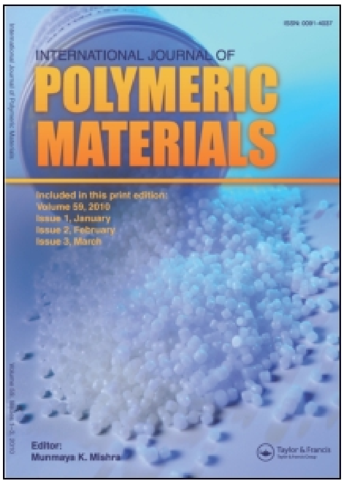

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Influence of Ether Linkages on the Properties of Resol Phenolic Resin

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Phenolic resol resin was synthesized using different formaledehyde/phenol ratios in the range 1.5 to 2.5. FTIR, TGA and mechanical property measurements were done on the samples. From relative intensity observations it is found that although the number of ether linkages increases with F:P ratio the mechanical properties of the resin do not improve beyond F:P = 1.75. This is because the number of phenolic –OH groups limits hydrogen bonding at higher F/P ratios. The overall performance of the cured resin is optimal at F:P ratio of 1.75.

Keywords: F:P ratio, FTIR, mechanical properties, phenolic resin, TGA

INTRODUCTION

Although phenolics were the first class of synthetic polymers discovered, they continue to be used widely. The excellent thermal and dimensional stability, moldability, chemical resistance, compressive strength, and surface hardness of these resins make them a natural choice for many applications. Some of these are foundry molds and cores, plywood and particle boards, grinding wheels and coated abrasives, adhesives and glues, coatings and varnishes, ablative composites and electrical and decorative laminates [1].

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Phenolic resins are prepared by the condensation reaction of phenol and formaldehyde in the presence of either acid or alkali [2–3]. The acid catalyzed phenolic resin in which formaldehyde to phenol (F:P) ratio is less than one, is known as novolac. Resols are alkali-catalyzed resins with F:P ratio greater than one; between 1 to 3. Resols are self-curing thermosets. Different basic catalysts like NaOH, $Ca(OH)_2$, $Ba(OH)_2$, amines, and so on are used for the condensation reaction [1,4]. The reaction between phenol and formaldehyde involves the substitution of methylol($-CH_2OH$) group at the ortho and para positions of phenolic $-OH$ group. The functionality of phenol being 3, the maximum number of methylol groups that can be substituted is three. Therefore, the reaction mixture contains a mixture of o- and p-monomethylol phenols, o,o- and o,p-dimethylol phenol, and 2,4,6-trimethylol phenol [5]. Apart from the initial F:P ratio, the relative proportions of various methylol phenols are determined by the reactivities of individual methylol phenols [5–6].

The curing of resols leads to a three-dimensional network structure. The molecular structure of resol resin is mainly determined by the initial F:P ratio [7]. For the formation of an efficient network structure, a F:P ratio $\sim$1.5 is sufficient. It has been reported that the properties of the cured resin are maximum when the initial F/P ratio is in between 1.3 and 1.4 [8]. During curing, methylol phenols condense to form methylene bridges and dibenzyl ether linkages. The amount of methylene and ether linkages present in the cured sample depends on the F:P ratio and the type of catalyst used [7,9]. Ether linkages are weaker than methylene linkages on the basis of bond energy. This can lead to inferior mechanical properties when there are more ether linkages. But, on the other hand, ether linkages can establish hydrogen bonds with the phenolic $-OH$ groups. This can have a positive effect on the properties of the resin. This study intends to investigate the influence of F:P ratio and consequently, the extent of ether linkages on the mechanical and thermal properties of the cured resin.

EXPERIMENTAL

Materials

Phenol for the resin synthesis was supplied by S. D. Fine-Chem Ltd., Mumbai. Formaldehyde (aqueous solution, 40 w/w), sodium hydroxide and glacial acetic acid were supplied by Merck Limited, Mumbai.

Resin Synthesis

Resol resins of varying F:P ratios 1.5 (R 1.5), 1.75 (R 1.75), 2.0 (R 2.0), 2.25 (R 2.25), and 2.5 (R 2.5) were synthesized in the presence of 0.25 mole NaOH. Phenol and formaldehyde (40% w/w) and 0.25 mole percentage of NaOH on a phenol basis were placed in a two-necked R B flask with a mechanical stirrer and a reflux condenser. The mixture was reacted for 90 min at 90°C. It was neutralized with glacial acetic acid after cooling until the pH reached ~7.0. The condensate was kept overnight. The aqueous layer was decanted off and the resin dehydrated by vacuum at ~760 mm of Hg.

Casting and Testing of Specimens

The dried resin was poured into teflon molds, fabricated as per ASTM standards (ASTM D 638 and D 790) and crosslinking was completed by heating in an air oven. The cure schedule lasted 24 h and the temperatures employed were 60°C—2 h, 70°C—15 h, 80°C—2 h, 90°C—1 h, 100°C—1 h, 110°C—1 h, 120°C—2 h, sequentially.

The cured samples were tested for tensile strength, tensile modulus, elongation at break, energy absorbed, flexural strength, modulus, and maximum displacement taking six samples for each case. The mechanical properties were tested on a Shimadzu Autograph Universal Testing Machine—AG I series (50 KN).

FTIR technique was used for comparing the extent of various chemical groups present in the cured resin sample.

A TA instruments TGA Q 50 analyzer was used to investigate thermal degradation of the samples. A temperature ramp was done from room temperature to 800°C at 20°C/min in N_2. The sample size was between 5 mg to 10 mg.

RESULTS AND DISCUSSION

FTIR Studies

The dibenzyl ether linkages in phenolic resin show absorption at ~1050 cm^{-1}. The relative intensity at 1610 cm^{-1} due to –C=C– stretching of benzene ring was almost constant in all cured samples and hence it was taken as a basis for comparison. Figures 1–3 show the FTIR spectra of cured resins in the region of interest.

The ratio of the relative intensities, I_{1050}/I_{1610}, as a function of the F:P ratio is given in Figure 4. The ratio of the relative intensities, I_{1050}/I_{1610}, increases with increase in the F:P ratio. This indicates that ether linkages steadily increase as the F:P ratio increases.

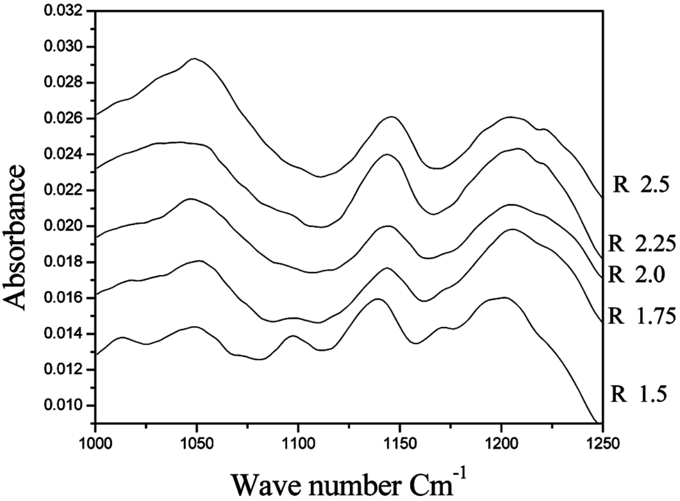

FIGURE 1 FTIR of cured resin in the region 1000–1250 cm^{-1}.

The –OH stretching frequency (3280 cm^{-1}) of the cured resin with F:P ratio 1.5 is slightly higher than for other samples. The shifting toward a lower frequency (~3272 cm^{-1}) for all other samples indicates a greater amount of hydrogen bonding at higher F:P ratios. Hydrogen bonding is possible between the phenolic –OH groups and ether linkages. Because the number of phenolic –OH groups remains the same, any change in the extent of hydrogen bonding is brought about by the change in number of ether groups. But beyond a certain concentration of ether

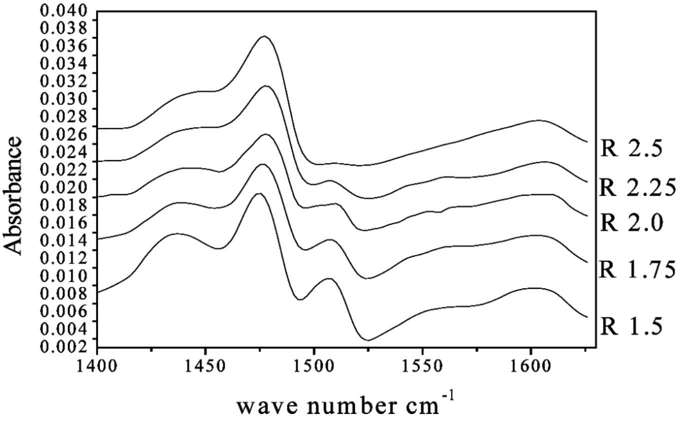

FIGURE 2 FTIR of cured resin in the region 1400–1650 cm^{-1}.

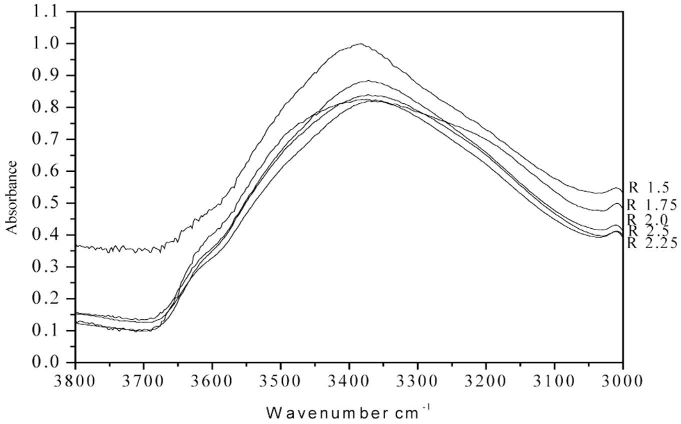

FIGURE 3 FTIR of cured resin in the −OH stretching region.

linkages no further shift in the frequency is observed because most of the −OH groups have been utilized for hydrogen bonding. So at higher F:P ratios, no positive effects of hydrogen bonding are noticeable.

Thermal Studies

The TGA curves of the various cured resins are shown in Figure 5. The results of TGA studies are summarized in Table 1.

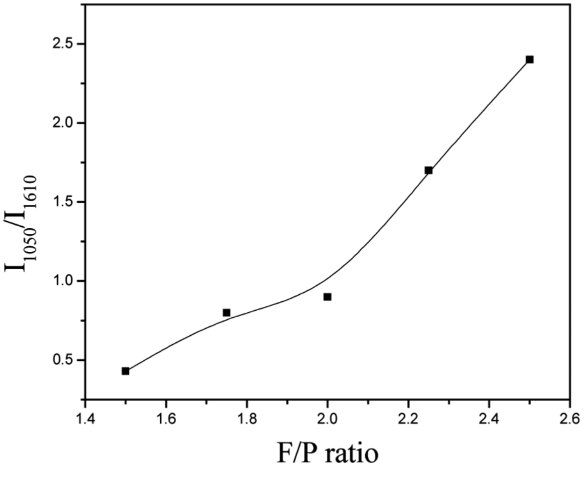

FIGURE 4 Variation in I_{1050}/I_{1610} with F:P ratio.

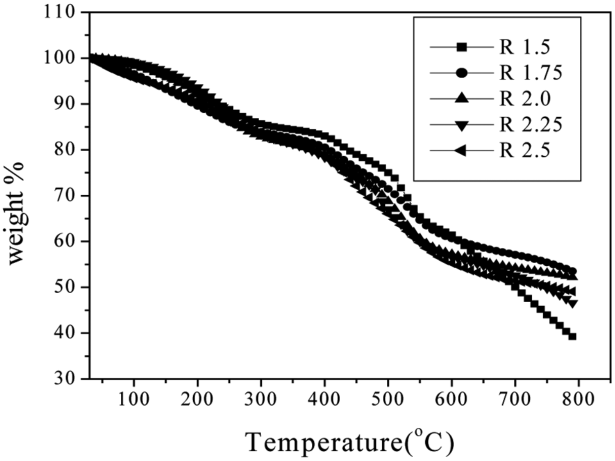

FIGURE 5 TGA of cured resins.

The onset temperature is maximum for the phenolic resin with F:P ratio 1.5. This contains the least number of ether linkages. The onset temperature steadily decreases with increase in the F:P ratio. This can be attributed to an increase in the number of ether linkages in the cured sample. The release of formaldehyde is the main degradation reaction in this temperature range [10].

The temperature at which the degradation rate is maximum (peak degradation temperature, Tp) shifts to a lower temperature range with increase in the F:P ratio. However, the resins with F:P ratios 1.5 and 1.75 are found to have the same T_p. The case with F:P ratio 1.75 yields the maximum residue and that with 1.5, the minimum. As can be seen from the mechanical property measurements given later, a F:P ratio of 1.75 gives the best performance. Hence, the overall performance of the cured resin is optimal at a F:P ratio of 1.75.

TABLE 1 TGA Studies on Cured Phenolic Resins

Sample	Onset temp. (°C)	Temp. of max. rate (°C)	Temp. of half loss (°C)	Residue at 800°C (%)
R 1.5	362	532.4	700	39.1
R 1.75	350	532.3	>800	53.4
R 2.0	348	518.7	>800	52.2
R 2.25	346	487.0	747	46.5
R 2.5	353	434.5	762	49.1

Mechanical Properties

Figures 6 to 9 show the variation in mechanical properties with F:P ratio.

Figures 6(a) and (b) show the variation in tensile strength and flexural strength with F:P ratio. The highest strength is shown by the resin with ratio 1.75. At higher F:P ratios it is possible that the presence of too many ether groups leads to a deterioration of properties. The positive effects of hydrogen bonding are offset by this effect so that there is a net fall in performance.

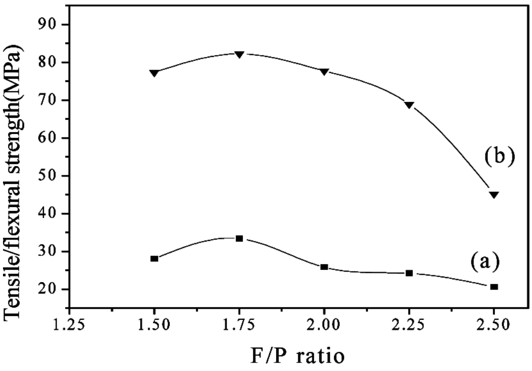

FIGURE 6 Variation in tensile strength (a) and flexural strength (b) with F:P ratio.

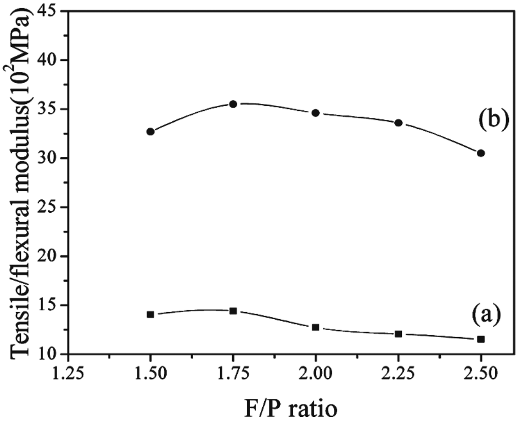

FIGURE 7 Variation in tensile (a) and flexural (b) modulus with F:P ratio.

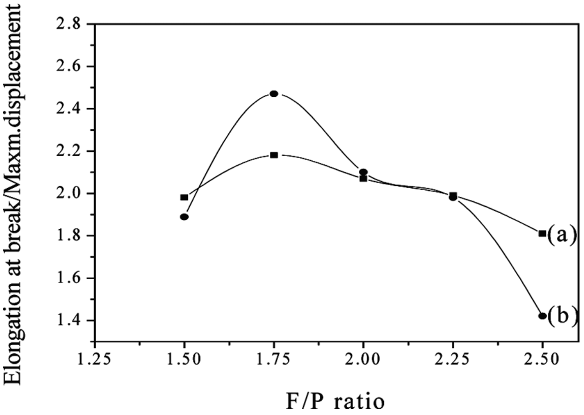

FIGURE 8 Variation in elongation at break (a) and maximum displacement (b) with F:P ratio.

Figures 7(a) and (b) show the variation in tensile and flexural moduli with F:P ratio. Modulus values are almost constant for the F:P ratios 1.5 and 1.75. The decrease in the modulus values at higher F:P ratios may be due to relatively higher amounts of ether linkages.

Figures 8(a) and (b) depict the variation in the elongation at break with F:P ratio. The elongation at break is maximum for a F:P ratio of 1.75. The lower strength of the cured resin at higher ratios reduces the elongation at break.

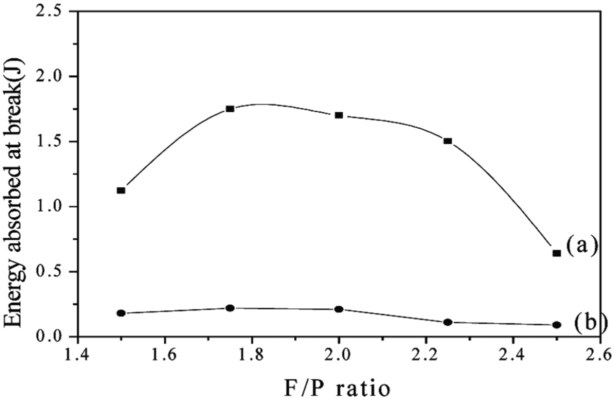

FIGURE 9 Variation in energy absorbed at break (a) tensile mode and (b) flexural mode.

Figures 9(a) and (b) show the variation in the energy absorption (toughness) with F:P ratio. The cured resin with F:P ratio 1.75 exhibits maximum energy absorption. The higher strength and the elongation showed by the cured resin at this F:P ratio is responsible for this.

CONCLUSION

The study reveals that the amount of ether linkages increases with increases in the F:P ratio. An excessive amount of ether linkages reduces the strength of the cured resin. However, the presence of a moderate amount of ether linkages leads to hydrogen bonding and an improvement in properties. The cured phenolic resin with F:P ratio 1.75 shows the best mechanical properties while retaining thermal stability.

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