

## **SYNTHESIS AND CHARACTERIZATION OF MODIFIED LOW CURING PHENOL-FORMALDEHYDE RESIN FOR MANUFACTURE OF WOOD COMPOSITES.**

**S.C.Sahoo<sup>1</sup>, Amitava Sil<sup>2</sup>**

<sup>1,2</sup> Scientist, Indian Plywood Industries Research and Training Institute, Field Station Kolkata

Email : <sup>1</sup> sadhu.ch.sahoo@gmail.com

### **Abstract**

The objective of this study was to develop a modified phenol formaldehyde resin to cure at low curing temperature than the conventional PF resin and its performance study in manufacturing of exterior grade plywood. In this study phenol formaldehyde resin was modified by using a combine catalyst based on propylene carbonate (C<sub>4</sub>H<sub>6</sub>O<sub>3</sub>), sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), Para toluene sulphonic acid (C<sub>7</sub>H<sub>8</sub>O<sub>3</sub>S) and ethyl formate (C<sub>3</sub>H<sub>6</sub>O<sub>2</sub>) at a certain reciprocal proportion. The cure –acceleration effect of resin properties by using catalyst were analyzed. The effect of shortening temperature and adhesion strength were determined by using catalyst concentrations starting from 0.25%, 0.5%, 1.0%, 2.0% and 3% on the basis of the weight of liquid resin. The pot life and adhesion performance of accelerated–Phenol formaldehyde resins (PF) were evaluated by studying variation of viscosity and both dry and wet glue shear strength of the plywood respectively. Results indicates that the modified PF resin after incorporation of catalyst effectively accelerates the curing performance at lower temperature (1200C) than the conventional PF resin used at present in plywood industries. FTIR Spectroscopy to characterize the Structure of resin and differential scanning calorimeter (DSC-TGA) measurement was carried to study the thermal curing behavior of PF resin. The results shows that PF resin synthesized under catalytic system shows that the adhesive can be cured at low curing temperature (1200C) and shorten gel time as compared with control sample. Hence the catalyst accelerated –Phenol formaldehyde resin (PF) can overcome the short coming of high curing temperature and improve the quality of plywood.

**Key words:** Modified phenol formaldehyde resin, modified phenol formaldehyde, FTIR Spectroscopy, DSC-TGA, Quality of plywood.

### **Introduction**

Phenol–formaldehyde (PF) resin is mainly used as a binder for bonding waterproof grade wood panels. Although extensively used PF resins cure more slowly in a hot press than aminoplastic resins [Lei, et.al 2006, Roll et.al 1999].

At elevated temperature these catalysts generate corresponding acids, which catalysis the resole reactions. [Werner, et.al, 2008, David. A et.al, 1993].

The choice of suitable latent catalyst can also reduce the peak exotherm temperature. Latent catalysts on the other hand improve the efficiency and economy of existing applications by an improved control of the curing process [George, et.al, 2006].

As to the cure-accelerating actions of PC, there are some discrepant experimental results and interpretations. (Pizzi, et.al, 1993) reported that PC reacted with phenols to form cross-linkages between phenolic rings. On the other hand, (Tohmura, et. al, 1993) compared the effect of PC with that of sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) and found that there was no difference between the effects of the two accelerators. They reported that the accelerating effect of PC was ascribed to the catalytic action of sodium bicarbonate (NaHCO<sub>3</sub>) formed by the hydrolysis of PC.

In this study PF resins were synthesized using combine catalyst to achieve its curing at low curing temperature and its performance studies for manufacturing of exterior grade plywood.

## Materials And Methods

### Materials :-

Phenol (99%), formaldehyde (37%), Sodium hydroxide(96%), Propylene carbonate (97%), Sodium carbonate(99.8%), Para toluene sulphonic acid (PTSA) 97%, Methanol and ethyl formate (97%) were analytical grade material purchased from Aldrich. Both core and face Veneer used for manufacture of plywood belongs to *Dipterocarpus sp.*(Gurjan).

### Complex catalyst preparation:-

20% Para toluene sulphonic acid (p-TSA) app. 1mole solution of homogeneous mixture was prepared in methanol under a mechanical magnetic stirrer at temperature between 45°C-60°C [Manikandan,et.al,2016].10% propylene carbonate(PC) appx. 1 mole and 8% ethyl formate appx. 0.1 mole and 25% sodium carbonate app.2.5 mole solution was prepared with distilled water. A combined catalyst was prepared by taking 30 parts Para toluene sulphonic acid, 20 parts propylene carbonate,40 parts sodium carbonate and 10 parts ethyl formate.The prepared combined catalyst was used as additive at a concentration starting from 0.25%, 0.5%, 1.0%, 2.0% & 3.0% on the weight % of liquid phenol formaldehyde resin synthesized.

### Phenol formaldehyde (PF) resin preparation:-

100 parts of molten phenol (98%) was charged into a three necked 1000 ml round bottom flask followed by 180 parts by weight of formalin (37%) fitted with a reflux condenser, a mechanical stirrer, a digital thermometer and 08 parts of caustic soda (50%) aqueous solution was added to it. The mixture was stirred for 10-20 minutes, and then slowly heated initially. Since the reaction is exothermicity, once exothermicity was reached heating was discontinued and temperature was maintained 90-92°C.The reaction was continued till the water tolerance became 1;8/9 and flow time in B4 ford cup (IS 3944:1969) was around 15 to 16 seconds. Then the resin was cooled up to 50-60°C and the prepared combined catalyst was added slowly under stirring and then cooled to room temperature. Six different resins were synthesized by varying catalyst concentration varying from 1 to 5% including control. The unloaded resin was kept for 12 hrs for complete polymerization and conditioning. The synthesized catalyst-accelerated phenol formaldehyde (PF) resin was taken for plywood manufacturing, shelf life and free formaldehyde determination.

### PF resin properties study:-

Gelation time, solids content, viscosity, and free formaldehyde of the resin were measured. The viscosity of the phenol formaldehyde resin was determined viscometer (DV-II+, Brookfield),. p<sup>H</sup> of the resin was checked in a digital p<sup>H</sup> meter at 27°C after calibration.

### Solid content :-

3.0 -5.0 Gms resin sample was taken into a evaporating dish (W1), the weight of the sample was taken exactly (W2).The resin sample was evenly spread throughout the dish and was kept in a hot air oven set at temperature 105°C and was allowed to dry for 3hrs. After which the sample was transferred into a desiccators to cool down to room temperature. The dish with dried resin was weighed (W3) Percentage weight by weight of the resin's solids content was calculated from this simple relation

$$\% \text{ solid content} = \frac{W3-W1(g)}{W2(g)} \times 100$$

### Measurement of gelation time :-

Gelation time of the catalytic accelerated Phenol Formaldehyde resin was measured with digital POLYTECH gellimer at temperature of 120<sup>0</sup>C of the liquid resin until the resin transferred to gel.

#### **Free formaldehyde of the resin:-**

(0.2 -0.5) gms. Of liquid resin was mixed with 50ml Iso-propanol and water mixture (Isopropanol :water -2:1 on v/v) using magnetic stirrer . Solution P<sup>H</sup> was adjusted to 3.5 by adding 0.1M Hcl. 25ml. of hydroxylamine hydrochloride solution (10% on w/w) was added under stirring and back titrated to P<sup>H</sup> 3.5 by using 0.1N NaOH. Free formaldehyde content of the resin was determined against the titration value of Blank and sample . (DIN EN ISO 9397).

#### **FTIR analysis of PF resin:-**

FTIR spectroscopy was carried to characterize the structure of the combine catalyst, propylene carbonate, PF resin and the prepared modified phenolic (PF) resins. FTIR spectra were recorded in the range of 400–4000 cm<sup>-1</sup> at room temperature.

#### **Differential scanning calorimeter (DSC) measurement:-**

The thermal stability and curing behavior of the accelerated –PF resin was studied using thermo gravimetric analysis by DSC/TGA with heating rate 10<sup>0</sup>C/min.

### **Results And Discussions**

#### **properties of catalyst- accelerated PF resin:-**

Table -1 shows the solid content pH, Viscosity, gel time, shelf life of the catalyzed –accelerated phenol formaldehyde resin. From the analysis data it was found that the solid content were similar for all resins, but viscosity varies greatly as the concentration of the catalyst increases. The viscosity of the resin at 3.0% catalyst concentration was 252cps higher than the viscosity of the lower concentration of the the catalyzed –accelerated resin especially the control resin with low viscosity of 186 cps. The pH of the resin decreases from 12.5 to 9.5 as the the concentration of catalyst increases. There was no significant effect of the free formaldehyde and free phenol of the the catalyzed –accelerated PF resin.

#### **Effect of gelation time of catalyst- accelerated PF resin:-**

Gel time can be used to evaluate the curing time of resin. Normally curing rate of the resin be accelerated by increasing the temperature In this study gelation time of the the catalyzed –accelerated PF resin reduced by reducing temperature up to 120<sup>0</sup>C by enhancing the curing rate The comparison of resin gel time, after adding catalyst by using laboratory synthesis phenolic resin as shown in Table-1.A gelation time reduction effect of about 30 to 40% was observed at 120<sup>0</sup>C compared to the control Phenol formaldehyde resin . Though increase in the concentration of the catalyst gelation time reduced, However, the reduction was not large and the shelf life of the resin reduced. The acceleration effect of the reduction of gelatin time is shown in Figure-7.

#### **FTIR Spectroscopy :-**

Fourier Transform Spectroscopy was carried for catalyst PC,Combine catalyst,PF resin,Modified PF resin using Spectrum RX1 Perkin Elmer and has been displayed below. This absorption spectrum having frequency range of 400 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>.

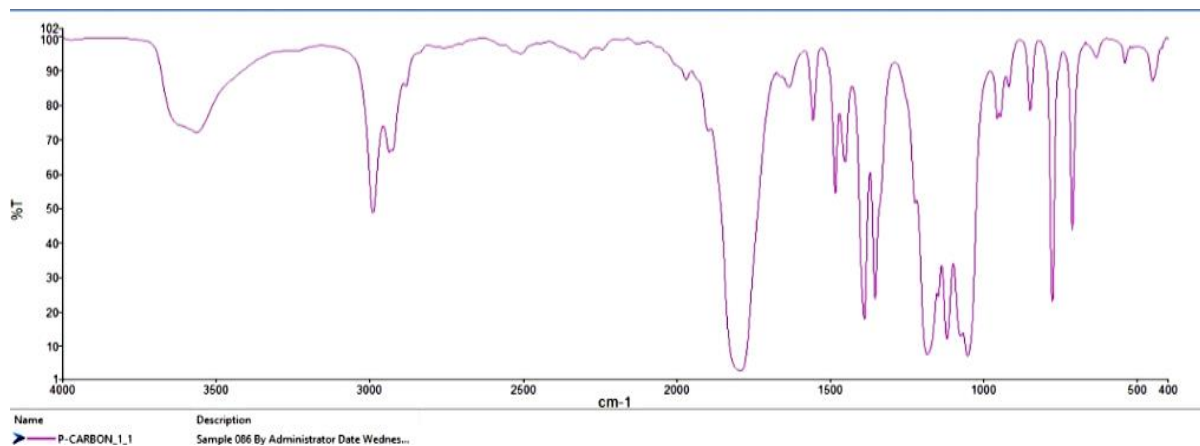


Figure -1 FTIR Spectrum of propylene carbonate

Wave number (cm <sup>-1</sup> )	Assignment
1709cm <sup>-1</sup>	C=O stretching of propylene carbonate
1022cm <sup>-1</sup>	C-H stretching
1223cm <sup>-1</sup>	C-O stretching vibration

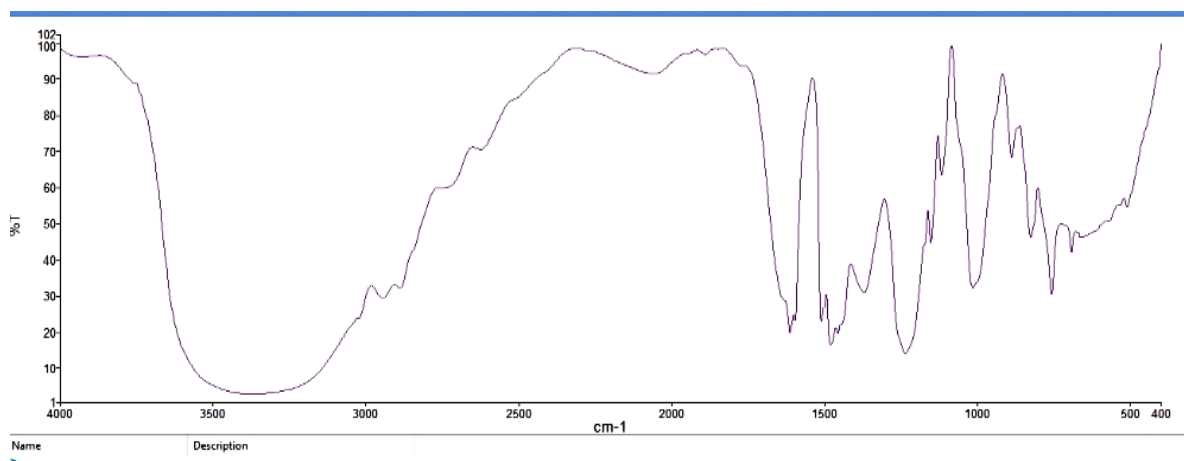


Figure -2 FTIR Spectrum of phenol-formaldehyde resin(control)

Wave number (cm <sup>-1</sup> )	Assignment
3363cm <sup>-1</sup>	O-H stretching vibration
2912cm <sup>-1</sup>	C-H stretching of methylene
1590cm <sup>-1</sup>	C=C elongation of aromatic ring
1260cm <sup>-1</sup>	C-O stretching vibration of phenolic C-OH
982cm <sup>-1</sup>	C-H stretching of vinyl

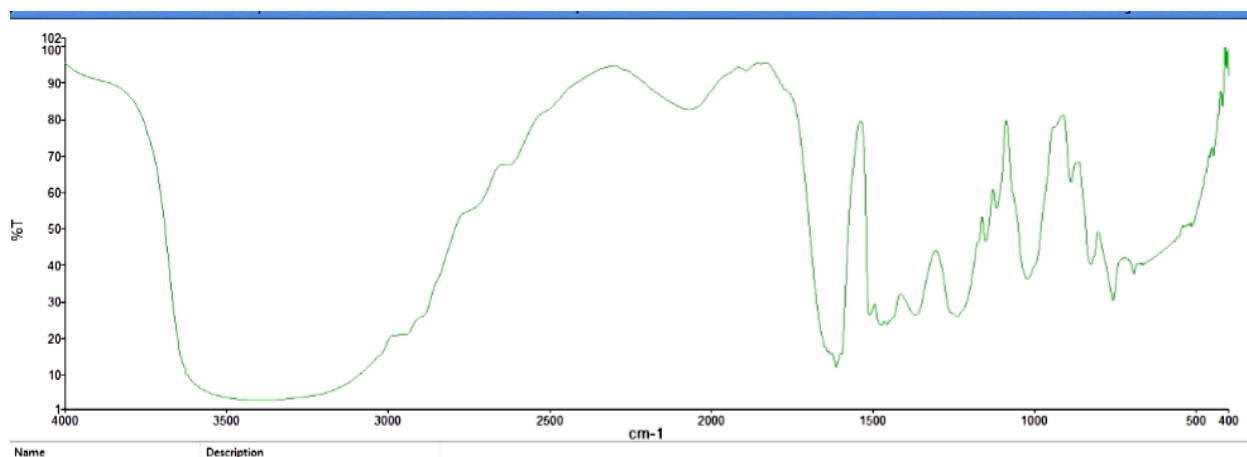


Figure -3 FTIR Spectrum of Modified phenol formaldehyde resin

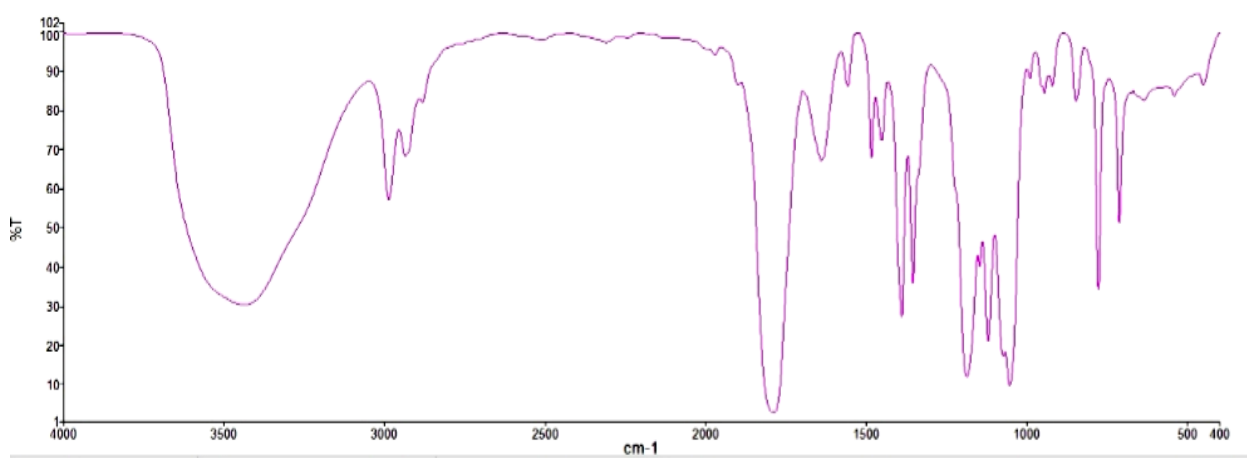


Figure -4 FTIR Spectrum of Complex catalyst

Wave number (cm <sup>-1</sup> )	Assignment
1272cm <sup>-1</sup>	C=O stretching of propylene carbonate
1140cm <sup>-1</sup>	O-O stretching of ethyl formate
1342cm <sup>-1</sup>	S-O stretching vibration of PTSA.

The structural change in the PF resin accelerated by catalyst FT-IR spectra were obtained. There were no significant difference between the spectra of catalyst-accelerated resin and the control sample which indicates structural similarity. Bands at 1020cm<sup>-1</sup> were ascribed to C-O stretching vibration of aliphatic C-OH, Aliphatic C-O and methylol C-OH. (fig. - 1 & 3).

**Thermal behavior of cured PF resin:-**

DSC/TGA was carried to perform the Curing characteristics of the resin. The stability of the cured adhesive was tested using a TGA instrument. (Fig -5). Weight loss appx. 75% was observed at starting in between 40 to 110 °C due to loss of solvent and appx. 50% weight loss was observed between 300 to 750 °C. The decomposition was major in between 500 to 650°C and stable up to 800°C.

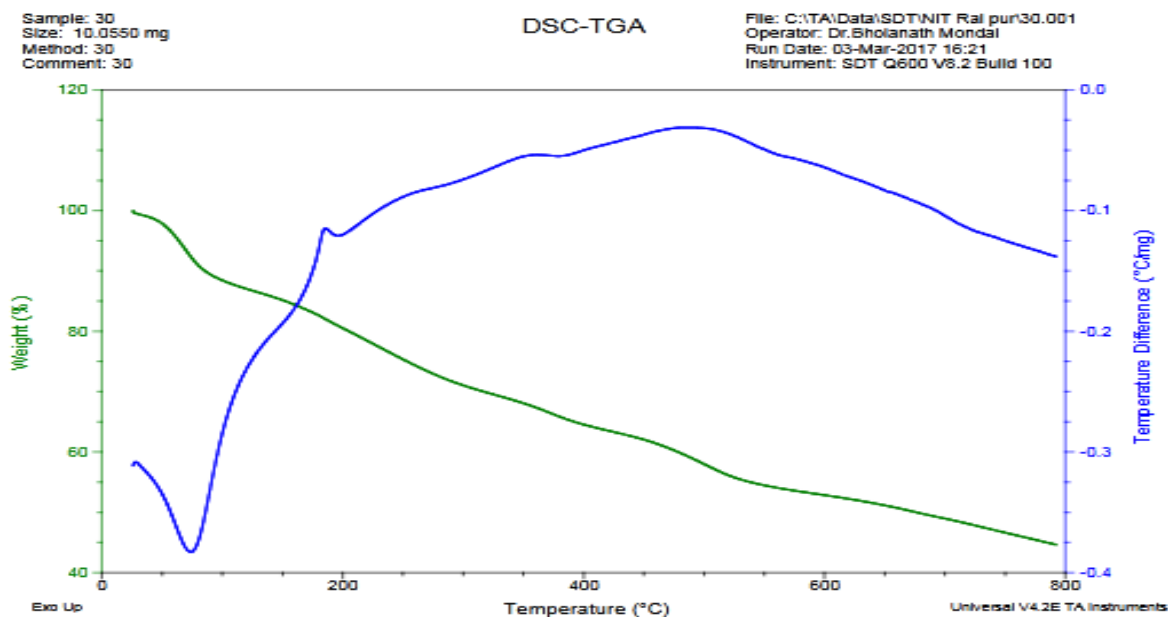


Figure -5 DSC/TGA Specturm of Modified PF resin

### Conclusion

The results and analysis of the studies carried at laboratory scale leads to the conclusion that the catalysed – accelerated phenol formaldehyde resin synthesized by using combine catalyst having concentration 2.0% (PF +2.0 % cat ) can cure the resin at 120-125°C. The gel time measured at 120°C decreased with increasing catalyst levels appx. 20-30% compared to the conventional phenol formaldehyde resin. (DSC-TGA) analysis of 2% of Catalyst is found suitable for reduced curing temperature of the phenol formaldehyde resin. These results suggest that this modification of PF resin meets the important criteria for its application in the manufacture of plywood with better quality at a lower curing temperature.

### Acknowledgment

The authors express their gratitude to Director, IPIRTI Bangalore for the timely encouragement, guidance and advices rendered during the course of the study.

### Reference

1. Lei H, Pizzi A, Despres A, Pasch H, Beer DG. Ester acceleration mechanisms in phenol–formaldehyde resin adhesives. *J Appl Polym Sci* 2006;100:3075–93.
2. Roll W. In: Christiansen A, Pilato LA, editors. *New developments in European wood adhesives: proceedings No. 7267: international contributions to wood adhesives research*. Madison (WI): Forest Products Society; 1999. p. 52.
4. George E. Myers, Alfred W. Christiansen, Robert Geimer, *Phenol-Formaldehyde Resin Curing and bonding in Steam-Injection Pressing, I. Resin Synthesis, Characterization, and Cure Behavior*, 2006,
5. Werner J. blank, Kurt Dietleker, Turja Jung, *Delayed (latent) catalysis in coatings*, Ciba schwazwaldalle, 2008, 215, 4002.
6. David.A. Hutchings, Tucker, *Latent catalyzed phenolic resole resin composition*, 1993, US patent 5243015, 3-6.
7. Pizzi A, Stephanou A (1993) On the chemistry, behavior, and cure-acceleration of phenol–formaldehyde resins under very alkaline conditions. *J Appl Polym Sci* 49:2157–2170
8. Tohmura S, Higuchi M (1995) Acceleration of the cure of phenolic resin adhesives VI. *Mokuzai Gakkaishi* 41:1109–1114.

**Tables :-**

TABLE -1 Properties of catalyst- accelerated PF resin

Sl.no	Type of resin	Flow Time (B <sub>4</sub> cup) seconds	Viscosity(cps)	Gel time(mints) @120°C	Solidcontent (%)	p <sup>H</sup>	Free formaldehyde (%)	Free phenol (%)	Shelf life (Hrs.)
01	PF (Control)	22	58	13.16	48.6	10.5	0.34	1.28	268
02	PF +0.25 % cat.	24	62	11.25	48.2	10.8	0.32	1.22	148
03	PF +0.5 % cat.	25	68	10.15	48.8	10.4	0.30	1.18	134
04	PF +1.0 % cat	27	70	9.48	48.3	9.9	0.33	1.16	126
05	PF +2.0 % cat	30	76	8.32	48.1	9.6	0.26	1.12	122
06	PF +3.0 % cat	31	80	7.16	48.6	8.9	0.27	0.98	108

TABLE -2 Properties of catalyst- accelerated PF resin

Sl.no	Type of resin	Flow Time (B <sub>4</sub> cup) seconds	Viscosity (cps)	Gel time(mints) @120°C	Solidcontent (%)	p <sup>H</sup>	Free formaldehyde (%)	Free phenol (%)	Shelf life (Hrs.)
01	PF (Control)	22	58	13.16	48.6	10.5	0.34	1.28	268
02	PF +0.25 % cat.	24	62	11.25	48.2	10.8	0.32	1.22	148
03	PF +0.5 % cat.	25	68	10.15	48.8	10.4	0.30	1.18	134
04	PF +1.0 % cat	27	70	9.48	48.3	9.9	0.33	1.16	126
05	PF +2.0 % cat	30	76	8.32	48.1	9.6	0.26	1.12	122
06	PF +3.0 % cat	31	80	7.16	48.6	8.9	0.27	0.98	108

**Figures :-**

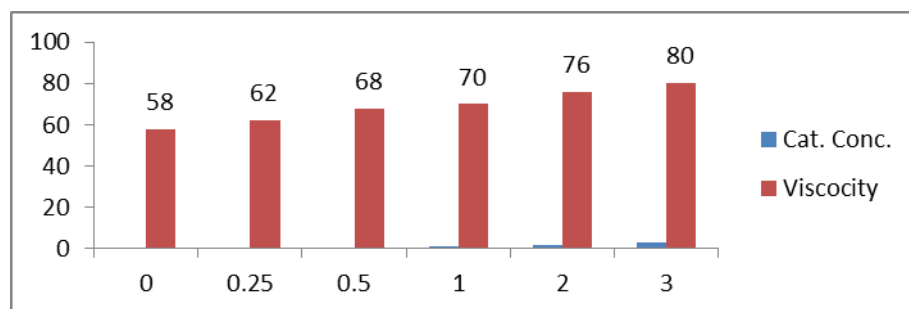


Figure -6 Concentration(%) vs Viscosity(cps)

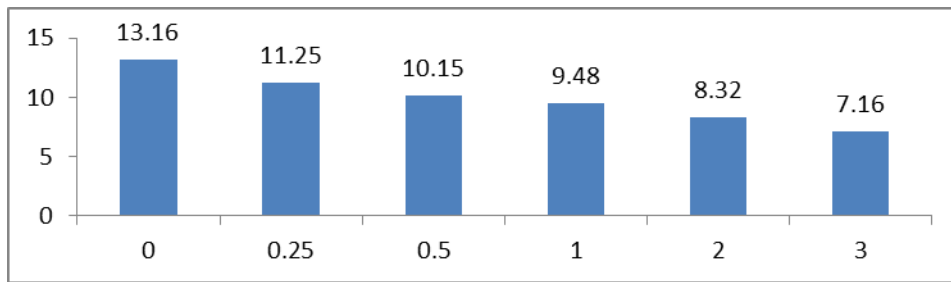


Figure -7 Concentration(%) vs Gel time(mnts.)

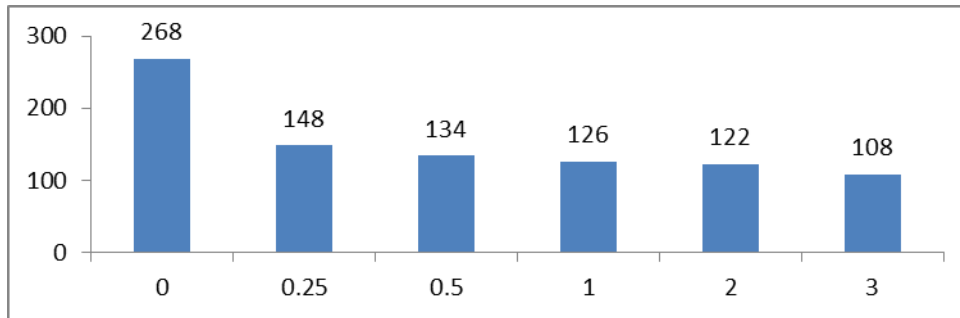


Figure -8 Concentration(%) vs Shelf life(Hrs)

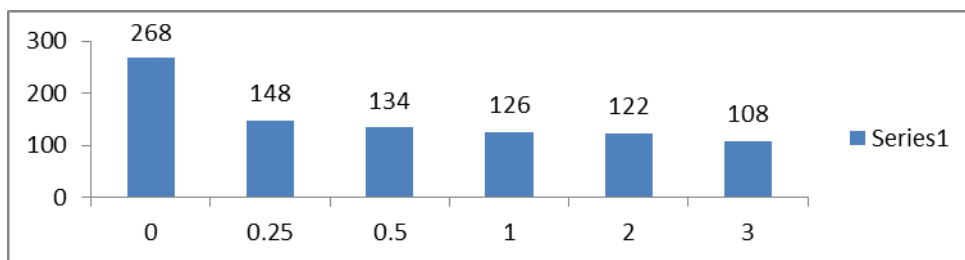


Figure -09 Concentration(%) vs Pot life (Hrs.)