



Effect of curing time on phenolic resins using latent acid catalyst

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Abstract: An investigation has been made to reduce the effect of curing time of phenol formaldehyde resin by incorporating latent acid catalyst at various percentages. The latent acid catalyst is used because of its capability to form more methylene bridge with phenol formaldehyde enabling fast curing at reduced temperatures and time. The curing of phenol formaldehyde takes place at higher temperature of about 110-140°C. Various latent acid catalysts are experimented and para-toluene sulphonic acid which is blocked by isopropanol is found best to serve as a latent acid catalyst. The characterisation techniques such as Fourier transform infrared spectroscopy, Differential Scanning Calorimetry and Thermogravimetric analysis were carried out. The latent acid catalyst of 40% para-toluene sulphonic acid and 60% isopropanol has been found. The amount of catalyst required to reduce curing time is determined to be 7 min 52 sec. It is observed that gel time (or) cure time of the phenol formaldehyde resin decreases with increasing catalyst content.

Keywords : Phenol formaldehyde, Para-toulene sulphonic acid, iso propanol, curing time, crosslinking polymerization, coatings, abrasives.

Introduction

Resins are generally used as binders, curable molding compositions, adhesives [1] and coatings. Phenolic resins continue to be the most important bonding systems of today's high performance products. Phenolic resins are thermoset polymers usually prepared and then cross linked by the effect of catalyst, heat and pressure. The typical systems are base catalyzed and water miscible, with water tolerances in the 50-300% range. Phenolic systems can be cured at fairly low temperatures (225°F/107°-121°C) [4].

Resoles and Novalac [5] are the two distinct types of phenol formaldehyde resins [3]. Resoles are prepared with an excess of formaldehyde and an alkaline catalyst which resembles the phenol alcohols and have methylol side or end groups [2]. They are capable of being cured by the application of heat and acids, cure resulting through condensation of the methylol groups[10].

Such phenol based resole resins cross link on heating & are used in adhesives applications[1,7]. The resole phenolics used in coating applications are made from monosubstituted phenols with phenol. The use of substituted phenols reduces the potential cross linking density. There are two broad categories of such resins (1) those that are soluble in alcohol & other low molecular weight oxygenated solvent commonly call as alcohol soluble , heat reactive phenolics and (2) those that are soluble in vegetable oils and are called oil soluble, heat reactive phenolics.

Alcohol-soluble, heat-reactive resole resins are prepared by reacting phenol and formaldehyde in the presence of a base catalyst at less than 60°C while removing water under vacuum. The catalyst is neutralized, alcohol is added. Potential cross linking is controlled by the ratio of formaldehyde to phenols and by reaction time.

Latent Acid Catalyst

The acid catalyst has only a limited life at room temperature, latent acid catalyst has been developed to overcome this problem [6]. At elevated temperature these catalysts generate corresponding acids, which catalyze the resole reactions[11,12]. 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[8].

Experimental Procedure

Preparation of Phenol formaldehyde

Phenol (91-94%), formaldehyde (37%), alkaline hydroxide (NaOH) (92-95%) along with latent acid catalysts (p-TSA / MSA + methanol / Isopropanol) are used in the formation of phenol formaldehyde resin [9].

Preparation of Latent acid catalyst

40% of p-TSA in the form of salt is taken and dissolved in 60% of Methanol at room temperature[11,12]. The mixture is stirred to form an homogeneous mixture and the temperature is maintained between 450C - 600C. Similar procedure is followed with 50% p-TSA and 50% Methanol, 60% p-TSA and 40% Methanol. The above experimentation is done by replacing p-TSA with Methane Sulphonic acid(MSA) and Methanol by Isopropanol.

Results and Discussion

Choice of Catalyst

Different catalyst combinations of equal weight has been taken as listed below and their gel time at 120°C for different compositions has been found out.

Catalyst 1 - MSA + Isopropanol

Catalyst 2 - MSA + Methanol

Catalyst 3 - p-TSA + Isopropanol

Catalyst 4 - p-TSA + Methanol

Table 1. Catalyst Concentration Vs Geltime at 120°C

Resin	Catalyst 1 Gel Time (min)	Catalyst 2 Gel Time (min)	Catalyst 3 Gel Time (min)	Catalyst 4 Gel Time (min)
Std PF	13:02	12:58	13:04	13:04
Resin +1% catalyst	12:52	11:30	11:25	11:35
Resin +2% catalyst	12:48	10:40	10:06	9:42
Resin +3% catalyst	12:09	09:50	09:15	7:21

Gel time for different catalyst composition has been tabulated above.

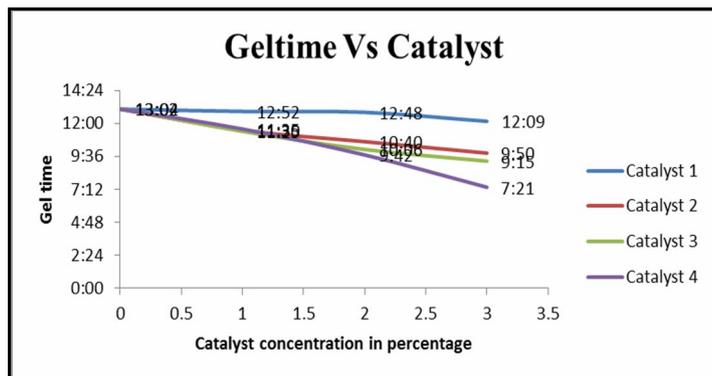


Figure 1. Geltime Vs Catalyst

Pot Life

Table 2. Pot life comparison for different Catalysts

S.no	Resin+ Catalyst	Hours	Days
1.	Catalyst 1	-	2
2.	Catalyst 2	4	-
3.	Catalyst 3	-	3
4.	Catalyst 4	4	-

Pot life of different catalysts are found out and represented above.

Comparing the results from tables 1 and 2, Catalyst 3 shows better results. It has reduced gel time and greater pot life comparing with the other catalysts. Hence Catalyst 3 is chosen for further analysis.

Gel Time for Selected Catalyst 3

Table 3. Comparison of Geltime for Catalyst 3A, 3B, 3C

Resin	Catalyst 3A Gel Time (min)	Catalyst 3B Gel Time (min)	Catalyst 3C Gel Time (min)
Std PF	13:04	13:04	13:02
Resin+1%catalyst	12:45	11:25	11:15
Resin+2%catalyst	11:55	10:06	09:10
Resin+3%catalyst	10:40	09:15	07:50

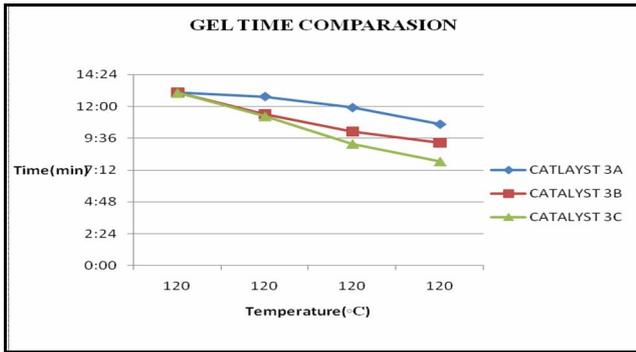


Figure 2. Gel time comparison with temperature for Catalyst 3A, 3B and 3C

Catalyst 3B, Catalyst 3C are selected ahead of Catalyst 3A since it gives the reduced gel time and also 3% by weight of catalyst shows reduced gel time for both the catalyst.

Analytical Results

FT-IR Spectroscopy

Fourier Transform Spectroscopy was carried on regular p-TSA, and selected Catalyst 3B and Catalyst 3C using Spectrum RX1 Perkin Elmer and has been displayed below. This absorption spectrum having frequency range of 400 cm-1 to 4000 cm-1.[7]

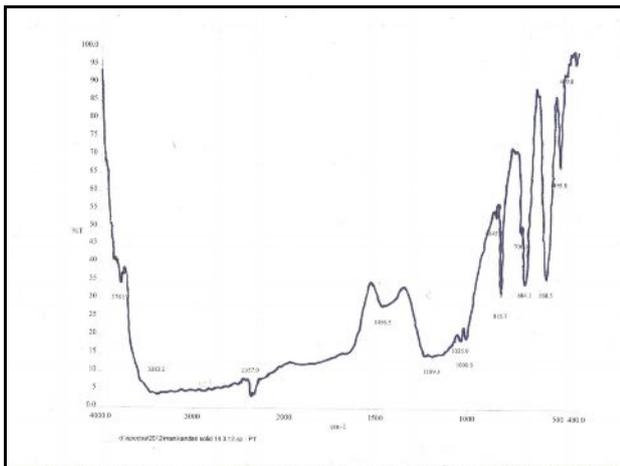


Figure 3. FT-IR Spectrum Regular Para Toulene Sulphonic Acid (p-TSA)

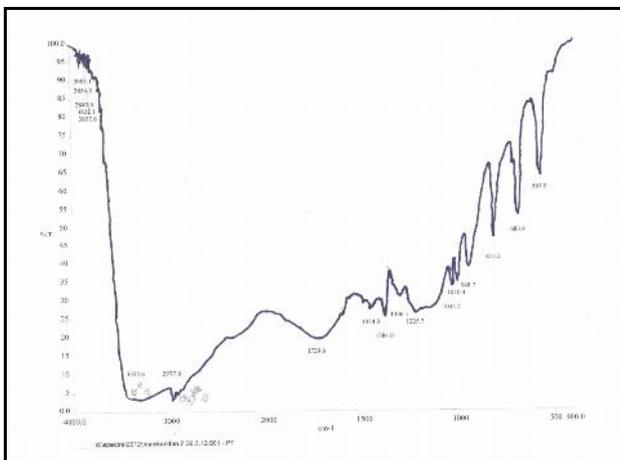


Figure 4. FT-IR Spectrum For Catalyst 3B

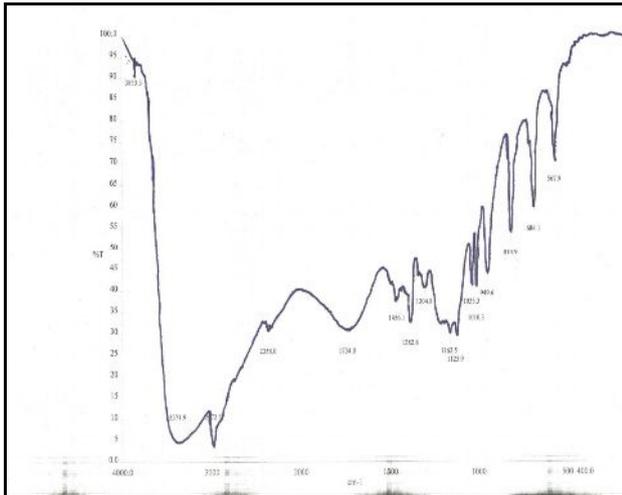


Figure 5. FT-IR Spectrum for Catalyst 3C

Differential Scanning Calorimetry

A metzsch DSC 204 phoenix was used to perform dynamic and isothermal cure experiments[12]. The measurements were done for standard phenol formaldehyde and phenol formaldehyde with catalyst 3B, 3C.

Table 4. DSC for Phenol Formaldehyde With Different Catalysts

Resin	Onset Temperature (°C)	Peak Temperature (°C)	Enthalpy J/g
Std PF	95	108.5	160
PF+ Catalyst 3B	95	106.3	106.3
PF+Catalyst 3C	95	100.5	84.77

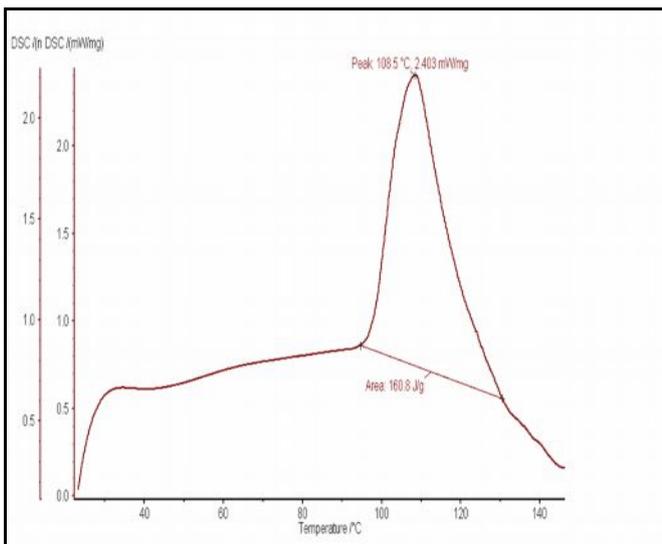


Figure 6. DSC Curve for Standard Phenol Formaldehyde

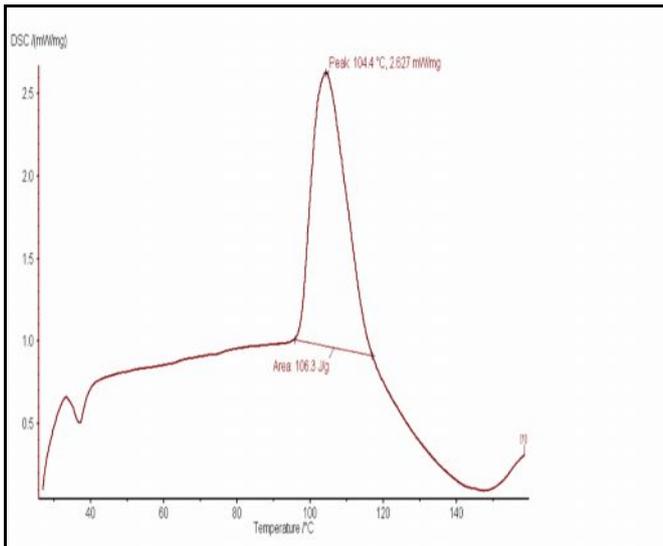


Figure 7. DSC Curve for Phenol Formaldehyde + Catalyst 3B

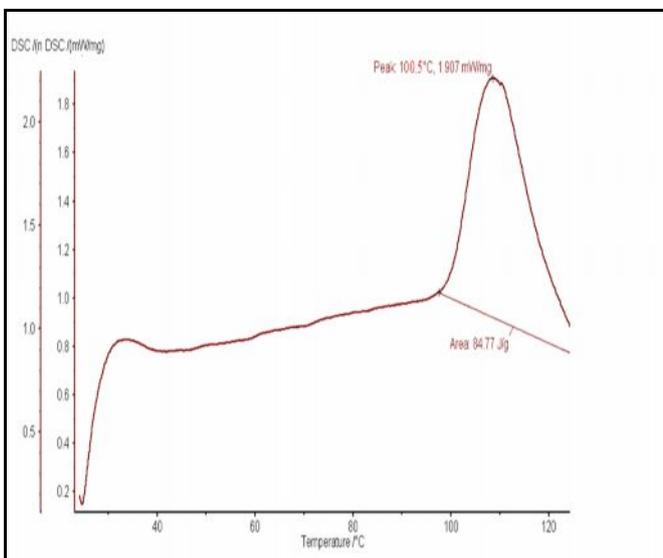


Figure 8. DSC Curve for phenol formaldehyde+ Catalyst 3C

Data of DSC thermogram are represented in table 4. It is (Figure 6, 7 and 8) observed that compared with standard phenol formaldehyde DSC curve, addition of both the catalyst 3B and 3C shows reduced exothermic peak temperature and the enthalpy was also reduced. The catalyst 3B has reduced the peak temperature of about 4°C and enthalpy nearly 25%. The catalyst 3C has reduced the peak temperature of about 8°C and enthalpy nearly 45%. Hence by comparing catalyst 3B and 3C, catalyst 3C was better for curing phenol formaldehyde.

Table 5. Gel Time Values for Phenol Formaldehyde and 3% Catalyst 3C at Various Temperatures

RESIN	TIME (min)
Std resin@120°C	13:09
Resin +3% catalyst 3C@120°C	7:52
Resin+3% catalyst 3C@110°C	10:48
Resin+3% catalyst 3C@100°C	14:15

Thermogravimetric Analysis for Standard Phenol Formaldehyde

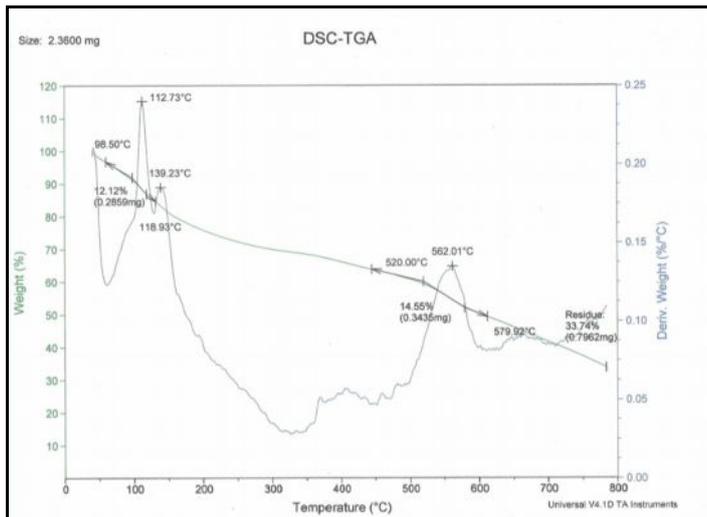


Figure 9. TGA curve for standard phenol formaldehyde

The TGA analysis of standard phenol formaldehyde resin is illustrated in the Figure 9.[12] The derivative curve is also shown in same Figure 9. The initial weight loss between 50°C and 200°C was due to loss of solvent entrapped in resin matrix. The gradual weight between 350°C and 780°C was due to degradation of resin. The degradation occurs in several stages, the initial decomposition between 350°C and 450°C was meager and 450°C and 650°C was more. The residue of 33.7% was observed and it was stable upto 800°C.

TGA Curve for Phenol Formaldehyde+Catalyst 3C

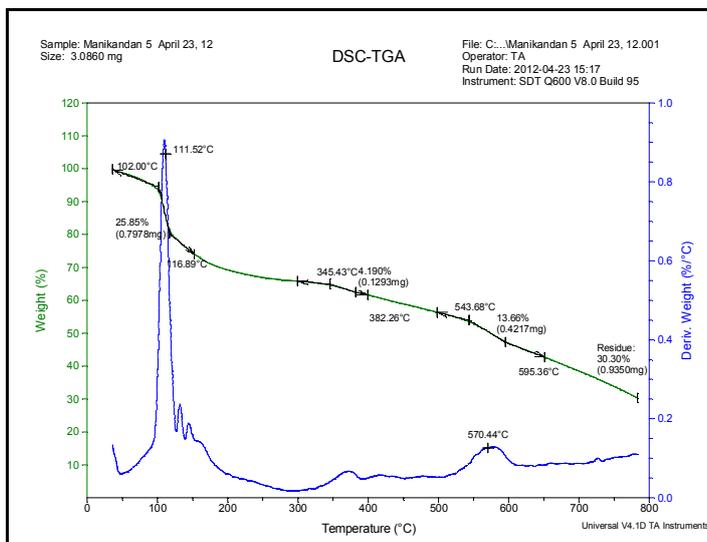
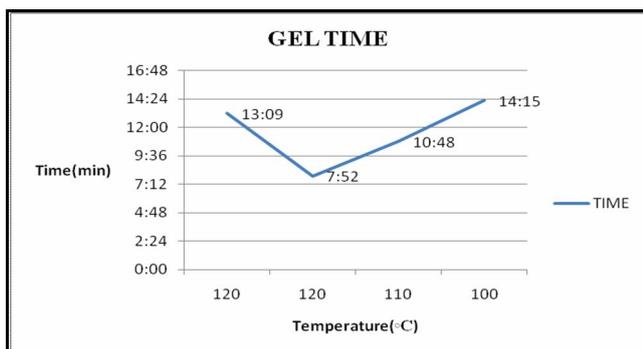


Figure 10. TGA curve for phenol formaldehyde + Catalyst 3C

The TGA analysis of standard phenol formaldehyde resin and phenol formaldehyde resin with catalyst 3C is illustrated in the Figure 10. The initial weight loss between 30°C and 150°C was due to loss of solvent entrapped in resin matrix. The gradual weight between 350°C and 780°C was due to degradation of resin. The degradation occurs in several stages, the initial decomposition between 350°C and 500°C was minor and 500°C and 650°C was major. The residue of 33.7% for standard resin and 30.30% for resin and catalyst was observed and was stable upto 800°C.

Comparing the Figures 9 and 10 TGA curves the addition of catalyst 3C does not alter the thermal stability of phenol formaldehyde and the thermogram is also similar.

Gel Time for Phenol Formaldehyde + Catalyst 3c at Different Temperatures**Figure 11. Plot between time and temperature for PF and 3% Catalyst 3C at various temperatures**

It is found from the table 3.5 that Phenol formaldehyde resin with 3% Catalyst 3C at 120°C has a minimum gel time of 7 min and 52 sec when compared.

Conclusion

The phenol formaldehyde resin used in coated abrasives has the curing temperature of 120°C. The curing time has been reduced as the latent acid catalyst such as para toluene sulphonic acid (p-TSA) and methane sulphonic acid (MSA) was freeze-dried and the solvents like methanol and isopropanol were selected. From the gel time and pot life results, Catalyst 3 (p-TSA and isopropanol) was selected since it has reduced gel time and greater pot life. Catalyst 3C (60:40) has been selected based on the characterization done by Fourier Transform Infrared Spectroscopy, Differential Scanning Calorimetry (DSC) and Thermogravimetric analysis (TGA). 3% of Catalyst 3C is found suitable for reduced curing time of the phenol formaldehyde resin thereby showing the same reproducibility performance as standard phenol formaldehyde resin. The curing time is found to be 7 min 52 sec.

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