Experimental investigation on characteristics of resole based phenolic resin

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Abstract: In this study, characteristics of two different resole based phenolic resin being used in aerospace application were investigated. Phenolic resins were advanced by conditioning to bring down its point of trouble. At this stage both resins were separately impregnated with PAN based carbon fabric as reinforcement and evaluated their rheology properties. Residues of free phenol, free formaldehyde and sodium content in resins were estimated for both the resins and compared. Also other properties such as neat resin cure characteristics, resin characteristic frequencies, molecular weight distributions, char yield of resins were evaluated and compared. A conclusion is drawn from the test results that char yield is affected by purity of phenolic resin viz presence of unreacted free phenol and free formaldehyde. Also viscosity plays a vital role in wetting of the reinforcement resulting in better interlaminar shear properties.

KEY WORDS: Resole based phenolic resin, Point of trouble, Char yield, Viscosity

1. INTRODUCTION

Base catalysed phenol-formaldehyde resins are made with formaldehyde to phenol ratio of greater than one (usually around 1.5). These resins are called resoles. Phenol, formaldehyde and a base catalyst (NaoH) are mixed in the desired amount, depending on the resin to be formed and are then heated. This can be mixed in different proportion to produce different resin formulations. Resole phenol-formaldehyde resin is a water soluble methylol (\(-\text{CH}_2\text{OH}\)) bearing thermoplastic. The curing process to the final thermoset material can be initiated by just heating the resole. Therefore, they usually contain unreactive hydroxymethyl groups and the action of heat is sufficient to cross-link a resole. When heated, resoles form larger molecules with methylene cross-links without the use or addition of a curing agent. The phenol-formaldehyde resin resinification reaction is a typical polycondensation reaction since water is given off as a by-product [1-2]. Resole phenolic resins are being used for making prepregs for aerospace application. Curing of the resin is carried out in three phases. The first step is referred as the A-stage or resoles stage; the second is the B-stage or resitol stage; and the third is the C-stage or resite stage. During the first stage, the resin becomes fusible and soluble. Heat must be generally be supplied to initiate the second step, in which the resin is transformed into a fusible solid having low solubility. Further heat drives the curing operation to the third stage in which the resin hardens and becomes insoluble and infusible [3]. Disadvantages of these resins include high curing pressures, longer curing times and short shelf life. The short shelf life is due to active methylol groups in acidic condition evolves water. However, the limited storage stability of resoles at ambient temperature must be taken into consideration. The shelf life of resole phenolic resin can be enhanced by storing them in sub-zero temperatures [4-5]. The viscosity of resoles is time dependent, and the viscosity may increase of an order of magnitude even at room temperature over a period of time. The resoles are therefore, stored at sub ambient temperature where the reaction is
relatively slow. The magnitude of changes in reaction depends on the storage temperature and other important variables [6-8]. The changes in viscosity associated with molecular weight distribution and also on point of trouble of resin. If the point of trouble reaches below 6ml, the increase in viscosity might even prohibit the use of resins for applications such as prepregging and filament winding. The Phenolic resins are known for their excellent thermal properties and chemical stability. In the field of advanced composite materials, phenolic based composites are known for their excellent flame resistance and are excessively used in the aerospace application because of their ablative characteristics [9-10]. The low viscosity and good wetting characteristics of resoles make them the choice materials for the fabrication of composite products for aerospace application.

In this paper, two different sources of solvent based resole phenolic resins being used in aerospace application were investigated for their neat resin physical, chemical and thermal properties with the aim that whether any resin characteristics affect the end applications.

2. MATERIALS AND METHODS

Commercially available resole phenolic resins PR-1 and PR-2 from two different sources are employed for the present investigation and their processing method is not revealed by the manufacturer. PAN based carbon fabric is used as reinforcement for making prepreg.

2.1. Materials
The average main properties of the resin from three batches are summarized below in Table 1.

| Parameter                        | PR-I            | PR-II           |
|----------------------------------|-----------------|-----------------|
| Appearance                       | Honey red in colour | Dark tan colour |
| Specific Gravity at 30°C         | 1.15            | 1.14            |
| Point of trouble, ml             | 10.5            | 10.8            |
| (at Specific Gravity: 0.860)     |                 |                 |
| Viscosity at 30°C, cP            | 162.3-163.5     | 130.2-131.7     |
| Volatile Content (% by wt.)      | 37.67           | 39.10           |
| Solid resin Content (% by wt.)   | 61.55           | 59.12           |
| Free Phenol, %                   | 4.38            | 5.90            |
| Free Formaldehyde, %             | 1.12            | 2.76            |

2.2. Testing Methods

2.2.1. Point of trouble.
This method describes the determination of point of trouble of phenolic resin at a definite specific gravity of the resin. It is a measure of the advancement of the polymerization of phenolic resin. The given phenolic resin is diluted with 99.98% purity ethyl alcohol to obtain the specific gravity of 0.860. The specific gravity of phenolic resin is adjusted to 0.860 by using Archimedes method. 10 ml of diluted phenolic resin is taken in a beaker and titrated against distilled water up to the turbidity point. The volume of distilled water consumed is point of trouble.

2.2.2. Viscosity.
Viscosity of the resin shall be measured by Brookfield Viscometer as per ASTM D2393

2.2.3 Volatile content.
Take 1-2 gm. of a resin sample from a well-mixed lot in a silica crucible weighed to an accuracy of 0.1 milligrams. The resin sample shall be heated at 160°C for 20 minutes in an oven. Crucible is then cooled to room temperature and weighed.
% Volatile Content = \frac{W_2 - W_3}{W_2 - W_1} \times 100

where,
\begin{align*}
W_1 (gm) & : \text{Net weight of the empty crucible} \\
W_2 (gm) & : \text{Weight of crucible + resin sample} \\
W_3 (gm) & : \text{Weight of crucible (with resin) after heating for 20 minutes at 160°C}
\end{align*}

2.2.4. Solid resin content.
The residue obtained in the volatile content test shall be heated again at 170°C for one hour to obtain the solid resin content.

% Solid Content = \frac{W_4 - W_1}{W_2 - W_1} \times 100

where,
\begin{align*}
W_4 (gm) & : \text{Weight of crucible (with solid matter) after heating for 1 hour at 170°C}
\end{align*}

2.2.5. Free phenol content.
The percentage of free phenol was evaluated according to bromometry method. Accurately weighed about 20g of resin sample in 1000mL round-bottomed flask. To that 100mL distilled water was added and the pH value of the solution was adjusted to 4 by 20% hydrochloric acid solution. Then steam distilled until the negative test for phenol with bromine water. The distillate was diluted to1000mL with double distilled water. A liquid of 50mL, was taken in Erlenmeyer flask and 25mL of 0.1N bromate-bromide solution and 5mL concentrated HCl was added. The flask was then closed and kept in dark for 15min. After that 18g potassium iodide was added and kept in dark for another 10min. Finally, the mixed solution was titrated with 0.1N sodium thiosulphate solution using starch as indicator. The free phenol was calculated by the following formula

% Free Phenol Content(by weight) = \frac{(V_1 - V_2) \times C \times 0.01568 \times 1000}{m \times 50}

where,
\begin{align*}
V_1 & : \text{Volume of 0.1N sodium thiosulphate solution required for blank} \\
V_2 & : \text{Volume of 0.1N sodium thiosulphate solution required for sample} \\
m & : \text{Weight of sample in gm} \\
C & : \text{Exact normality of sodium thiosulphate solution}
\end{align*}

2.2.6 Free formaldehyde content.
The free formaldehyde content of the resins was determined by the hydroxylaminehydrochloride method. Accurately weighed about 30 or 50g of resin sample was transferred into 250mL beaker and dissolved in 50mL methyl alcohol or 50ml 75% isopropyl alcohol. Simultaneously, the pH value of the solution was adjusted to 3.5 by adding 1N hydrochloric acid solution. 25mL of 10% hydroxylamine hydrochloride solution was added and stirred for 10min. Finally, the mixture solution was titrated with 0.1N or 1N sodium hydroxide solution. Free formaldehyde content was calculated by using following formula.

% Free Formaldehyde Content = \frac{(V_1 - V_0) \times 3 \times C}{m}

where,
\begin{align*}
V_1 & : \text{Volume of sodium hydroxide solution required for sample} \\
V_0 & : \text{Volume of sodium hydroxide solution required for blank} \\
m & : \text{Weight of sample in gm} \\
C & : \text{Exact normality of sodium hydroxide solution}
\end{align*}
2.3. Conditioning of phenolic resin
Conditioning of phenolic resin carried out in an oven at 50°C and estimated their physical properties. Conditioning of Phenolic resin is required before prepregging in order to achieve the optimum tackiness on the prepreg. Phenolic resin shall be conditioned by keeping the resin drums in an oven heated at 50±2°C till the point of trouble reaches level of around 6.5 ml which is the standard practice being followed. During conditioning, once in 4 hours the resin drums are to be taken out and rolled/shaken so that the resin homogeneity is maintained. Before commencement of conditioning of the day, sample would be drawn from the resin container and check for the point of trouble. The conditioning should continue till the point of trouble reaches around 6.5 ml. The viscosity of resin is inversely proportional to its point of trouble. Point of trouble is a easily measurable one whereas viscosity is a time and temperature dependent property and that is the reason point of trouble is generally used to know the condition of the resin before usage. In this study also, point of trouble of resins are measured and brought down to same level for better comparison and understanding. The properties of resin after conditioning is given below in Table 2.

Table 2 Properties of resin after conditioning

| Parameter                        | PR-I         | PR-II        |
|----------------------------------|--------------|--------------|
| Point of trouble, ml             | 6.6          | 6.6          |
| Viscosity at 30°C, cP            | 302.9 to 303.4 | 244.1 to 245.6 |
| Volatile content (% by wt.)      | 37.02        | 37.63        |
| Solid resin content(% by wt)     | 61.78        | 60.44        |
| Specific gravity                 | 1.15         | 1.13         |

3. VARIOUS STUDIES AND RESULTS:

3.1. FTIR Spectra:
FTIR run for both liquid neat resins using Bruker spectrophotometer. IR spectra show identical characteristic functional groups for both resins and are shown in figure 1 and figure 2.

![Figure 1 FTIR-Spectra of PR-I](image1)
![Figure 2 FTIR-Spectra of PR-II](image2)

Table 3 FTIR Spectra results of PR-I and PR-II

| Parameter                        | PR-I         | PR-II        |
|----------------------------------|--------------|--------------|
| –OH functional group             | 3343.47 cm\(^{-1}\) | 3334.21 cm\(^{-1}\) |
| Inphase stretching vibration of –CH2 | 2975.6 cm\(^{-1}\) | 2975.32 cm\(^{-1}\) |
| Out of phase stretching vibration of –CH2 | 2892.65 cm\(^{-1}\) | 2966.33 cm\(^{-1}\) |
| -C=C-aromatic ring               | 1610.86 cm\(^{-1}\) | 1597.17 cm\(^{-1}\) |
| -CH aliphatic                    | 1511.59 cm\(^{-1}\) | 1597.61 cm\(^{-1}\) |
| -CH aliphatic                    | 1479.74 cm\(^{-1}\) | 1479.97 cm\(^{-1}\) |
| -OH in plane                     | 1371.93 cm\(^{-1}\) | 1373.91 cm\(^{-1}\) |
Assymetric stretch of phenolic \(-C-C-OH\) 1236.00 cm\(^{-1}\) 1235.55 cm\(^{-1}\) 
\(-C-O\) assymetric stretching 1152.17 cm\(^{-1}\) 1151.34 cm\(^{-1}\) 
Single bond C-O stretching 1042.57 cm\(^{-1}\) 1043.10 cm\(^{-1}\) 
\(-CH\) out of plane 879.78 cm\(^{-1}\) 879.11 cm\(^{-1}\) 
\(-CH\) out of plane para substituted 827.08 cm\(^{-1}\) 825.97 cm\(^{-1}\) 
\(-CH\) out of plane ortho substituted 756.54 cm\(^{-1}\) 757.03 cm\(^{-1}\) 
Adjacent 5H 692.48 cm\(^{-1}\) 692.50 cm\(^{-1}\)

The results of the characterization of phenolic resin by FTIR is shown above in Table 3. IR spectra show identical characteristic functional groups and frequencies for both resins. The identified characteristic frequencies are in tally with the resole phenolic resin frequencies as shown in literature [11].

3.2. DSC Analysis:
DSC tests are performed on Perkin Elmer Modulated DSC instrument. Dynamic heating experiments are conducted under 20ml/min nitrogen flow. Each resin sample around 10 mg is placed in an aluminum pan and placed opposite to the empty reference pan in the DSC chamber. The DSC is set up for temperature range of 25° to 300° with heating rate of 10°/min. DSC curves are shown in figure 3 and figure 4.

![Figure 3 DSC Spectra of PR-I](image)

![Figure 4 DSC Spectra of PR-II](image)

DSC curves show that at around 80°C sovent evaporation takes place by endothermic reaction. After 100°C gelation starts with condensation polymerisation reaction with an exothermic reaction having \(T_{peak}\) around 175°C followed by steep endothermic reaction peak around 180-190°C. In both cases, the steep endothermic peak is considered to have been caused by evaporation of condensation by-products after completion of cross linking.

3.3. Rheological Analysis:
The rheological analysis was carried out by Rheometer dynamic run as shown in figure 5 and figure 6 with a heating rate of 1°C/min aiming to know the gelation time (gel time) of both resins seperately on PAN carbon fabric-phenolic prepreg, using the fact that at this gel time, the storage moduli\((G')\) is equal to loss moduli \((G'')\). The gel time for PR-I at 119°C is 88.95 minutes and gel time for PR-II at 121°C is 91.39 minutes.
Resin flow test was carried out according to a procedure developed by Putnam et al.[12]. To study the flow, five square shaped samples of 5 X 5 cm dimension were cut from PAN carbon-phenolic prepreg, and they were stacked on each other and placed between the two release films. The sandwich was heated to 160°C under a load of 25kg weight for 30 minutes. Then the sandwich assembly was allowed to cool down and the overflown resin was wiped out from the edges of the specimen before being reweighed. The change in weight as a percentage of the original was expressed as the resin flow and given in Table 4.

| Table 4 Resin flow in carbon prepreg |
|-------------------------------------|
| Resin flow, % | PR-I | PR-II |
|----------------|------|-------|
| Un-conditioned prepreg | 11.2 | 10.7 |
| Conditioned prepreg | 4.8  | 5.2  |

In the conditioned prepreg partial advancement of resin took place with lower volatile content in the prepreg with improved tackiness. This is the ideal condition for fabrication of composite products.

3.4. Char yield by TGA:

| Table 5 Weight loss of both resins |
|-----------------------------------|
| Temperature | Weight (%) |
| Sample PR-I at 700°C | 61.98 |
| Sample PR-II at 700°C | 59.66 |
| Sample PR-I at 1000°C | 36.16 |
| Sample PR-II at 1000°C | 33.02 |

Cured neat resin TGA tests are performed on TA Instrument. The results of the weight loss of the resin, obtained at a constant heating rate of 10 °C/min in an inert atmosphere, are presented in figure 7. From the TG curve, four temperature ranges of weight loss of the resin can be noticed. In the first range 0–200 °C, the weight loss was 2%, in the second range 200–400 °C the weight loss was 7%, in the third range 400–700°C there was a sharp decline of the curve, i.e., the weight loss of the resin was higher, approximately 33%, and in the fourth range 700–1000 °C, the weight loss of the resin was approximately 25% for the both resins. Both resins have almost all same char yield, however, at higher temperatures there is a variation in test results and are given in Table 5. It is evident that char yield is influenced by the purity of phenolic resin. The left out free phenol and free formaldehyde in the resin which are unreacted molecules, in free state do not participate in the reaction and influences the char yield formation at higher temperatures and hence the variation.
3.5. Mass spectra:

The molecular weight distributions of resins PR-I and PR-II are compared in figure 8 and figure 9. Molecular weight distributions in the resin depend upon manufacturer’s process conditions and also on point of trouble of resin. During conditioning the resin undergoes partial cross linking of pre-polymers randomly resulting in higher molecular weight polymeric groups. Both resins consist fewer low molecular weight species and higher molecular weight species. The free phenol, having no methylol groups, would be less likely than low molecular weight methylol groups to take place in any condensation reactions during the conditioning of phenolic resins. The molecular weight distribution for PR-I is 1344-3334 with an average molecular weight of 2140 for PR-II 1378-3528 with an average molecular weight of 2041.

3.6. Sodium content by Flame photometer:
Traces in phenolic resin can be determined by emission spectra using Flame photometer. For this, solid resin content of the resin taken in a platinum crucible and heated at 1100°C in a muffle furnace for 1 hour. Cool the crucible and add 10 ml. of dil. Hydrochloric acid (1:3) to the crucible containing Na in traces and warm. Transfer the contents quantitatively to a 100ml. standard flask. Wash the crucible thoroughly and transfer the washing to the flask. Make up to volume with distilled water. Switch on the flame photometer and set the instrument and allow it to stabilize. Aspirate distilled water and adjust the reading to zero. Aspirate the calibration standards of 1, 2, 3, 5 and 10 ppm of sodium solutions and take the emission readings. Plot the emission intensity readings of the calibration solution against concentration of sodium in ppm to obtain calibration graph.
\[ \text{Sodium in the Sample in ppm} = 100 \times \frac{A}{W} \]

where,
A: Concentration of Sodium in ppm in the test sample
W: Weight of the solid resin in gm

| Parameter | PR-I | PR-II |
|-----------|------|-------|
| Sodium content, ppm | 700  | 1400  |
|             | 1100 | 900   |
|             | 800  | 750   |

It is observed from the test results given in Table 6 that the sodium content is varying from batch to batch of resins. This is due to improper washing of resin after the reaction to remove the catalyst. In general, sodium content should be as low as possible for better ablative performance and batch with lowest and closest sodium content from PRI and PRII is chosen for this study.

3.7. Interlaminar shear strength:
Interlaminar shear strength (ILSS) was evaluated as per ASTM D 2344 after conditioning both the resins PR-I and PR-II for the point of trouble range of 6-7 ml in steps of 0.1ml with PAN based carbon fabric as reinforcement. It is observed that the ILSS values evaluated with resins having point of trouble of 6.4-6.6 ml are found to be higher and the average values of ten samples are given in Table 7.

| Property | PR-I | PR-II |
|----------|------|-------|
| ILSS (MPa) | 22.12 | 27.45 |

4. CONCLUSION

The viscosity of resoles is time dependent and also is inversely proportional to its point of trouble. During conditioning, resins undergo partial condensation with an increase in viscosity which is in agreement with the test results. The change in viscosity is associated with molecular weight distribution. Uniform molecular weight distribution with optimum viscosity provides better penetration and wetting of reinforcement resulting in better interlaminar shear properties which was clearly evident from the results. From the thermal study, it is evident that both resins undergoing complete cross linking between 160-200°C and have excellent thermal stability. The TGA patterns for two sources of resins are nearly the same up to 700°C with four stages of weight loss and slight variation at 1000°C due to unreacted substances evident from results. Based on the test results, it is concluded that optimum viscosity and unreacted substances present in phenolic resin play a vital role in thermal performance of composite.

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