

Synthesis, Characterisation and Cure behaviour of Phenol – Crotonaldehyde Resins

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Abstract - Phenol-crotonaldehyde (PC) resins with varying mole ratio of phenol to crotonaldehyde were synthesised by base catalyst. The PC resins were characterised by physic-chemical methods. PC resin presumably undergo both addition and condensation reactions. However, the gel time data of Table 2 were interpreted to show that the rate of polymerization varies with the reactant ratio. The number average molecular weights of the resins were found to be in the range of 1110-1245 g mol⁻¹. The resins were found to exhibit thermoplastic behaviour and the molecular weights as well as softening temperatures increases with increasing amount of cross-linking agent. Post curing of these resins with cross-linking agent at elevated temperatures(180 °C) yielded infusible thermosets.

Key words - Phenol-Crotonaldehyde resin, base catalyst, thermoplastic, cross-linking agent, thermoset.

1 INTRODUCTION

Polymers are a large group of molecules or macromolecules, which are designed by the combination of many smaller molecules. These smaller units are called as monomers and the group of monomers further reacted with themselves and get converted into polymers.¹ In fact, the word “polymer” has a Greek origin, “many members.” Phenol-formaldehyde materials were first discovered in 1872 by the German chemist Adolph Von Baeyer. In 1907, the use of phenolic resins, also known as Bakelite, was developed by L. H. Baekeland, the “father of the phenolic resins”.²⁻⁷ Phenolic resins are the first synthetic resins to have acquired a significant commercial success and as such most thoroughly investigated.⁸⁻¹³

There is a growing need for new polymer material development and it is aimed at improving the range of service of polymers to meet practical needs. Phenolic resins on the other basis of α , β unsaturated aldehydes are the subject matter of continued research¹⁴⁻³⁴ for the development of modified polymeric materials. Even though there is an extensive literature¹⁴⁻³⁴ on the synthesis and characterisation of phenolic resins based on α , β unsaturated aldehydes, work on base catalysed (resol type) phenol-crotonaldehyde resins are very limited. In an earlier study, we have reported³⁵⁻

³⁶ the results on thermal degradation kinetics of base catalyst phenol-crotonaldehyde resins and Synthesis, characterisation and cure behavior of Phenol-crotonaldehyde-resorcinol resins.

Objective of working on Crotonaldehyde:

- Crotonaldehyde is a byproduct of the Sugar Industry, an agro based renewable resources, which is abundantly available in India.
- Because of the presence of α, β -unsaturation, the resin developed was expected to be more flexible than with formaldehyde.
- Higher reactivity nature due to the presence of double bonds.
- Addition as well as condensation reaction is possible⁶ and hence the synthesized resin can give better thermal and insulation resistance properties.
- The composites made with this synthesized resin can also exhibit flexibility than those of formaldehyde based system.

This communication deals with the synthesis, characterization and cure behaviour of the base catalyst phenol-crotonaldehyde resins. The effect of mol ratio and catalyst concentration on resin properties as well as the effect of the temperature and amount of cross-linking agent on the cure behaviour of the resin and on the properties of the cured resins are also reported. The results are compared with those obtained for phenol-formaldehyde (PF) resins of similar composition.

2 EXPERIMENTAL

2.1 Reagents

Phenol was a product of Hindustan organic chemicals. Crotonaldehyde was obtained from Somaya organic and chemicals. Crotonaldehyde was distilled before use and its purity was checked by GC and was found to be 99% pure. Analytical reagent grade sodium hydroxide, and hexamethylenetraamine (hexa) were used. Formaldehyde of 37% strength was obtained from western India chemicals and was used as received.

2.2 Synthesis

The synthesis of the resins was performed in a glass vessel at 100 °C temperature for 1 h time, by varying the mol ratio of crotonaldehyde and Sodium hydroxide (NaOH) base catalyst. The mol

ratio of phenol was kept in constant i.e. 1 equivalent (eq.) for the all reactions. The crotonaldehyde concentration varied from 1.2-3.0 eq. while the Sodium hydroxide (NaOH) concentration varied from 0.01-0.3 mol. The polymerization reactions were monitored by the means of refractive index, Gel time and free phenol and free crotonaldehyde in the reaction mixture via thin layer chromatography(TLC). After the set reaction time (1 h) was over, the reaction was stopped and the reaction mixture was cooled. The resinous products formed were red to dark brown colour in both form solid and viscous liquid PC1 to PC8, as shown in **Scheme 1**. The crude resinous product was purified washing it with water several times to remove excess base and further purified using hexane mixture (80: 20) to remove the unreacted starting material as well as the additives in it. The purified and dried resinous samples were used for further characterization.

Final product **PC1** to **PC8** were obtained according to the mole ratio of reactant, as shown in **Scheme 2** and **Table 1**.

The refractive index was tested with an Abbe –refractometer (DIN53491) and specific gravity was determined with the pycnometer (DIN 53217). The gelation time was determined for each phenolic resin according to the ASTM D 4640 by placing approximately 0.5 g of the resin on an electric hot plate at constant desired temperature under continuous agitation. Using a stopwatch, the time taken for the resin to become a soft elastic rubbery or solid is reported as the gel time. The acetone solubility also checked for the elastic rubbery mass or solid to identify the nature of the gelling characteristics.

The number average molecular weights were tested with Knauer-vapour pressure osomometer and Benzil was used as the internal standard and the Tetrahydrofuran(THF) was used as a solvent. The sensitivity range was maintained 8, Bridge voltage- 100% and temperature at 40 °C. The elemental analysis was carried out on a Hosli rapid carbon and hydrogen analyzer.

3 RESULT AND DISCUSSION

3.1 Synthesis, reaction mechanism and resin properties

The planned synthesis for the Phenol-crotonaldehyde resin was showed in below **Scheme 1**. Synthesis began with the use of simple starting material phenol, crotonaldehyde and NaOH. In a stirred solution of phenol (1 eq.) and crotonaldehyde (1.2-3.0 eq.) at room temperature for 5-10

minutes, 20 % NaOH (0.01-0.3 eq.) solution was added drop wise into resulting solution for 5-10 minutes at room temperature. The addition of base is an exothermic reaction, may be due to formation of phenoxide ion; during addition of NaOH solution, the exothermic reaction was controlled under stirring by using water bath and reaction mixture temperature was maintained up to 50°C. Again, the reaction temperature was raised and maintained the reflux stage at 95°C to 100°C for 1 h.

Scheme 1. Synthesis of phenol-crotonaldehyde resins

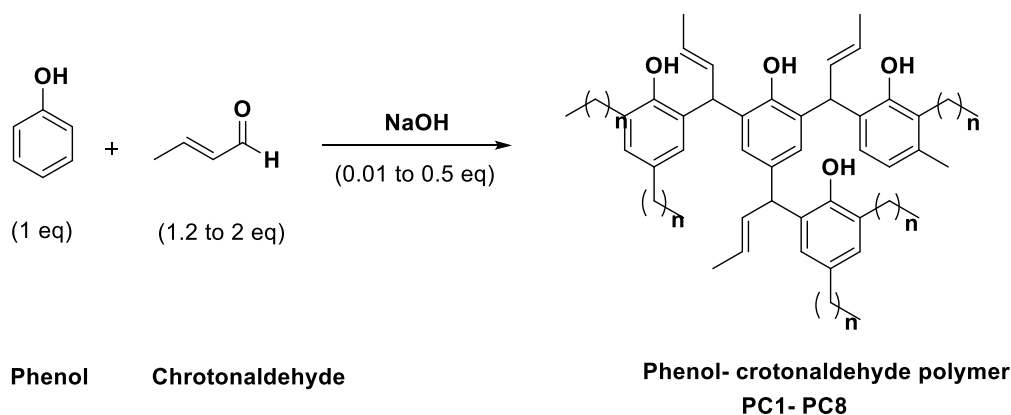


Table 1. Crotonaldehyde mol fraction in the polymer

Synthesis	Resin Code	Mol ratio (P:C:S) ^a
1	PC1	1:1.2:0.3
2	PC2	1:1.6:0.3
3	PC3	1:2.0:0.3
4	PC4	1:2.5:0.3
5	PC5	1:3.0:0.3
6	PC6	1:2.0:0.1
7	PC7	1:2.0:0.05
8	PC8	1:2.0:0.01

^aP: Phenol; C: Crotonaldehyde; S: Sodium hydroxide

The varying mole ratio of crotonaldehyde, we have studied the different properties of resin such as **pH**, refractive index(initial reaction mixture & final synthesized resin) and gel time as described in below **Table 2**.

The increasing amount of crotonaldehyde in the reaction showed increasing Gel time of resins. Particularly, PC1, PC2, PC3, PC4 and PC5 shows drop to 93 seconds respectively. Further, decreasing catalyst % also studied in the reaction which indicated that decreasing amount of catalyst increases gel time and in case of PC7it was very high and PC8 does not exhibit the polymerization and gets evaporated on the Hot plate. The Refractive index initial reaction mixture of final synthesized product readings shows polymerization is stable up to PC5, but further polymerization drop was observed with the reducing amount of catalyst for PC6 to PC7, and PC8 does not show any indication of polymerization at **pH** 6.85.

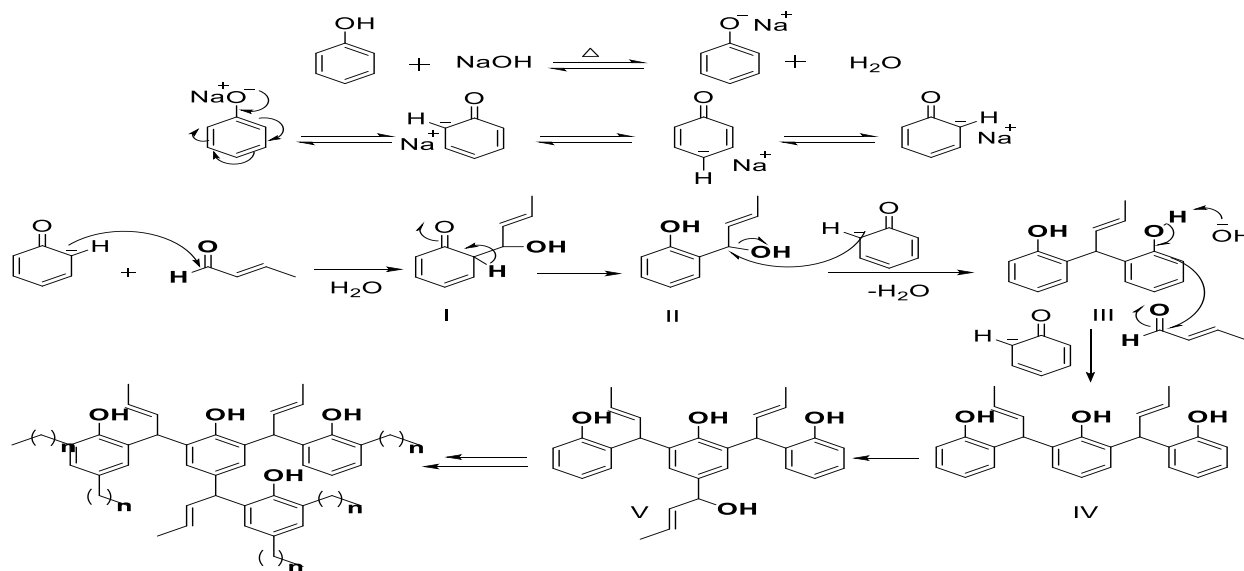
TABLE 2

pH, Refractive Index (initial & final) and Gel time of synthesized resins

Resin Code	Mol. ratio (P:C:S)^a	pH	Initial Refractive Index at 25 °C	Final Refractive Index at 25 °C	Gel time (Sec) at 170 °C
PC1	1: 1.2: 0.3	11.30	1.490	1.530	80
PC2	1: 1.6: 0.3	11.35	1.495	1.535	95
PC3	1: 2.0: 0.3	11.38	1.498	1.535	122
PC4	1: 2.5: 0.3	11.31	1.502	1.533	104
PC5	1: 3.0: 0.3	11.36	1.508	1.534	93
PC6	1: 2.0: 0.1	10.90	1.492	1.528	148
PC7	1: 2.0: 0.05	10.15	1.485	1.520	No gel behavior(> 600)
PC8	1: 2.0: 0.01	6.85	1.473	1.485	Evaporates on hot plate

^aP-Phenol; C-Crotonaldehyde; S-Sodium hydroxide

The possible reaction mechanism of phenol-crotonaldehyde resin is as shown **Scheme 2**. In basic medium, phenol react with NaOH to form a phenoxy anion, then aromatic ring goes to resonance form (as shown in **Scheme 2**). The same molecule can be called nucleophilic species that were attacking the electrophilic atom or group. In crotonaldehyde molecule there were two electrophilic positions one was aldehyde and another one was double bond but in the present reaction case it was attacking to the aldehyde carbonyl carbon only and not a double bond. The ^1H NMR spectra graph, clearly showed peak at double bond region and there was no peak that was observed in the typical aldehyde peak region i.e. δ 9-10. Hence, according to ^1H NMR clearly showed a nucleophilic attack at the aldehyde group. After, attacking of the aldehyde carbonyl carbon group, it formed a compound **I** (as shown in **Scheme 2**), which formed on aromatic compound **II**, via tautomerisation.



Scheme 2. Possible reaction mechanism of phenol-crotonaldehyde polymer

The nucleophilic attack took place from **compound II** at hydroxyl group carbon which removed

a water molecule and formed compound **III**. The reaction was basic a medium, so hydroxyl OH group again from phenoxy anion then the nucleophilic attack takes place from remaining active position of benzene group to form compounds **IV**, **V** and final addition reaction polymer. As per the reference literature report, they have mentioned same reaction mechanism of phenolic molecule with a basic condition.¹⁶ The final phenol-crotonaldehyde resin addition reaction product can be a mixture of intermediate compounds.

We have studied the effect of molecular weight on increasing amount of crotonaldehyde with constant of other reactant. The mole ratio and molecular weight of PC1 to PC7 is showed in **Table 3**. In PC1 resin amount of crotonaldehyde in a reaction 1.2 eq. and its molecular weight is 1205 g mol⁻¹. Where as in PC2 quantity of crotonaldehyde resin was increased by 0.4 eq. i.e. 1.6 eq. its showed 1222 g mol⁻¹ mass. Further, in PC3, PC4, PC5 increased ratio of crotonaldehyde in the reaction and it observed 1245, 1140 and 1110 g mol⁻¹ mass respectively. It was also observed that the micro analysis data does not show much changes in the readings and it indicates that the structure of polymer with increasing or decreasing amount of crotonaldehyde or catalyst is going to be similar. We predict that based on the molecular weight(1110 to 1245) and elemental analysis data(Total Carbon-864 and it becomes 72.30 % and Hydrogen- 91,becomes 7.61% and balance Oxygen – 240, becomes 20.08% in total molecular weight of 1195).

Table 3

Number average molecular weight (g mol⁻¹) data for PC resins by GPC.

Mol ratio (P:C:S) ^a	Resin Code	Micro analysis data		(Mn) g mol ⁻¹
		C	H	
1: 1.2: 0.3	PC1	72.22	7.56	1205
1: 1.6: 0.3	PC2	72.13	7.64	1222
1: 2.0: 0.3	PC3	72.18	7.70	1245
1: 2.5: 0.3	PC4	72.41	7.31	1140
1: 3.0: 0.3	PC5	72.38	7.46	1110
1: 2.0: 0.1	PC6	72.33	7.62	1165
1: 2.0: 0.05	PC7	72.12	7.74	1210

^aP: Phenol; C: Crotonaldehyde; S: Sodium hydroxide

3.1.1 Infra –red analysis

The IR spectra of the uncured resins with and without conventional cross-linking agent, hexa are shown in figures 6a and 6b. **Fig 1a** represents uncured PC resins formation in presence of NaOH. The peaks at 810 and 740 cm^{-1} represent the characteristic bands of the aromatic substitution at 1, 2, 1, 4 and 1, 2, 4 positions.

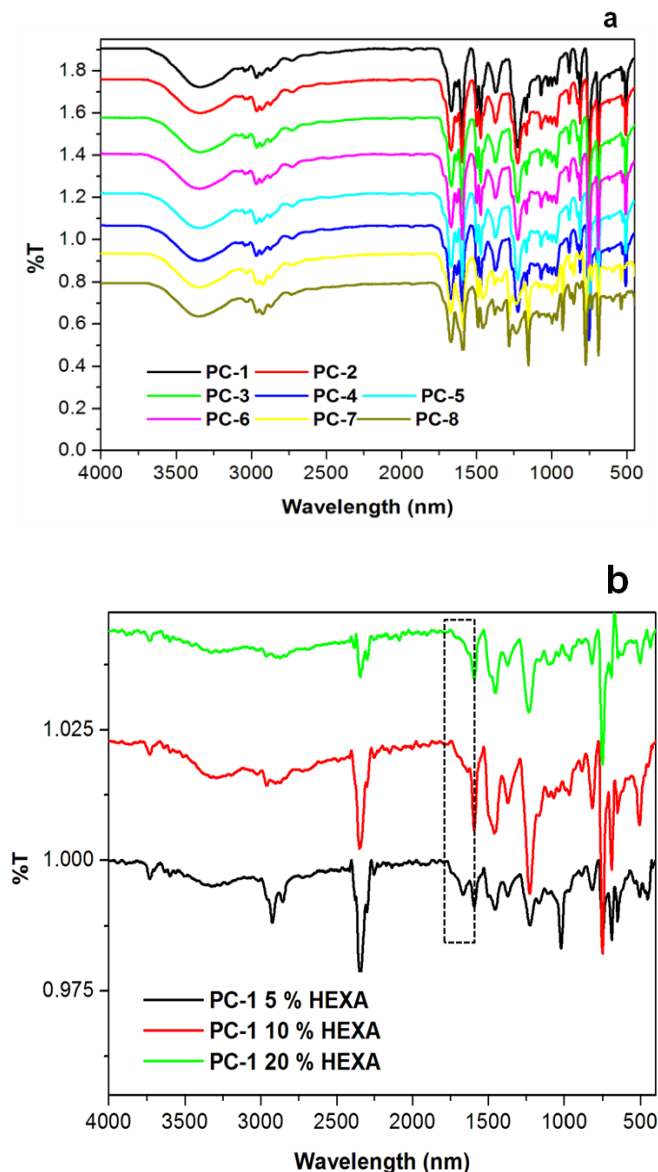


Fig 1. FTIR spectra of a) uncured resins without conventional cross-linking agent, hexa b) uncured resins with conventional cross-linking agent hexa

The characteristic bands of the C-O were observed at 1160 cm^{-1} , peaks at 3431 and 1672 cm^{-1} are due to the presence of phenolic hydroxyl and aldehyde groups respectively. It was observed that the resin absorbed at IR frequencies to C=C double bond at 1640 cm^{-1} where as the this regions indicating that there is presence of unsaturation. The sharp peak at 1007 cm^{-1} was observed only in **Fig. 1b**, represents the presence of methylol group at 1019 cm^{-1} which is characteristic of hexa. All the PC resins exhibited almost identical infra-red spectra irrespective of the mol ratio of crotonaldehyde and catalyst as seen from **Fig. 1a & 1b**.

3.1.2 Proton NMR analysis

The proton NMR spectrum measured in 500 MHz Bruker instrument. The PC3 resin ^1H NMR as given in **Fig. 2** revealed that the signals situated in the range of δ 0.6-2.4 ppm, belongs to $-\text{CH}_3$ groups.

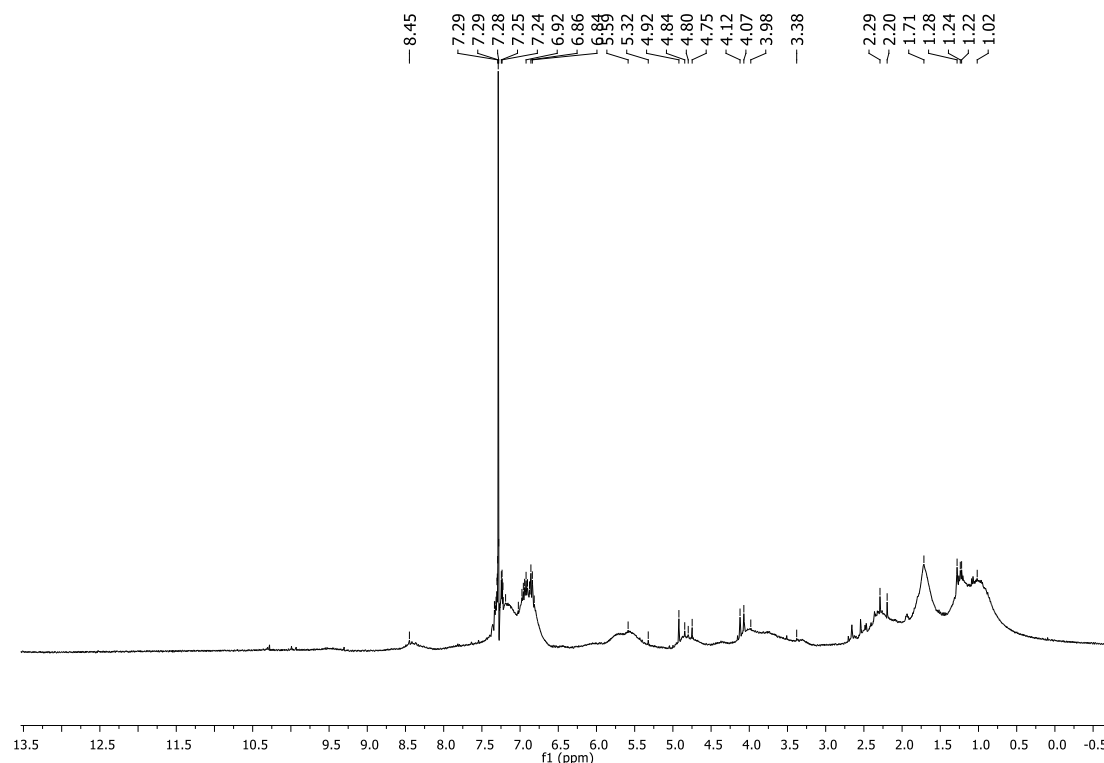


Fig. 2a Representative ^1H NMR of PC resin (PC3)

^1H NMR of PC2 resin

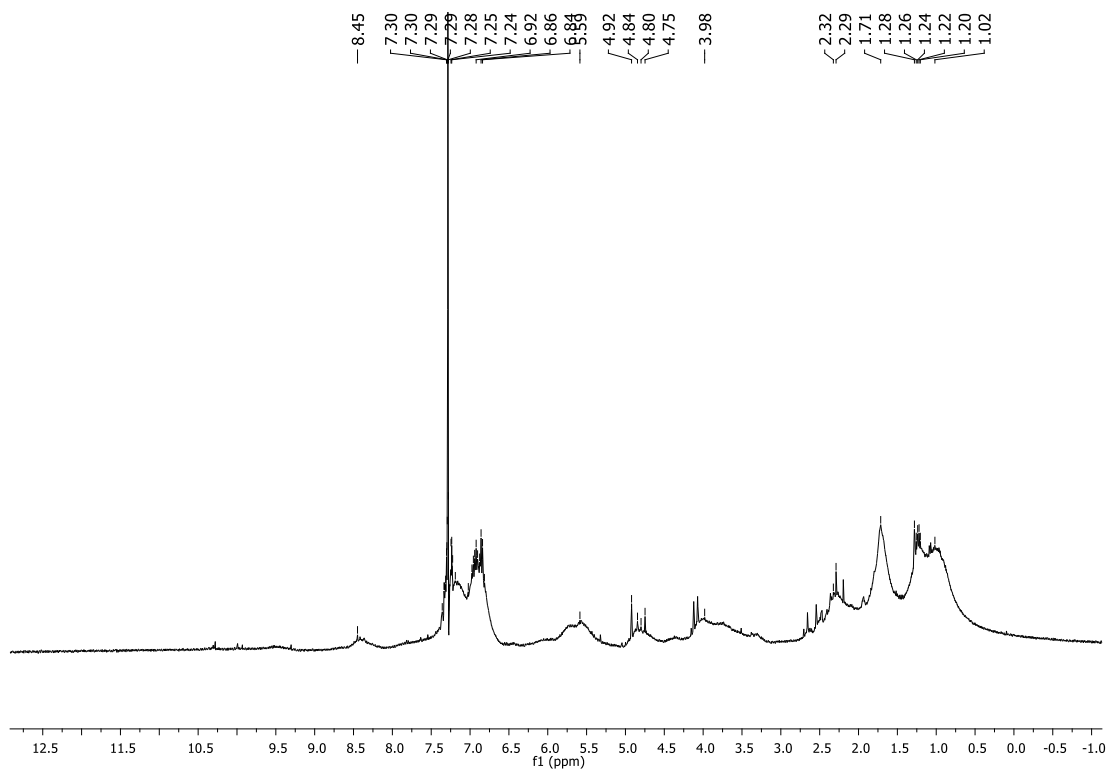


Fig. 2b Representative ^1H NMR of PC2 resin

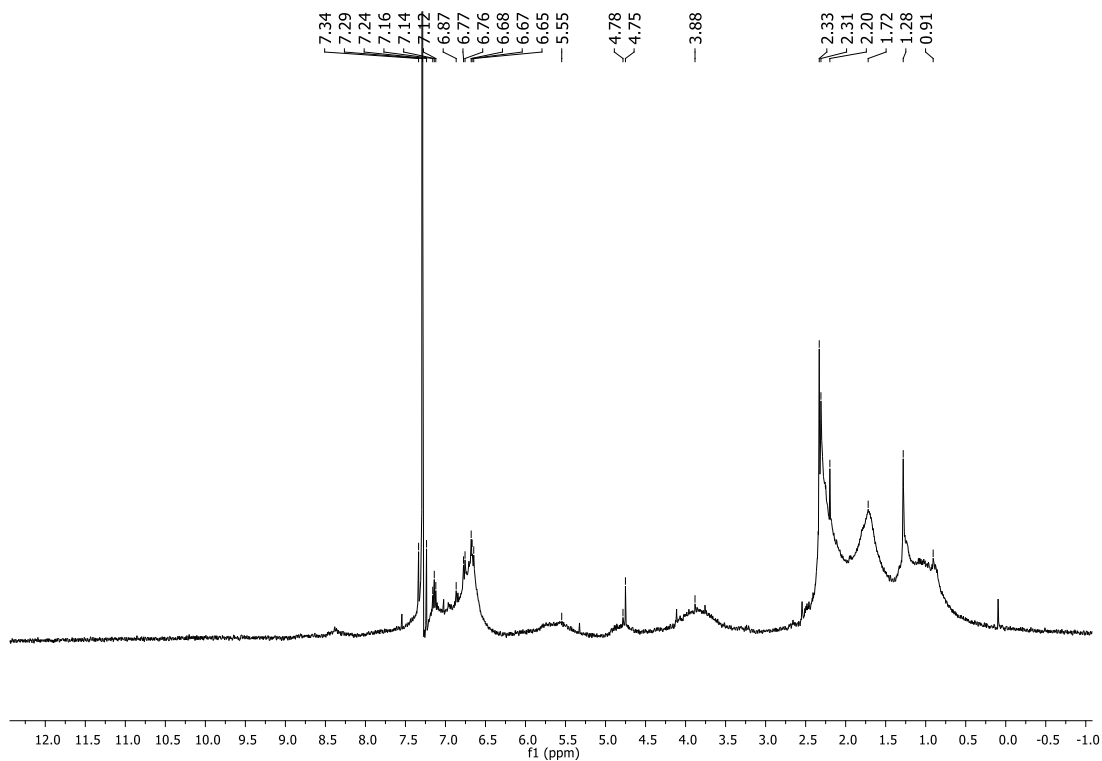


Fig. 2c Representative ¹H NMR of PC5 resin

The signals between δ 3.25 - 4.25 belong to $>CH$ and δ 5.4-5.6 ppm are related to $C=C$, $>CH-OH$ or $>CH-O$ groups respectively. In aromatic region signal observed δ 6.75- 8.45 which indicating aromatic $C=C-H$ peak

3.2 Cure behavior and softening temperature studies

The cure behavior studies of PC are presented in **Table 4**. It was noted that PC resins are thermoplastic in nature and the purity cured samples were soluble in acetone, whereas the PF resin (commercially available taken) evaluated under similar conditions exhibited infusible insoluble thermostat characteristics. The influence of the chemical reactivity of the curing agent

with PC resins at a low temperature was not apparently seen. However, it is evident from **Table 5** that the cross-linking with the use of hexa at higher temperature improves the characteristics.

Table 4

Effect of curing temperature on cure behaviour of PC resins

Mol ratio ^b	Curing Temperature(°C)	Softening point at 25 °C	10% Hexa	°C/ Acetone*
				solubility with 10% hexa
1.2	120	120-125	140-144	Soluble
	140	150-154	175-179	Soluble
	160	163-167	205-210	Partially Soluble
	180	220-225	infusible	Insoluble
2.0	120	134-138	150-155	Soluble
	140	154-158	185-190	Soluble
	160	165-170	208-213	Soluble
	180	235-240	infusible	Insoluble
2.5	120	136-140	158-163	Soluble
	140	148-154	163-166	Soluble
	160	158-163	202-207	Partially Soluble
	180	215-220	infusible	Insoluble

^b Mole ratio of phenol to formaldehyde

This peculiar behavior offers interesting processing possibilities. It may be partially possible to cure these resol resins with an addition of cross-linking agent up to 20% process on an injection moulding machine to attain thermoplastic product shapes, followed by post-curing of the moulded part in the oven to impart the desired thermostat characteristics. This cure behaviour indicates that the base catalysed PC reactions behave as PF of novolac type rather than resols and requires additional cross-linking agent unlike conventional PF resins.

Fig. 1b shows the IR spectra of partially cured PC material with hexa. The difference in the shapes of the peaks with and without hexa (**Fig 1a**), at 1600 cm^{-1} and in the range of $1400\text{-}1100\text{ cm}^{-1}$ are clearly seen. It was reported that the change is attributed to three dimensional network formations as the cure rate increases. It was observed that the curing reaction produces a band at a 1007 cm^{-1} , which is not present in the reactants and peak intensities decrease with hexa based cured resin sample (**Fig. 1b**) as cited to an increase in cure rate and is assigned due to the stretching of the azomethane group (-C=N-).⁴⁴

The amount of hexa on the cure behaviour and molecular weights of PC resins was investigated and the data are presented in **Table 5**.

TABLE 5

Effect of amount of hexa on the cure behaviour and molecular weight of PC resin (PC3, aldehyde –phenol mol ratio 2.0)

Sr. No.	% of hexa	Softening Temperature ($^{\circ}\text{C}$) after curing for 30 min		(Mn) ^c g mol ⁻¹
		140 $^{\circ}\text{C}$	180 $^{\circ}\text{C}$	
1	5	170-178	Infusible	1430
2	10	185-190	Infusible	1470
3	20	218-224	Infusible	1580

^c molecular weight tested after curing at $140\text{ }^{\circ}\text{C}$ for 30 min.

The amount of hexa on the cure behaviour and molecular weights of PC resins was investigated and the data are presented in **Table 5**. It is evident that the softening temperature and molecular weight increased with increasing hexa concentration indicating that the cross-linking reaction with hexa is operative. However its exact mode of reaction, as in conventional PF resins could not be established so far. The cure behaviour of mixed PC and PF resins (aldehyde to phenol mol ratio 1.0:2.0) are presented in **Table 6**. It was observed that the mixing of the PF resin with the PC, enhanced the curing rate of PF (high gel time) and no phase separation was seen.

TABLE 6
Cure behaviour of mixed PC3 and PF 3resins (aldehyde –phenol mol ratio 2.0).

Resin composition PC:PF (%w/w)	Gel time at 130 °C (seconds)	Gelled / Solidified mass characteristics after post curing ^d		
		Softening temperature range before post curing (°C)	Softening temperature range after post curing (°C)	Acetone solubility
100:0 ^e	160	110-115	148-152	Soluble
80:20 ^e	103	1220-130	160-165	Soluble
60:40 ^e	85	138-143	260-265	Soluble
40:60	61	240-250@	Infusible	Insoluble
20:80	42	Infusible	Infusible	Insoluble
0:100	30	Infusible	Infusible	Insoluble

^d Post curing at temperature 160 °C for 60 minutes

^e Resin samples from PC: PF composition 100:0% to 60:40% were all soluble in acetone

Resol type PF resin possess abounded free methylol group (reactive sites) and curing these resins even at low temperatures (below 140⁰C exhibited fast reactive (low gel time) thermostat characteristics. The PC resins, are of thermoplastic nature due to lack of reactive sites. It was also observed that the curing of PF resin with higher PC loading (above 40% by weight) showed thermoplastic behavior. It may be due to the steric hindrance of the bulkier moieties of the phenol ring of the PC resin, leading to the inhibition of the cross-linking reaction of PF and PC. Thus, PC resins require additional reactive sites and loading up to 60% by PF that could only transform them into infusible thermostats.

3.3 FESM study

Morphology study of PC3, PC5 and commercially available PF resin were carried out by using FESM. The morphology images are showed in below **fig.3**.

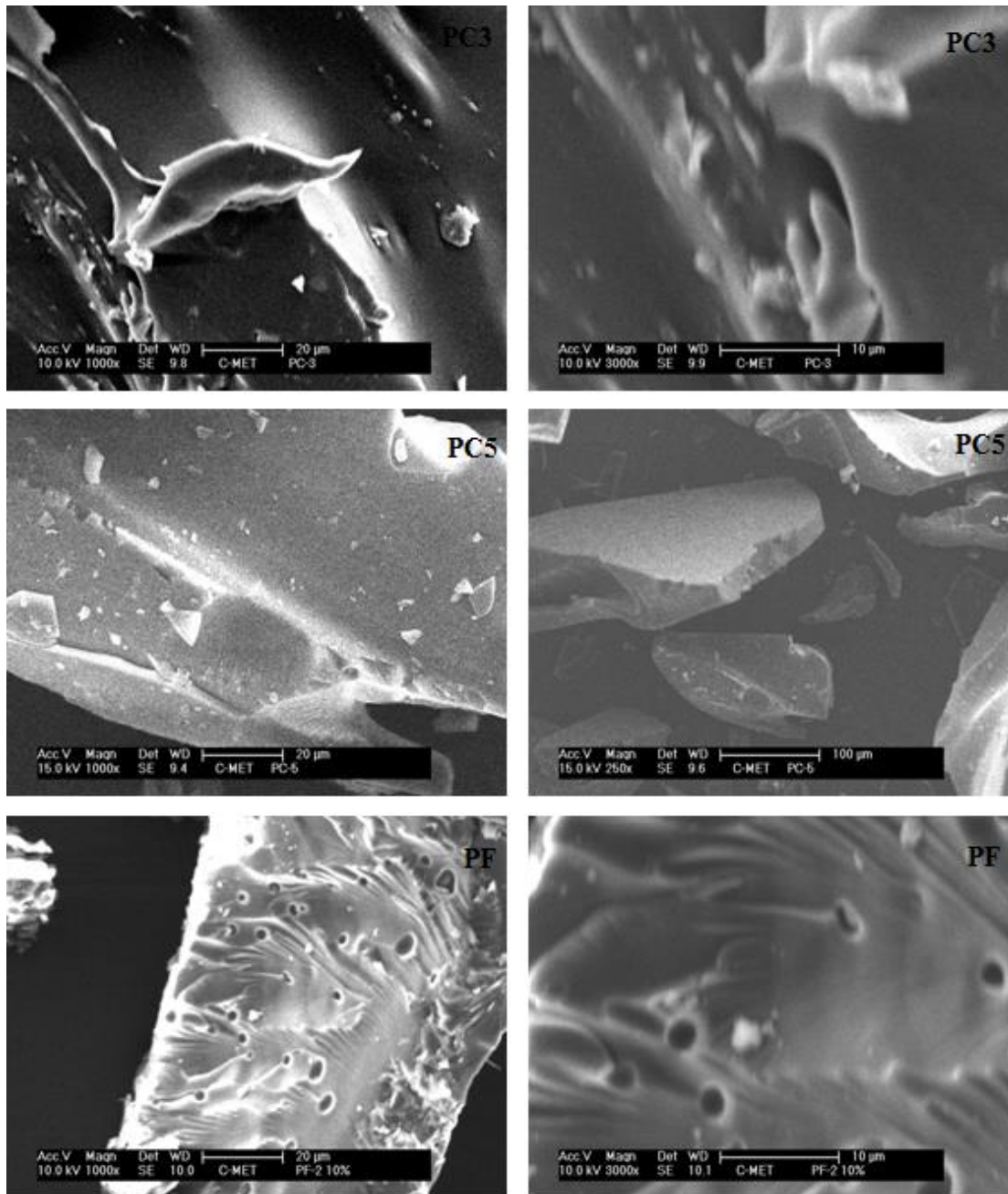


Fig.3. FESM images of PC3, PC5 and Commercially available PF resin

In PC3 images of FESM showed the surface of resin are not sharp or plane as compared to PC5 images. In PC3 resin surface showed hole and also small patches. Whereas, in PC5 resin surface are plane and having sharp image. PC5 images seen plane and having sharp edges, particle size

of PC5 resin was around 100-500 μm . In PC5 image the shoe structure like stone. The PE resin showed morphology like PC3 resin, its having patches and hole in surface. The PC3 and PF resin showed somewhat identical images.

4 CONCLUSIONS

The reaction of phenol with crotonaldehyde under base catalysed medium is similar to those found with formaldehyde however, due to the presence of double bond in crotonaldehyde, the PC reactions undergo addition as well as condensation reactions. The physico-chemical spectral analysis revealed that the reaction product formed has six benzene rings, bound together by bulky four carbon atom side chains. Because of the presence of such bulky side chain on the benzene ring, these resins exhibited thermoplastic behaviour. There is no much influence seen on the mole ratio of crotonaldehyde on reaction mechanism and all the PC resins exhibited almost identical infra-red and proton NMR spectra. The catalyst NaOH concentration followed by *pH* influences the polymerization and at higher alkaline (*pH* >10) conditions only polymerization takes place. The cross-linking agent, hexamethylenetetraamines was found to influence the reaction only at elevated temperature by converting them into thermostat materials. The addition of PF resin in to PC resin over 50% helps to increase the polymerization even at temperature 160°C and convert in to thermoset behaviour. This peculiar behaviour offers interesting processing possibilities and indicates that desired product shapes of thermostat materials can be obtained.

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