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Synthesis and Modification of Low-Formaldehyde Resol Resin using Sodium Sulphite and Hydroxylammine Hydrochloride

V.C. Resmi, S.K. Narayanankutty*

Department of Polymer Science & RubberTechnology, Cochin University of Science & Technology, Kochi, Kerala, India.

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ABSTRACT
Phenolic (PF) resol resins contains unreacted free formaldehyde which continues to be released from the products after manufacturing process is completed. Formaldehyde is incredibly volatile, has an unpleasant odour which irritates the eyes and nasal passages and may cause other health problems. Hence an efficient method is necessary to decrease the amount of free formaldehyde in PF resol resin. In this study we have investigated the synthesis of resol resin using sodium sulphite (SS) and hydroxylammine hydrochloride (HH) as formaldehyde scavengers. These scavengers form reversible adducts with formaldehyde. The effect of these scavengers on the free formaldehyde content (FFC) of the new modified resol resin was analyzed by Walkers titration method. With the incorporation of sodium sulphite and hydroxylammine hydrochloride, the free formaldehyde content was reduced to zero. The scanning electron micrographs of tensile fractured surfaces were used to investigate the morphological changes on scavenger addition. The physical, mechanical and thermal properties of the PF resins were improved on modification with these scavengers.

Keywords: *PF resol resin, free formaldehyde content, Scavenger, Scanning Electron Microscopy*

1. INTRODUCTION

Phenolic resins (PF) are one of the most widely used thermosetting polymers. They are polycondensation products of phenol and formaldehyde. These are widely used because of their thermal stability, water resistance, binding strength, chemical resistance, electrical insulation and dimensional stability. These have attracted special interest because of their large range of industrial applications in adhesives, casting, molding and in structural parts. PF resins are synthesized by reacting phenol with formaldehyde in the presence of an acid or alkali. Depending on the ratio of phenol to formaldehyde and the type of catalyst used, these are classified as resols and novolacs. Novolacs are prepared with a formaldehyde to phenol (F/P) molar ratio <1.0 in the presence of an acid catalyst whereas resols usually have F/P molar ratio >1.0 and employ an alkali catalyst. Of these two types, resoles are reactive type resins. These can be cross-linked by application of heat, without any catalyst [1-5].

*Corresponding Author:
Email: e-mail: sncusat@gmail.com
Phone: +91 9995300093

polynuclear hydroxymethylphenols which are stable at room temperatures, but are transformed into three dimensional, crosslinked, insoluble and infusible polymers by the application of heat. The unreacted, excess formaldehyde continues to be released from the products after of heat. The unreacted, excess formaldehyde continues to be released from the products after manufacturing process is completed. Formaldehyde is very volatile, has an unpleasant odour which irritates the eyes and nasal passages and may give rise to other health problems. Large portion of the work on these aspects are protected under patents work on these aspects are protected under patents [6-8].

The aim of the present study is to develop a low free formaldehyde PF resol resin using formaldehyde scavengers Sodium sulphite and hydroxylammine hydrochloride. Sodium sulphite at 0.1-2% concentrations and hydroxylammine hydrochloride at 0.5-2 weight % are incorporated as a formaldehyde scavenger for PF resin. The free formaldehyde content (FFC) of the new modified resol resins was analyzed by titration method. The mechanical, thermal and morphological studies of the neat and modified resin are reported.

2. EXPERIMENTAL

2.1. Materials

Phenol (MW, 94.11, M.P=39-41^{0}C), formaldehyde (37% solution in water), Sodiumsulphite, Hydroxylammine hydrochlorie and glacial acetic acid were laboratory reagent (LR) grade, Kochi, Kerala.

2.2. Synthesis of PF resol resin

Resol prepolymer resin was synthesized with F/P molar ratio1:1.8 in presence of NaOH catalyst in a 1000 ml RB flask fitted with a reflux condenser, a mechanical stirrer, a digital thermometer. Condensation of phenol and formaldehyde was conducted at 90 °C. Reaction vessel was heated to the same reaction temperature. Resin was prepared by reacting the required amounts of phenol (~99%) with formaldehyde (37% solution in water,) in the presence of the catalyst. The resulting reaction mixture was stirred and heated to 90–95 °C until the mixture became cloudy. Afterwards, the free formaldehyde content of PF resin was analyzed. Then scavengers (SS and HH)) at different weight percentages were added and stirred for 1 hour at room temperature and free formaldehyde was determined.

2.3. Free formaldehyde content analysis

The percentages of the free formaldehyde in the resin were determined using a modified version of Walker's hydroxylamine hydrochloride method using methanol, HCl, hydroxylamine hydrochloride and NaOH.

2.4. Tensile properties

The tensile properties were determined using dumb-bell shaped specimens on a Schimadzu Autograph Universal Testing Machine (ASTM D 638) at a cross head speed of 50 mm/min.

2.5 Scanning electron microscopic analysis (SEM).

Studies on morphology of the tensile fractured surfaces of pure PF and scavenger modified PF were carried out using a JEOL Model JSM 6390 L scanning electron microscope(SEM).

2.6. Thermogravimetric analysis (TGA)

Approximately 5mg of each of the cured samples were subjected to TGA in a nitrogen atmosphere at a heating rate of 20°c/min from room temperature to 800^{0}C with a thermogravimetric analyzer TGA Q-50 thermal analyser (TA Instruments)

3. RESULTS AND DISCUSSION

3.1. Free formaldehyde content analysis

Figure 1 shows the variation of FFC in increasing scavenger loading. It is seen that both the scavengers are excellent in reducing the FFC of the PF resin. In the case of SS the decrease is very sharp and shows a 99% reduction at 0.3% loading. At still higher loadings there is no further reduction in FFC. The reduction in FFC for SS is due to the formation of reversible adducts as given below.

Na_2SO_3+CH_2O↔ $OHCH_2NaSO_3$+NaOH

This reaction reduces the free formaldehyde left behind in the resol resin, reducing the emission of formaldehyde. As the adduct formed is reversible the formaldehyde can be made available during the curing reaction. HH is also very efficient in reducing the free formaldehyde of PF resin. With the addition of 1.5% of HH, 98% reduction in FFC is observed. The reduction in FFC for HH is due to the formation of formaldoxime derivatives.

HCHO+NH_2OH.HCl→CH_2=NOH+HCl+H_2O

Oximes regenerate formaldehyde when treated with dil HCl.

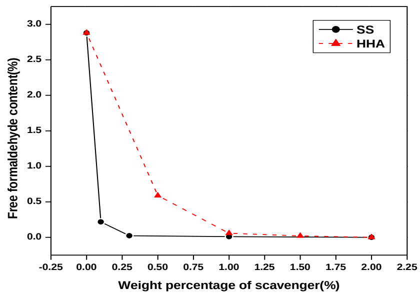

Figure1. Variation in percentage of free formaldehyde content with weight percentage of scavengers.

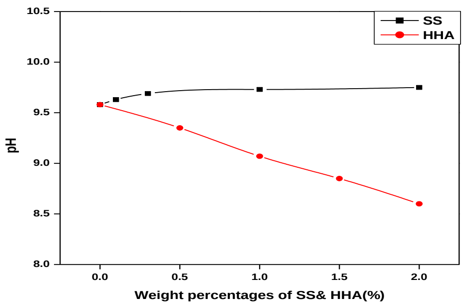

Figure 2. The variation of the pH with weight percentages of SS&HH

3.2. pH.

Figure 2 shows the variation of pH of the scavenger modified resins. The pH remains almost same in the case of sulphite modified samples. But in the case of HH modified samples shows decrease in pH. The general lowering of pH in HH containing resols is due formation of formaldoxime derivatives.

3.3. Tensile properties.

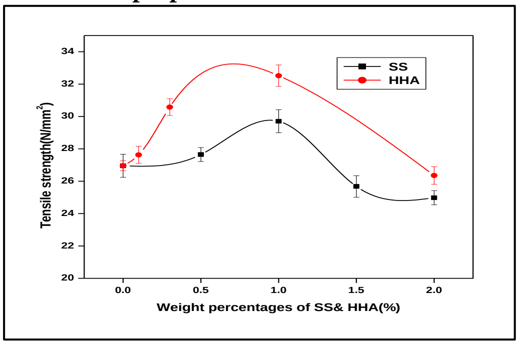

Figure 3. The variation of the tensile strength with weight percentages of SS&HH.

The effect of SS& HH on the tensile strength of the resol resin is shown in the fig. 3. In the presence of both sodium sulphite and hydroxylamine hydrochloride, the tensile strength increases. About 31% improvement in tensile strength is shown by SS modified resins and about 28% improvement is shown in the case of HH modified resins. The improvement in tensile strength may be attributed to the decrease in the void content. It is again confirmed from the SEM fractured surfaces. Further addition of these scavengers causes a reduction in tensile strength.

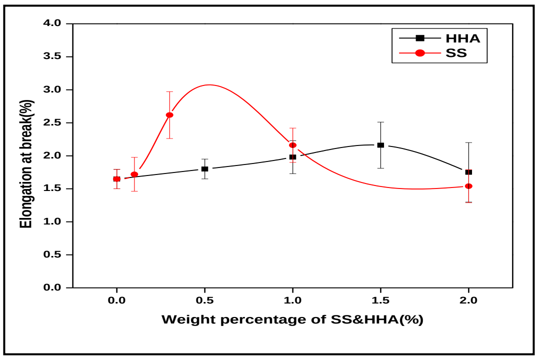

Figure 4. The variation of elongation at break with weight percentages SS&HH.

The effect of SS & HH addition on the elongation at break is shown in the fig. 4. The addition of 0.3% SS produces the greatest increase in elongation up to 59%. A maximum increase 32% of elongation is shown by the resin modified by 1.5% HH. The reduction in micro voids contributes to the increase elongation.

3.4. Thermogravimetric analysis (TGA)

Figures 5 and 6 show the variation in derivative weight (%) with temperature (^{0}C) of SS and HH modified PF resol. Their inset shows respective thermograms. The thermal degradation characteristic of the resins is shown in table 1. For the neat resin the degradation starts at 468^{0}C. For SS-modified PF resol there is a considerable improvement in onset of degradation. At 0.3% SS

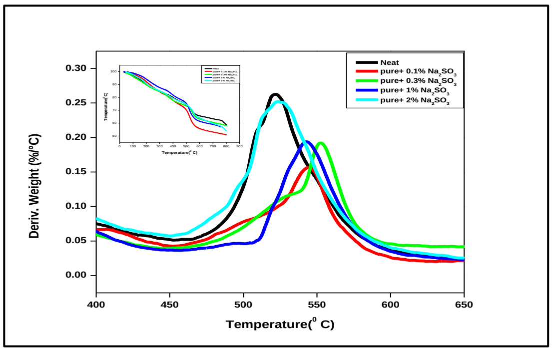

Figure 5. Variation in derivative weight (%) with temperature (^{0}C) of SS modified resol.

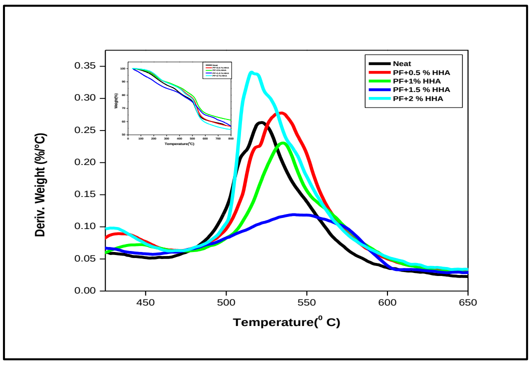

Figure 6. Variation in derivative weight(%) with temperature (^{0}C) HH modified resol.

loading the onset degradation temperature is raised from 468 ^{0}C to 502^{0}C and at 1% SS loading the onset is shifted to 512^{0}C. It is observed that the maximum degradation is shifted towards higher temperature for the resins containing different amounts of SS. With the addition of 0.3% of sulphite the maximum degradation temperature shifted from 521^{0}C to 552^{0}C. The rate of maximum degradation of the neat resin is 0.2612 %/^{0}C. As the percentage of SS in the resin increases, a gradual decrease of peak rate of degradation can be noticed, consistent with the increased thermal stability. In the presence of 0.3 % SS the rate of the maximum degradation is reduced to 0.1873 %/^{0}C. Further addition of the SS also shows reduction in the rate of the maximum degradation. These results suggest that the SS- modified phenolic resin are thermally more stable than the neat phenolic resin.

In the case of HH- modified PF resol, the temperature at the onset degradation is raised from 468^{0}C to 491^{0}C. The temperature at maximum degradation is shifted from 521^{0}C to 542^{0}C, and the

Table 1. Thermal characteristics of the Neat and modified resols.

Samples	Onset of Degradation (^{0}c)	Temperature at maximum degradation (^{0}c)	End of Degradation (^{0}c)	Rate of maximum degradation(%/^{0}C)
Neat PF	468	521	602	0.2612
SS (weight %)				
0.1	471	543	603	0.1187
0.3	502	552	601	0.1873
1.0	512	542	605	0.1545
2.0	466	526	599	0.2508
HH(weight %)				
0.5	491	532	612	0.2765
1.0	490	536	614	0 .2304
1.5	465	542	603	0.1187
2.0	490	515	586	0.3281

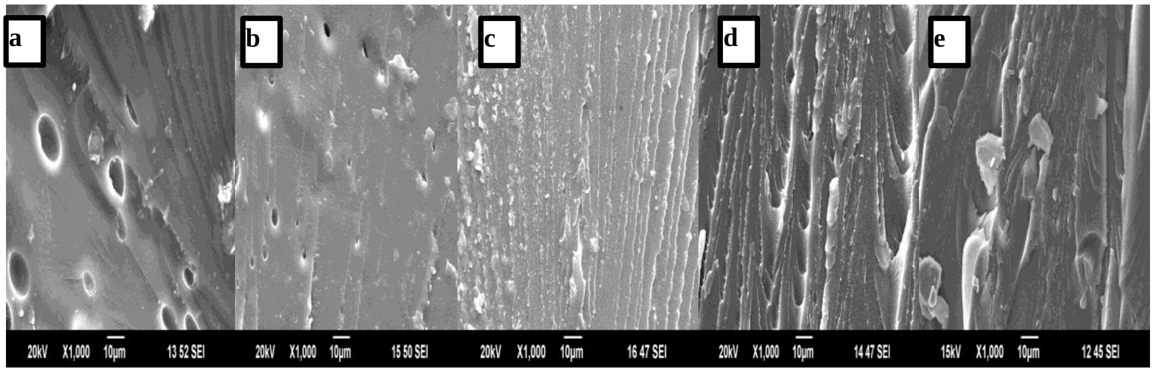

Figure 7. Scanning electron photograph of fractured surfaces of a) Neat resol b) 0.1% SS c) 0.3% SS d) 0.5%HH and e) 1.5 %HH modified resols.

rate of the maximum degradation is 0.2612%/^{0}C reduced to 0.1187 %/^{0}C, indicating higher thermal stability. The thermal analysis shows the higher thermal stability of the sodium sulphite & HH modified PF resol resin

3.5. Scanning electron microscopic analysis

Fig. 7 shows the SEM images of fractured surfaces of neat (a), SS modified (b & c) and HH modified resols (d &e). The SEM photograph of fractured surface of neat resol shows a smooth fracture with large number of voids. The voids may be due to the emission of free formaldehyde during the curing of resol resin. In the case of SS and HH modified resols the morphology is entirely different. It is clear from SEM photographs that for SS and HH modified resol resins the number of voids is less or absent. This may be due to the fact that free formaldehyde content is reduced in the presence of these scavengers. The fractured surfaces of the modified samples are rough compared to neat PF.

4. CONCLUSION

Sodium Sulphite and hydroxylammine hydrochloride can be used as formaldehyde scavengers which form a reversible adduct with the formaldehyde in the PF resol resin. The free formaldehyde content is reduced to zero in the presence of these scavengers. The optimum loading of the sulphite is 0.3% and hydroxylammine hydrochloride is 1.5%. The tensile properties of the PF resin are improved on modification with scavengers. The void formation is reduced in the presence of the modifiers. The thermal properties of the PF resin are significantly improved on modification with these scavengers.

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