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On the Solvent-Mediated Stabilisation of Phenol-Formaldehyde Resole Resin- A Revisit

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Abstract

The aging of phenol formaldehyde resole (PF) resin was monitored from an increase in viscosity, indirectly measured from its flow time though a capillary. A way to arrest the self-condensation reaction responsible for aging, is addition of a solvent so as to retards the kinetics of the crosslinking reaction. Conventionally, ethanol was used and is still preferred as the diluent for PF resin. However, no rationale has been given for this preference. On re-investigation, we too found that alcohols are the best diluents to arrest or retard aging of resoles. A detailed study of the evolution of viscosity with time for different alcoholic solution, concentrations and temperatures vis-à-vis a reference solvent, Methyl, Ethyl Ketone (MEK) led to the conclusion that alcohol causes stabilisation of P-F resins by (i) sharing of the non-bonding electrons on the oxygen of alcohols with the electrophilic carbon of the H_2**C**-OH groups of methylol, which quenches the latter's reactivity towards another methylol phenol, (ii) the nucleophilicity of the OH group, (iii) the ease of proton transfer from the alcoholic -OH groups that facilitates the formation of benzyl alkyl ether with reduced reactivity towards phenols. The efficacy of the alcohol depends mainly on its nucleophilicity and steric environment. For these reasons, the stabilising effect of the alcohols decreased in the order tertiary> primary > secondary. Though the tertiary alcohols are the best, they are expensive and has, in general, a noxious ordure. The next choice falls on a primary alcohol that is sterically least hindered and has adequate nucleophilicity Though methanol appeared to be a good choice, its high volatility and toxicity impede its preference. The next choice is ethanol which is comparatively a strong nucleophile, is less toxic and volatile, easily available, low priced and is also an excellent solvent for P-F resin. Thus, the choice of ethanol as a preferred stabilising solvent for P-F resin is scientifically rationalised.

Keywords: P-F resin, resole, resin aging, solvent stabilisation, methylol condensation, ethanol stabilisation

1. Introduction

Resole type phenol-formaldehyde resins are in great demand as the phenolic-wood composite industry is proliferating and that its demand in other areas of technology is on the increase. This thermosetting resin, prepared by the reaction of phenol and formaldehyde under alkaline conditions comprises of a mixture of isomeric (ortho and para) methylol phenols with practically little polycondensates[1]. Coupled with silica fibre / powder, these resins constitute excellent ablatives for rocketry due to their highly favourable characteristics in terms of processability, strength, heat resistance, char strength, lightweight of the cured resin and cost[2]. Phenolic matrix composites provide superior ablative characteristics, high char yield and retention of the strength and mechanical properties at elevated temperature. This, particularly makes it the resin of choice for ablative thermal protection systems in atmospheric re-entry space missions[3]**.** Silica-phenolic composites used in liquid engines in rocketry have to withstand very high thermal and mechanical stresses[4].

The P-F resins are known to be stored in alcohol especially in ethanol under refrigerated conditions for pretty long time, without much aging. Ethanol used to serve as the solvent right from the inception of the resin, probably because of the easy availability, low cost, compatibility with the resin and reduced toxicity of this alcohol in contrast to many other solvents. This practice is being followed even now without any scientific reasoning other than those mentioned above. Not much study has been devoted to understand the role of ethanol as a solvent of preference for P-F resin.

There have been many attempts to enhance the shelf-life of P-F resins by diminishing the crosslinking reaction rate. The crosslinking happens through condensation of the methylol groups among themselves in the absence of an alcoholic solvent even under refrigerated conditions. This happens as the methylol condensation needs very low activation energy. The activation energy varies from 15- 17kJ/ mole only, for different F/P ratios[5], while a typical epoxy resin curing needs like 45-60 kJ/ mole[6]. There have been many attempts to overcome this situation by way of designing modified P-F resins. One approach was to synthesise addition-curable P-F resins. These are basically low molar mass novolac resin incorporating addition curable groups like maleimide, acetylene, propargyl ether etc[7]. Most of these are low melting solids. Though high temperature resistant and high char-yielding, these have poor fiber wetting characteristics as the resins are only moderately hydrophilic.

The stabilisation efforts on resole include designing a urea-extended phenol-formaldehyde resin stabilized with alkanolamines and monosaccharides or disaccharides as per a US Patent,WO1998053001[8]. Phenol-formaldehyde-urea-ammonia resins are reported to be stable at pH 3 with desirable cure profiles[9]. This one is a copolymer with increased shelf-life but has inferior thermal stability**.** Another method was to modify the resole by way of allylation of the phenolic as well as methylol OH groups to produce phenyl allyl or benzyl allyl ethers with diminished reactivity towards phenols. Yet another method is to synthesise ortho methylol rich resole by using polyethylene glycol as a template[10]**.** Ortho methylols are less reactive than the para isomer. All these methods are, though, in theory acceptable, practical difficulties associated with these modifications are many; like lack of knowledge about their effect on cure behaviour, aging characteristics of the cured resin etc.

Though alcohols have not been subjected to any systematic studies for this purpose, during the preparation of this paper, a report on the use of methanol for P-F resin's discolouration and stabilization surfaced[11]. Prior to this, there was a report by A.W. Ahmed on the same subject[12]. The enhanced stability of the resin in this case is attributed to etherification of methylol group by methanol. The etherified methylol is less reactive towards another methylol phenol unlike its precursor (i.e. methylol phenol). Methanol, however, is toxic and cannot be used on a large-scale. Meanwhile, there are reports that methanol increases the curing rate and crosslink density of phenolic resole resins[13]. Thus, contradictory reports exist in its utility for resole stabilisation.

An ideal system should be the one where the stabilising additive shall be non-toxic, moderately volatile, compatible with the resin, not interfering with its application, cure schedule and affect the properties of the cured resin. This implies that it should have only a fugitive role. If the stabilising additive is a compatible liquid, it reduces the resin's viscosity and makes the application easier thus, achieving two objectives at a shot.

Ethanol is in use since the resin's inception as back as in 1907. However, it is understood that, that was the practice from those days onwards as this particular solvent was freely available and meet all requirements for P-F resin. So, it was of interest to see if ethanol or alcohols *per se* have any stabilising effect on resoles.

While the reasons for the instability of PF resins are fairly well understood, very few studies only have been devoted to unearthing the real reason behind. With a view to unravel the role of solvents, particularly the alcohols in stabilisation of resole, the present study was undertaken. We investigated the stabilisation of the resin from their time-viscosity (flow-time) profiles under specified conditions of concentration and temperature. Alcohols of different structures were used in comparison to a reference non-alcoholic solvent, methyl ethyl ketone(MEK).

2. Experimental

2.1. Materials

Phenol (99.9% purity), formalin (35-37% aqueous solution), sodium hydroxide (Reagent grade), ethanol, EA (AR grade), tetrahydrofuran (THF) ethyl methyl ketone, MEK (AR grade), isopropyl alcohol, IPA (AR grade), t-butyl alcohol, TBA (AR grade) were procured from M/s Finar Chemicals (Cochin) and were used as such.

2.1.1. Synthesis of resole

PF resole resin was synthesised from phenol and formaldehyde in a specified mole ratio using sodium hydroxide at 70°C by a proprietary method developed at VSSC. No additive was used. The resin was neutralised using acetic acid and the resultant coagulated resin was dried in vacuum at 45-50°C for 4 hrs. The study was carried out by making solutions of 2.5, 5.0 and 10% (wt/volume) of the resin in various alcohols including a non-alcoholic solvent viz: ethyl methyl ketone (MEK). The solutions were manually stirred thoroughly, filtered to remove any suspended particles and used for the flow-time studies. In some cases, the viscometer along with solutions was immersed in a water bath at different temperatures, and their flow-times were measured at these temperatures with reference to the corresponding solvents.

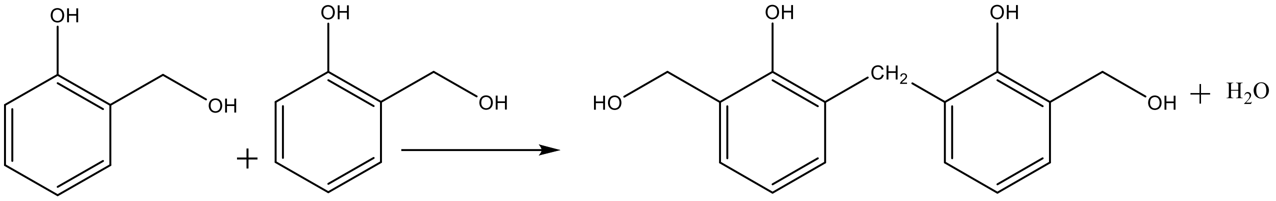
2.2. Characterisation

2.2.1. Determination of flow time

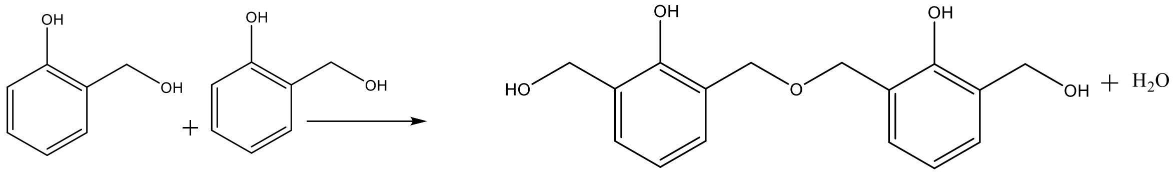
The viscosity was indirectly monitored by measuring typically the flow time of a solution of the resin in the concerned solvent using a thermostated Ubbelohde viscometer. Typically, the capillary was chosen with constant **k** approximately 0.003 and dia of 0.47 mm. This gave a flow time of about 80 seconds for MEK. Flow time measurements were repeated till concordant time of flow was obtained for each case. For higher temperature experiments, the resins were kept in an oil bath, tight closed and magnetically stirred at the specified temperature. After the aging, the flow times were measured in the viscometer kept in a water bath maintained at the required temperature.

3. Results and discussion

If left alone, resoles condense among themselves as per the following scheme. Methylol phenol can react with another molecule to form a longer chain methylol phenolic oligomer (Scheme 1) or form dibenzylic ether (Scheme 2).

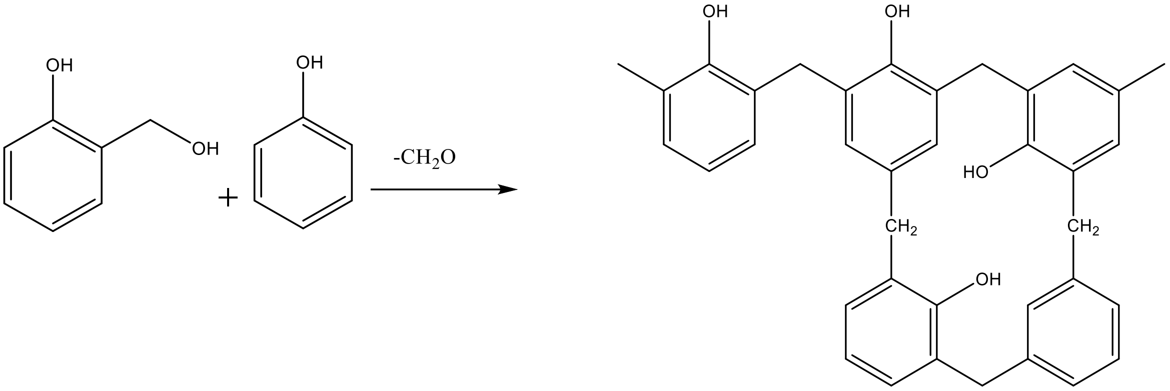


Scheme 1 Formation of methylol phenol oligomer



Scheme 2. Formation of dibenzyl ether

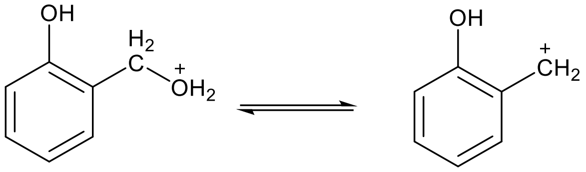
The main curing reaction is condensation between the hydroxymethyl and unsubstituted active hydrogen of another phenol ring, cleavage reaction of ether bond, accompanied by the release of water and formaldehyde, ultimately to form the three-dimensional poly (methylene phenols) as shown in Scheme3**[14]**.



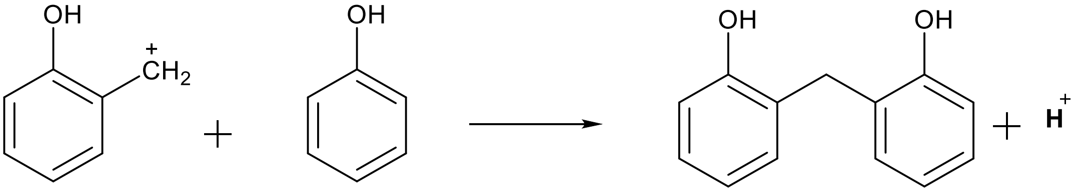
Scheme 3: Crosslinked phenolic resole network

Formation of multiple self-condensates of the methylols leads to flow-time increase and ultimately to cross-linking of the PF resins. The low activation energy values for condensation between ortho and para methylol phenols lead to an easy condensation between them. These routes lead to ready cross linking and gelation of the resin. Concerning the chemical stability of the resole resins, there is hardly any solid study on the stabilisation of the formed resoles.

Yet another way for stabilisation, apart from diminishing the temperature is to dilute the resin using a solvent. Dilution reduces the reactivity of the resole and also makes their application easier. Since polycondensation of methylol is understood to follow a second order kinetics, the dilution has a significant influence in diminishing the overall rate, e.g. if the concentration is made half of the the original, the rate should get reduced to ¼. However, our interest was in identifying a solvent that reduces the rate or reactivity not only by dilution but also by some mechanism that slow down the polycondensation of resole by intervening in the crosslinking process. The resole polycondensation proceeds via a partial carbo-cationic intermediate originating from methylol groups as depicted in Scheme 4. The polycondensation occurs via reaction with phenol (Scheme 5).

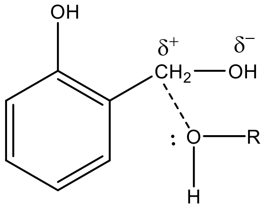


Scheme 4 Carbocation intermediate formed from methylol groups



Scheme 5. Electrophilic attack by the carbo cation and formation of methylene bridges

Resole condenses with phenol and among themselves too. Methylol phenols, the first-generation products do not have appreciable viscosities, but once they start condensing among themselves, the viscosity and henee, the flow-time starts to build-up. Therefore, the shelf-life of these resins is limited by the time the viscosities increase dramatically. In neutral and acidic medium, it is the methylol group that attacks the phenol while in alkaline medium, the phenolate anion nucleophilically attacks the -CH-OH group of the methylol phenols. If methylol is the attacking species, then it should precede by the polarisation of the reactive -CH-OH group as follows and the attack is electrophilic in nature (Scheme 6). Alcohols compete with phenols as better nucleophiles towards the electrophilic benzylic cation (partially polarised).



Scheme6. Co-ordination of alcoholic OH with partially polarised benzyl alcohol group

Normalisation of viscosity

For a solution of P-F resin in any solvent, the solvent independent viscosity factor is actually the relative viscosity defined as:

Flow Time (FT) of solution/FT of solvent = viscosity of solution/viscosity of solvent…… (ii)

Since it is difficult to determine the absolute viscosity of both solvent and the solution every time, we used a near related parameter called normalised FT = FT of solution/viscosity of a solvent. This gives a viscosity parameter of the polymer independent of the solvent. Such analytical practices have been resorted to by Kasaai *etal* for explaining the solvent-assisted fragmentation of chitosan[15].

The solvent viscosity data for this were obtained from literature. If the viscosity of the solvent at a given temperature is not reported, the same could be deduced from the viscosity-temperature relation as:

$$\eta = \eta_o \times e^{(E/RT)} \ldots\ldots\ldots\ldots \quad \textbf{(if)}$$

E activation energy for the flow, R universal gas constant

$$\text{Ln}\,\eta = \text{Ln}\,\eta_o + E/RT$$

Therefore, a plot of Ln η versus I/T will give a straight line with E/R as slope and Ln ηo as y intercept. Such a plot each for ethanol and isopropyl alcohol are shown in Figure 1 and in Figure 2 respectively. Using the data available in literature and with the help of the above equation, we could assess the viscosity of any liquid at any temperature (until its boiling point).The normalised viscosity has the unit mPa. This normalisation exercise does not alter the profile of the individual Time-Viscosity profile, but gives the true representation of the polymer characteristics within the solvent. This treatment also helps offset graphs along the y-axis direction and thus helps disentangle the overlapping graphs in FT-time plots. The viscosity data of pure solvents were taken from literature. Table 1 shows typical viscosity data for different solvents and temperatures used.

Table 1. Representative viscosity data for different solvents used in this study

Solvent	**Viscosity(mPa)**		
	Ambient	60°C	70°C
MEK	0.43	0.35	0.32
IPA	2.08	0.40	0.33
TBA	3.38*	0.53	0.44
EA	1.10	0.43	0.37

*at **25 °C**

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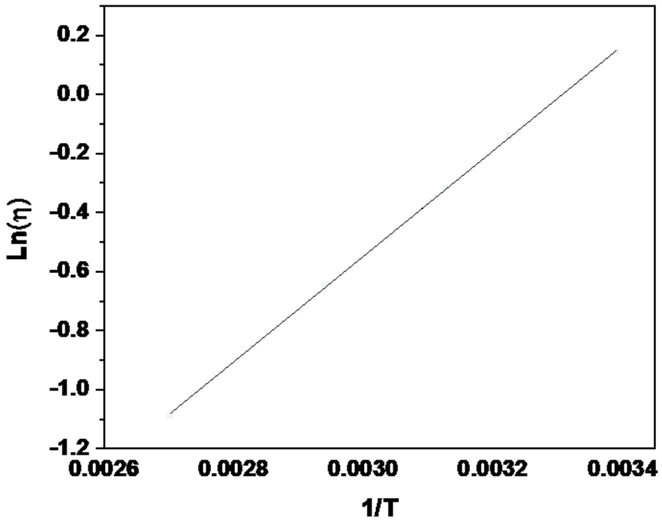

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Figure 1: Temperature- viscosity linear plot for ethanol

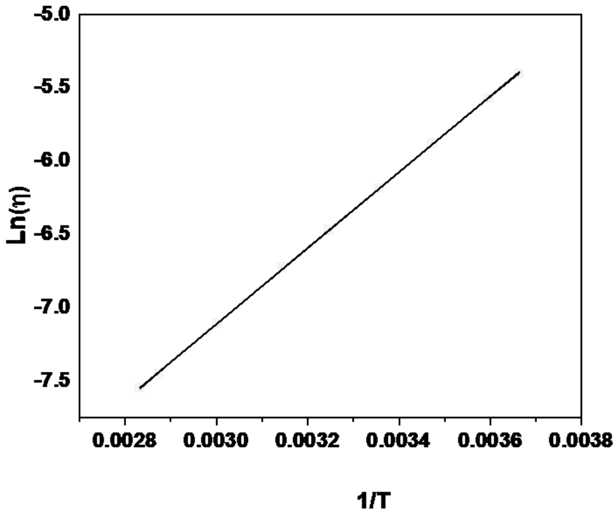

Figure:2, Viscosity-Temperature plot for IPA

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Determination of gel time (t_{gel})

In all cases, the gel time (t_{gel}) was obtained from the cross section point of the two tangents drawn to the two sides of the inflection point in the FT- aging time graph. If the data *per se* do not conform to a pattern as shown in Figure 3,then t_{gel} is obtained after fitting the data to a polynomial equation to get a plot as seen in the same Figure and then drawing two tangents on either side of inflection point. The cross point is the gel point corresponding to the gel time. Typical-plot is shown in Figure 3

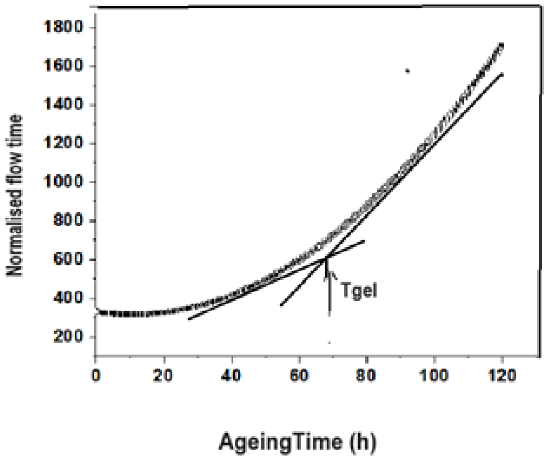

Figure 3 Determination of gel time with data from viscosity (FT)- time profile

Figure 4 shows the normalised viscosity-aging time profile for a solution of PF resin in two different solvents, EA and MEK at 60°C. In MEK, the viscosity shoots up sharply at around the 70th hour, while the one in ethyl alcohol undergoes only a moderate flow-time build-up during this period and that the increases in viscosity after 350 h is only about 250 %. Gelation was not observed even up to 350 hrs at 60°C as the flow-time profile manifests.

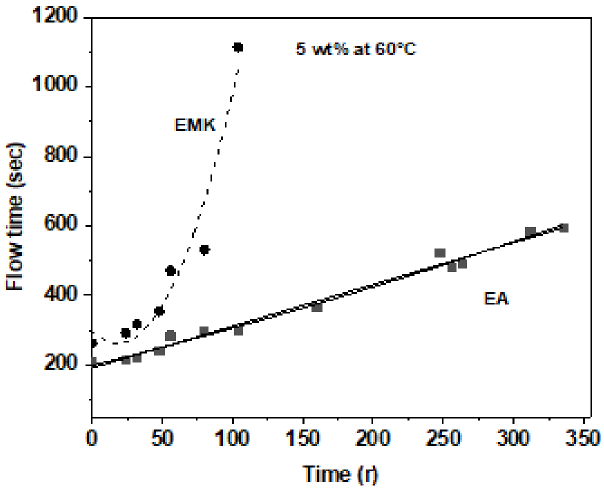

Figure 4 . Normalised flow time-Ageing time plot for 5% solution of the resin in different solvents at 60^{o}C

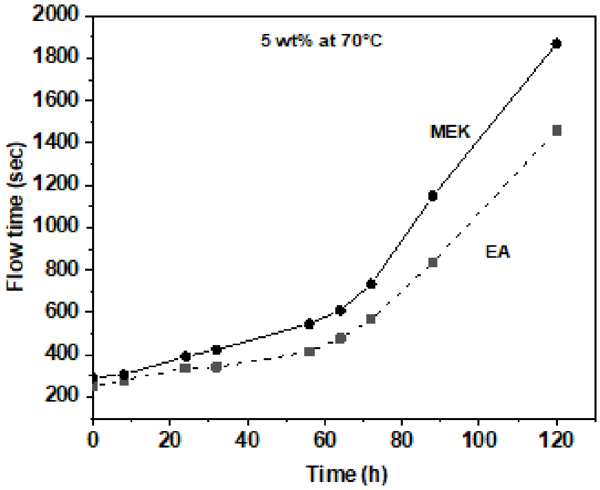

Figure5. Flow time for 5 % solution of PF in Ethanol (EA) and methyl ethyl ketone (MEK) at 70°C

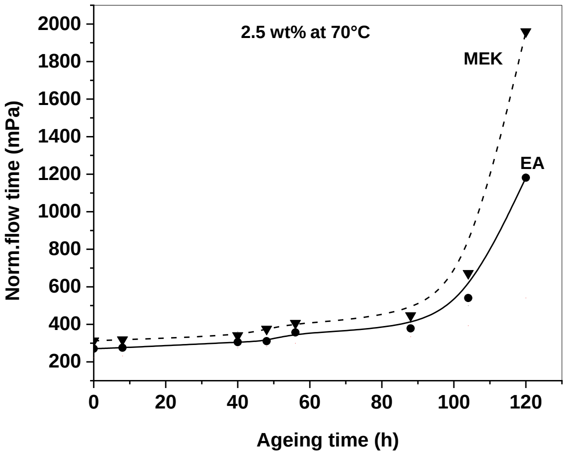

Figure 6. Flow time for 2.5 % solution of PF in Ethanol (EA) and methyl ethyl ketone (MEK) at 70°C

As can be seen from Figure 5, when the temperature is increased to 70°C, the two profiles are identical as far as the x-axis is concerned and grow parallelly. However, the viscosity and its build-upis more for the MEK solution. The trend in gelation is unlike the one at 60°C. Gelation occurs at around 110 h for MEK and at 100 h for the solution in EA. The FT gap between alcoholic solvent and the aprotic MEK solution goes on increasing as the temperature increases.

When the solution is further diluted to 2.5 %, and temperature reduced to 60, the overall profile has the same look but with a shift in the time scale towards right along the X-axis (Figure 6). In all these cases, the resin was more stable in Ethanol than in MEK. The aging data collected from these plots are compiled in Table 2

Table 2 Concentration dependency of gel time for EA- and MEK-solutions

Sl No	Concentration of polymer solution (weight/vol%)	Temperature (°C)	t_{gel}(h)	
			EA	MEK
1	7.5	70	80	60
2	5	70	110	100
3	2.5	60	>170	112

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Comparison of different alcohols

If the alcohols' mechanism of stabilisation is as proposed above, then the nature of the various alcohols should make a difference in viscosity build-up profile. For this, typical primary, secondary and tertiary alcohols were examined at varied concentration of 2.5% (Figure7) and 5% resin(Figure 8) both at 70°C.

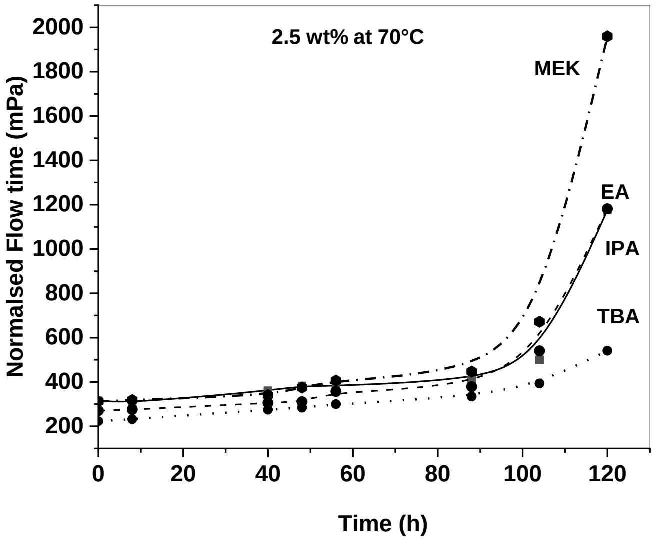


Figure7: Time-viscosity profiles of a 2.5% solutions of PF resin in four different solvents at 70°C

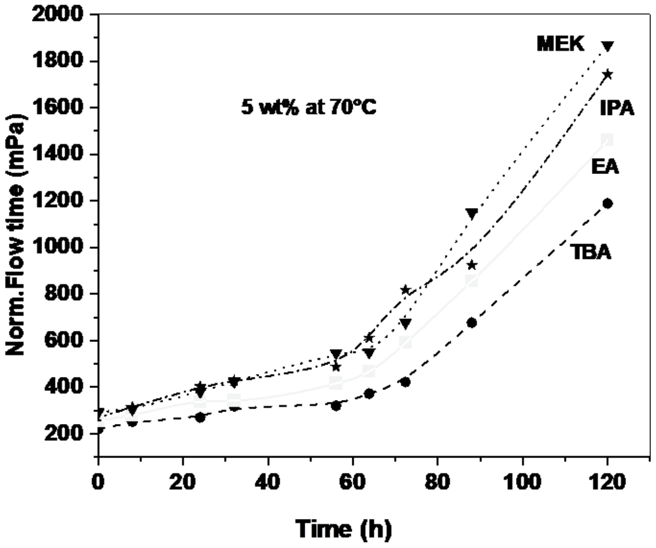


Figure8: Time-viscosity profiles of a 5% solutions of PF resin in four different solvents at 70°C

Figure 7 demonstrates the time-viscosity profiles of a 2.5% solutions of PF resin in four different solvents among which three are. constituted by a primary (EA), secondary (IPA) and a tertiary (TBA) alcohol. The fourth one is the reference solvent MEK. When they make up a 2.5% solution, their normalised viscosities at a given time increased in the order TBA<EA<IPA<MEK. Interestingly, the apparent gel time **followed a reverse** trend. TBA out-bet all other solvents inclusive of EA in stabilising the resin. Surprisingly the normalised FT was the lowest for this solvent, and the rate of viscosity build-up was also the slowest in this case. Propanol and ethanol have near overlapping profiles. The solution with 5% resin at 70 °C also presented a similar pattern (Figure 8) like the 2.5% solution except that the gel time was advanced by 20-30 hours. The other graphs with higher concentration of solutions also showed similar trend. The data corresponding to other temperatures and concentrations are compiled in Table 3.

The gel times are compiled in Table 3. When the concentration was on the lower side (2.5%), the gel point was difficult to be identified. At this concentration, on raising the temperature to 70 ^{o}C, though the overall profile remained the same, the time for gelation decreased by 50 to 60 h. Increasing the concentration to 5% at 60^{o}C had the same effect as increasing the temperature to 70^{o}C at 2.5% concentration. At this concentration, the overall pattern remained the same while the gel time got advanced by about 50-60 h. At 5% concentration (Figure 8) when the temperature was enhanced to 70^{o}C, the overall trend is the same as in Figure 7 in the sense, the solution viscosity (normalised) increased in the order TBA<EA<IPA<MEK at a given time. The gel time also increased in the same order (Refer Table 3). As temperature and concentration increased, gel time dropped significantly.

Table 3. Gel time for different alcoholic solutions and temperatures for a 2.5 % solution at 60°C and 70°C

Sl no	Solvent	t_{gel} (h)		Remarks
		60°C	70°C	
1	TBA	>175	>120	No gelation till this time
2	**EA**	**170**	**108**	
3	**IPA**	**165**	**105**	
4	**MEK**	**155**	**100**	

In print,F scheme
data missed in the table

It is shown beyond doubt that tertiary butyl alcohol is the best stabiliser for PF resin among the diverse alcohols, as this molecule presents least steric hindrance while its OH group acquires maximum nucleophilicity to intervene in the rate-determining step of the aging reaction. This happens thanks to the +I inductive effect of the three methyl groups that push the electrons towards the OH group.(see Figure 9). In ethanol and isopropanol, this effect is limited to two methyl groups or one ethyl group. Ethanol has slight advantage over isopropanol. MEK, though possesses a pair of nonbonding electron on its oxygen, is not capable of offering any advantage despite possessing an ethyl and a methyl group on either sides of the ketonic group (see Figure 10)

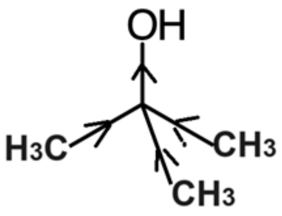


Figure 9: +I inductive operative in TBA

Generally, the reactivity of alcohols in esterification reaction follows the order: methyl alcohol > tertiary butyl alcohol > ethyl alcohol>isopropyl alcohol. This means it is not only the nucleophilicity of the alcohol, but their steric hindrance factor has also a big say in this (Figure 10). Methanol with least nucleophilicity and least steric hindrance however tops the list, followed by 3^obutanol, ethanol and isopropanol being the least reactive ones. This means that a trade-off between nucleophilicity and steric factor decidse their reactivity in this kind of reactions.

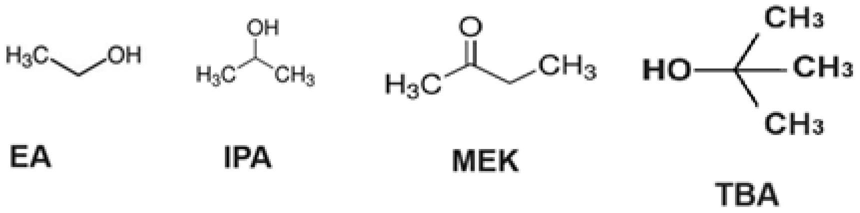


Figure: 10: Structures of alcohols

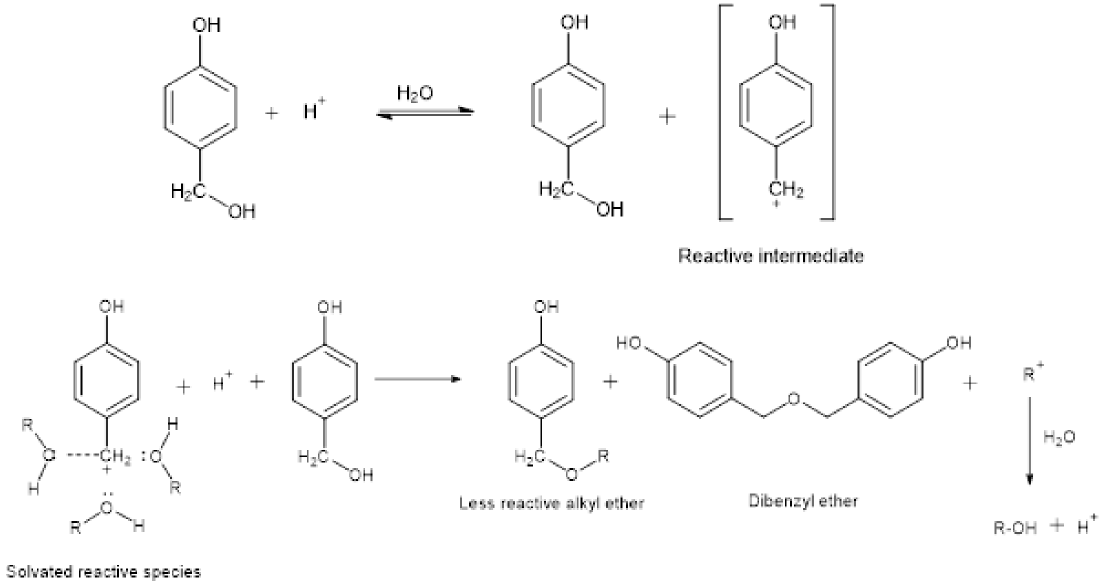
Tertiary and the high electron density on the Oxygen atom renders it the best butanol has very high nucleophilicity thanks to the three CH_3 groups that push the electron density towards the central carbon and from there to the oxygen (Figure 9). The electron density is pumped through +I inductive effect of the three methyl groups that are projecting on the opposite side of the OH group does not pose much steric hindrance in these reactions felt nucleophilic oxygen.(Figure 10)

The solvent like MEK is also capable of diminishing the reactivity of resole as it contains an oxygen atom with two pairs of non-bonding electrons capable of interaction with the benzyl cation as described above. However, it can't transfer the proton in the intermediate step unlike the alcohols. So it can vbe concluded that the capability of the alcohol in stabilisation of PF resins depend upon the nucleophilicity of the oxygen, steric hindrance and the ease with which it can transfer the proton in the intermediate stage.

It is however not capable of proton transfer unlike the alcohols. Their efficiency, therefore, is lower than that of any alcohol investigated here. Since TBA has a noxious ordure and that it is least volatile which make it inacceptable. Methanol is highly volatile and not so nucleophilic like IPA or EA,. Hence, the choice falls on the next acceptable alcohol, i e ethanol. It has further advantages like moderate volatility, comparatively less toxicity, easy availability and bettere nucleophilicity (next to TBA). Hence, the choice falls on this alcohol as the next most suitable one Thus, the choice of ethyl alcohol for stabilising the resole resin is scientifically justified.

Conclusions

Normalised flow-time studies of resoles in various solvents reveal that solvents do have a role in reducing the viscosities and viscosity build-up of the solutions over a period of time. Protic solvents like alcohols diminish the rate of aging by intervening in the crosslinking reaction. It is concluded that the alcoholic OH groups stabilises the partially formed benzyl carbo cation intermediate by way of coordination of the non-bonding electrons of the oxygen with it. This quenches the electrophilicity of these species and reduces their propensity to react with the other phenyl methylol molecules (Scheme 7).



Scheme7. Mechanism of quenching the reactivity of resole by alcohols

This was in the midst of conclusion

The release of protons from alcohol can lead to formation of benzyl alkyl ether which is less reactive than the corresponding methylols. The efficiency of alcohol in diminishing the reactivity of resoles is in the order: Tertiary >primary > secondary.. Steric factors that intervene with the electron coordination with the partially formed benzyl cation.

Coordination ~~and~~ can also play havoc with the stabilisation effect of the alcohol. Though Methanol may appear as the alcohol of choice for this purpose, its toxicity, volatility and not so high nucleophilicity are disfavouring factors. There are contradictory reports that it accelerates the aging. Thus, one narrows down to ethyl alcohol as the solvent of choice for diluting and stabilizing resole resin. Its reduced toxicity, easy availability and high volatility are added advantages.

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