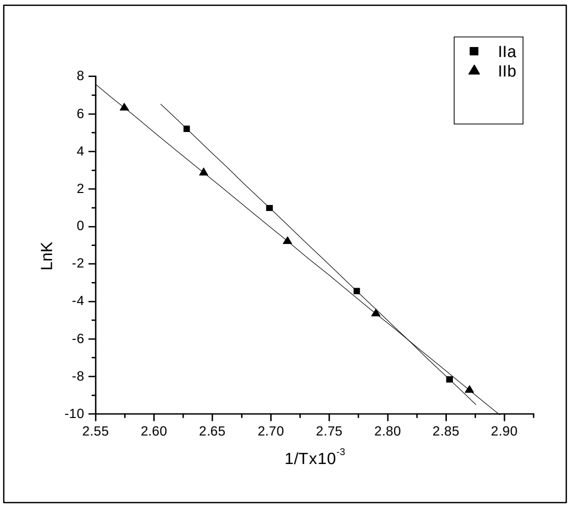


Figure 9. Arrhenius Plot for UPE II_a and II_b resins

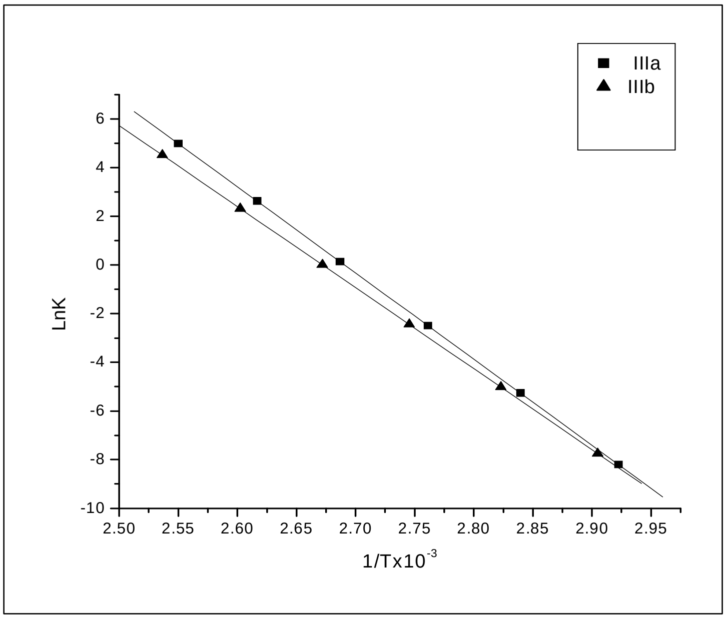


Figure 10. Arrhenius Plot of UPE III$_a$ and III$_b$ resins

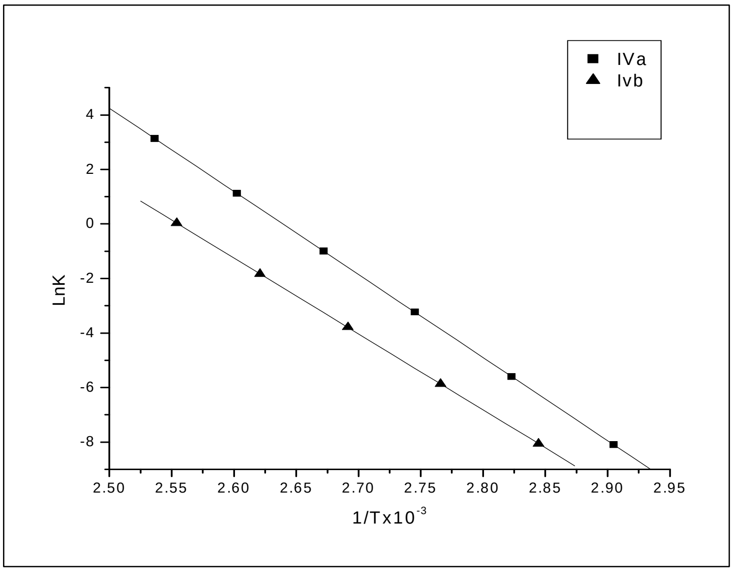


Figure 11. Arrhenius Plot of UPE IV$_a$ and IV$_b$ resins

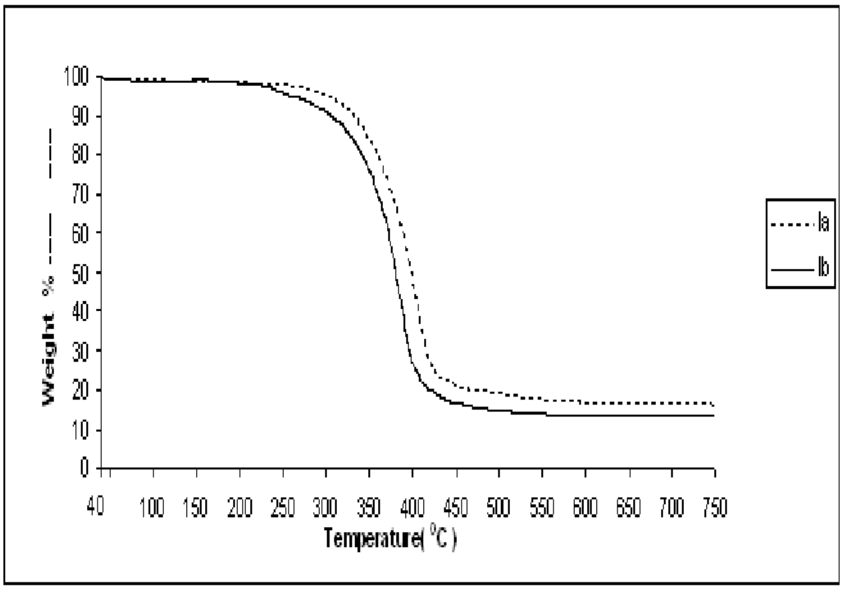


Figure 12. TGA thermograms of UPE I_a and I_b resins

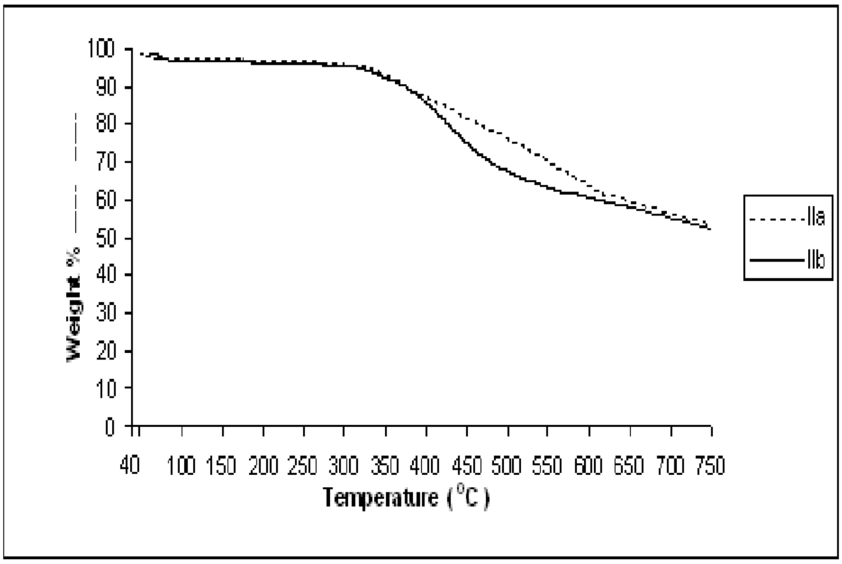


Figure 13. TGA thermograms of UPE II_a and II_b resins

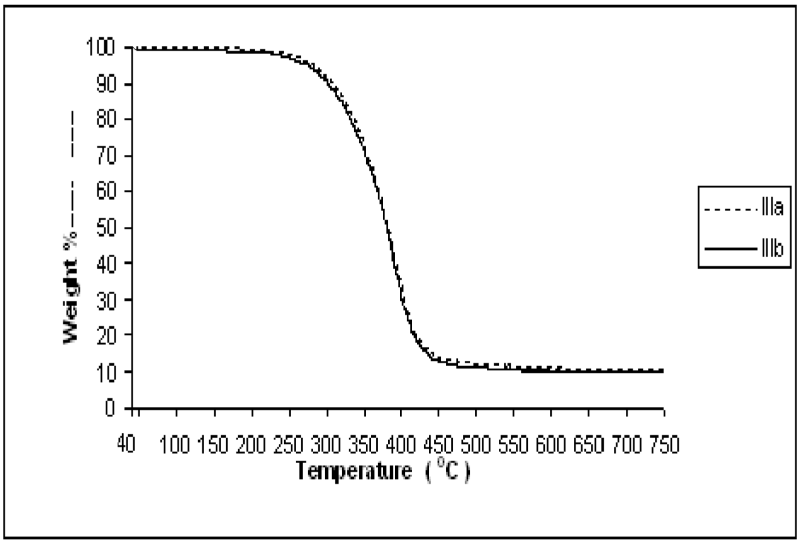


Figure 14. TGA thermograms of UPE III_a and III_b resins

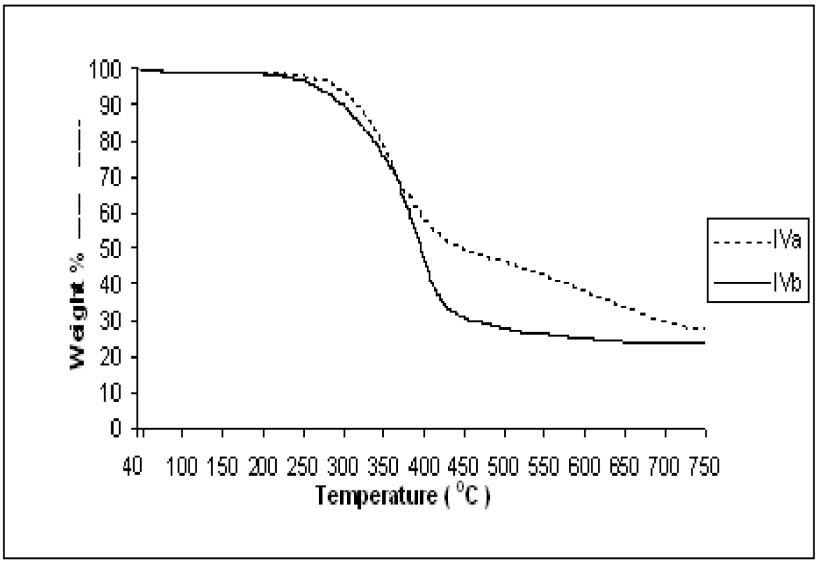


Figure 15. TGA thermograms of UPE IV_a and IV_b resins

Table 1. Characterization of modified CHF and UPE resins

Sample	**Number of double bonds per repeating unit**	**Number of -OH group per repeating unit**	**Number average molecular weight $\overline{Mn}$**
P$_a$	2.9	2.98	1616
P$_b$	2.8	2.96	1278
UPE-I$_a$	3.1	3.99	8264
UPE-I$_b$	2.9	3.97	5940
UPE-II$_a$	3.0	4.1	9404
UPE-II$_b$	2.9	4.0	9091
UPE-III$_a$	3.2	3.99	8823
UPE-III$_b$	3.0	3.98	6329
UPE-IVI$_a$	3.1	4.0	7874
UPE-IV$_b$	2.9	3.99	5660

Table 6. DSC data of unsaturated polyester (UPE) resins

UPE Sample	**T_i °C**	**T_p °C**	**T_f °C**	**Activation energy Kj/mole Ea**	**Heat of reaction J/g**
I$_a$	76.43	100.85	127.75	283.4	43.2
I$_b$	81.03	105.12	123.16	200.2	42.2
II$_a$	75.67	90.33	123.16	493.8	154.3
II$_b$	77.96	90.46	114.73	247.2	42.2
III$_a$	68.77	91.47	125.45	294.2	62.9
III$_b$	71.84	93.25	124.69	276.6	53.7
IV$_a$	71.84	92.50	125.45	253.5	69.1
IV$_b$	78.73	106.62	123.16	231.5	50.1

Table 9. Mechanical and electrical properties of UPE glass reinforced composites

UPE composite	**Flexural strength (MPa)**	**Compressive strength (MPa)**	**Impact strength (MPa)**	**Rockwell hardness (R)**	**Electrical strength (in air) (kv mm^{-1})**
I$_a$	285	230	260	125	24.1
I$_b$	253	210	216	120	21.4
II$_a$	364	290	300	140	26.1
II$_b$	360	285	290	138	26.8
III$_a$	259	221	219	129	23.8
III$_b$	240	195	215	125	19.2
IV$_a$	320	280	275	135	24.6
IV$_b$	290	240	270	132	24.3

Table 2. ^{1}H NMR spectral data for tetrahydrophthalated CHF (P_a) resin and UPE (I_a-IV_a) resins: δ ppm (DMSO-d6)

Sample **Assignment**	**P_a**	**I_a**	**II_a**	**III_a**	**IV_a**
COO**H**	12.442	-	-	-	-
Proton on the double bond of the cyclohexenyl ring	5.594-5.616	5.553-5.602	5.547-5.590	5.567-5.603	5.553-5.601
Other protons on cyclohexenyl ring	2.358-2.770	2.305-2.629	2.305-2.656	2.301-2.611	2.302-2.508
Hydrogen of cyclohexanone	1.875-2.290	1.760-2.211	1.757-2.039	1.761-2.173	1.756-2.040
-C**H**$_2$COO α to cyclohexanone	4.077	4.117	4.076	4.044	4.034
-C**H**$_2$COO	-	4.271	4.206	4.269	4.276
-C**H**-OH	-	3.375	3.351	3.357	3.352
-CH-O**H**	-	3.604	3.585	3.604	3.607
O-C**H**$_2$-CHOH	-	3.893-3.983	3.600-3.897	3.758-3.822	3.623-3.896
Aromatic hydrogen	-	6.833-8.587	7.482-8.626	6.940-8.608	6.824-8.586
Methyl hydrogen in epoxy moiety of DGEBA	-	1.560	1.621	-	-
Hydrogen of 1, ĺ cyclohexane in epoxy moiety of DGEBC	-	-	-	1.437-2.170	-
Methylene hydrogen in epoxy moiety of DGEBF	-	-	-	-	3.954

Table 3. ^{1}H NMR spectral data for tetrahydrophthalated CHF (P_b) resin and UPE (I_b-IV_b) resins: δ ppm (DMSO-d_6)

Sample **Assignment**	**P_a**	**I_a**	**II_a**	**III_a**	**IV_a**
-**C**OOH	176.31	-	-	-	-
Carbon of double bond of cyclohexenyl ring	124.37-125.76	124.39-126.14	125.23-125.48	125.56-126.98	124.34-125.57
-**C**OO	174.77	173.79	172.95	173.07	173.14
Carbonyl of cyclohexanone	212.78	212.31	212.65	212.21	212.31
CH$_2$COO α to cyclohexanone	64.50	63.93	63.62	63.91	63.28
CH$_2$COO	-	67.45	67.48	67.50	67.49
Carbon of methylene ether	-	69.62	71.06	70.45	70.47
-**C**H-OH	-	68.47	68.78	68.49	69.97
Aromatic carbon in epoxy moiety	-	114.36-129.86	117.81-131.47	114.60-130.02	114.85-130.29
Tertiary carbon in epoxy moiety of DGEBA	-	41.61	42.46	-	-
Methyl group in epoxy moiety of DGEBA	-	31.22	31.83	-	-
Carbon of 1, ĺ cyclohexane in epoxy moiety of DGEBC	-	-	-	23.06-36.97	-
Methylene carbon in epoxy moiety of DGEBF	-	-	-	-	43.57

Table 4. ^{13}C NMR spectral data for tetrahydrophthalated CHF (P_a) resin and UPE (I_a-IV_a) resins: δ ppm (DMSO-d_6)

Sample **Assignment**	**P_b**	**I_b**	**II_b**	**III_b**	**IV_b**
COO**H**	12. 303	-	-	-	-
Proton on the double bond of the cyclohexenyl ring	5.584 – 5.615	5.555 -5.601	5.593 -5.609	5.565 – 5.610	5.505 – 5.599
Other protons on cyclohexenyl ring	2.384 -2.632	2.351 – 2.672	2.302 -2.675	2.337 -2.612	2.358 – 2.512
Hydrogen of cyclohexanone	1.768 -2.347	1.761 -2.260	1.752 -2.282	1.764 – 2.298	1.760 -2.253
-C**H**$_2$COO α to cyclohexanone	4.071	4.115	4.072	4.109	4.157
-C**H**$_2$COO	-	4.272	4.234	4.301	4.303
-C**H**-OH	-	3.341	3.361	3.322	3.304
-CH-O**H**	-	3.605	3.603	3.538	3.594
O-C**H**$_2$-CHOH	-	3.792 – 3.987	3.620 – 3.924	3.607 – 3.878	3.610 – 3.893
Aromatic hydrogen	-	6.825 – 8.583	7.481-8.632	6.826 – 8.614	6.827 – 7.146
Methyl hydrogen in epoxy moiety of DGEBA	-	1.561	1.623	-	-
Hydrogen of 1, Í cyclohexane in epoxy moiety of DGEBC	-	-		1.439-2.174	-
Methylene hydrogen in epoxy moiety of DGEBF	-	-		-	3.927

Table 5. ^{13}C NMR spectral data for tetrahydrophthalated CHF (P_b) resin and UPE (I_b-IV_b) resins: δ ppm (DMSO-d_6)

Sample **Assignment**	**P_b**	**I_b**	**II_b**	**III_b**	**IV_b**
-**C**OOH	176.31	-	-	-	-
Carbon of double bond of cyclohexenyl ring	124.32-125.58	124.41-126.19	124.37-126.09	124.40-126.23	124.14-126.01
-**C**OO	174.75	173.21	172.91	172.01	173.95
Carbonyl of cyclohexanone	212.11	212.01	212.51	212.71	211.93
CH$_2$COO α to cyclohexanone	64.53	64.02	63.64	63.29	63.35
CH$_2$COO	-	67.52	67.54	67.62	67.50
Carbon of methylene ether	-	69.66	71.12	70.48	70.50
-**C**H-OH	-	68.47	68.85	69.85	70.07
Aromatic carbon in epoxy moiety	-	114.43-129.87	117.76-131.47	114.65-131.82	114.86-130.00
Tertiary carbon in epoxy moiety of DGEBA	-	41.66	42.52	-	-
Methyl group in epoxy moiety of DGEBA	-	31.24	30.16	-	-
Carbon of 1, Í cyclohexane in epoxy moiety of DGEBC	-	-	-	23.06-36.98	-
Methylene carbon in epoxy moiety of DGEBF	-	-	-	-	44.51

Table 7.Thermogravemetric analysis of the cured UPE resins

Reagents	**% Change**													
	H_2SO_4 25% v/v		**HCl 25% v/v**		**NaOH 25% w/v**		**Ethanol**		**Acetone**		**DMF**		**THF**	
UPE composites	**Thickness**	**Weight**	**Thickness**	**Weight**	**Thickness**	**Weight**	**Thickness**	**Weight**	**Thickness**	**Weight**	**Thickness**	**Weight**	**Thickness**	**Weight**
I_a	1.18	1.96	0.95	1.30	0.82	1.31	0.30	0.45	0.26	0.41	1.20	1.44	0.63	0.85
I_b	1.20	1.98	0.97	1.32	0.84	1.33	0.32	0.47	0.28	0.43	1.22	1.46	0.65	0.87
II_a	1.11	1.76	0.89	1.23	0.75	1.23	0.21	0.36	0.20	0.33	1.05	1.23	0.52	0.77
II_b	1.14	1.77	0.91	1.24	0.77	1.25	0.22	0.38	0.21	0.34	1.09	1.24	0.55	0.78
III_a	1.19	1.97	0.96	1.31	0.83	1.32	0.31	0.46	0.27	0.42	1.21	1.45	0.64	0.86
III_b	1.21	1.99	0.98	1.33	0.85	1.34	0.33	0.48	0.29	0.44	1.23	1.47	0.66	0.88
IV_a	1.17	1.95	0.94	1.29	0.81	1.30	0.29	0.44	0.25	0.40	1.19	1.43	0.62	0.84
IV_b	1.19	1.96	0.96	1.31	0.82	1.31	0.30	0.45	0.27	0.41	1.21	1.45	0.64	0.86

Table8. Chemical resistance properties of UPE resins glass reinforced composites

UPE Sample	**Weight loss (%)at various temperatures**							**Decomposition temperature °C**			**Char yield (%) at750 °C**
	100 °C	**200 °C**	**300 °C**	**400 °C**	**500 °C**	**600 °C**	**700 °C**	**T_o**	**T_f**	**50% wt. loss temperature °C**	
I_a	0.62	1.22	4.79	52.69	81.26	83.03	84.01	356.01	450.11	397.88	15.94
I_b	0.79	1.46	9.18	73.50	85.43	86.67	87.17	340.02	405.03	380.20	12.78
II_a	0.89	2.12	4.08	12.83	23.74	36.21	43.74	348.80	607.12	-	53.60
II_b	0.9	2.98	4.53	14.22	32.52	39.48	44.91	340.51	583.30	-	52.50
III_a	0.15	0.48	8.18	66.91	87.93	88.81	89.13	318.42	431.61	381.85	10.85
III_b	0.50	1.20	9.61	69.60	88.76	89.50	89.83	310.54	423.73	380.46	10.15
IV_a	0.89	1.19	6.34	41.59	53.55	61.78	69.68	311.53	450.05	448.99	27.92
IV_b	0.90	1.40	10.36	52.88	72.05	74.96	75.80	267.55	430.08	396.06	24.20

CONCLUSION

The salient features of the investigation are:

- Novel UPE resins were obtained in which the CHF resin was modified with tetrahydrophthalic anhydride reagent and reacted via carboxylic acid group with different types of epoxy resins in the presence of a base catalyst. The UPE resins thermally cured in the presence of BPO.
- The increment in the resin functionality resulted in a new group of UPE resins, and the cross-linked resins showed good thermal stability, mechanical resistance, chemical and electrical properties. These resins may be used as structural matrix in glass fabric –reinforced composites and in the field of electrical and electronic industry
- UPE resins based on CHF resin of 300 OHV showed better thermal stability, mechanical resistance, chemical and electrical properties than those based on CHF resin of 235 OHV.
- Thermal stability of UPE resins, as measured by TGA, is good enough to permit processing of these types of resins using conventional laminated composite techniques.

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