Control of Microvoids in Resol Phenolic Resin Using Unsaturated Polyester

P. S. Parameswaran,[1,2] M. G. Bhuvaneswary,[1,3] Eby Thomas Thachil[1]

[1]*Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi, Kerala, India*
[2]*Department of Chemistry, SD College, Alappuzha, Kerala, India*
[3]*Department of Chemistry, SNM College, Maliankara, Ernakulam, Kerala, India*

ABSTRACT: A major drawback of cured phenol formaldehyde resin is the presence of microvoids, resulting from the liberation of condensation byproducts. In an attempt to rectify this, phenolic resol resin was blended with unsaturated polyester (UP). UPs with various maleic anhydride (MA) to phthalic anhydride (PA) ratios were synthesized and later mixed with resol resin in various proportions. The best MA/PA ratio was found out by determining the specific gravity, acetone-soluble matter, and volatile content of the cast blend, cured under a satisfactory time–temperature schedule. The influence of acid value of the UP and the most desirable UP content were also investigated on the basis of the quality of the modified phenolic samples. The structural changes in the modified resin were studied using FTIR spectroscopy. Scanning electron micrographs (SEM) of the fractured surfaces were obtained to ascertain the extent of microvoids in the modified resin. Both thermogravimetric analysis results and SEM micrographs confirm the effectiveness of UP in reducing the microvoids in the cast resol resin. The tensile and impact strengths of the samples also reflect the superior quality of the resol phenolic resins that have been modified by UP. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 802–810, 2009

Key words: resins; modification; voids; impact resistance

INTRODUCTION

Phenolic or phenol-formaldehyde (PF) resin is one of the oldest polymeric materials of commercial value. It is still widely used as a staple thermoset resin, mainly because of high reliability under severe conditions. Its excellent ablative properties, thermal and dimensional stability, structural integrity, and chemical resistance facilitate application in a broad range of fields such as thermal insulation materials, molding compounds, foundry, wood products industry, coatings, adhesives, and composite materials.[1–7] The main disadvantages of phenolic resin are microvoid formation in the cured resin and the brittle nature resulting from a high degree of crosslinking.[8–10]

PF resin is a synthetic polymer whose processing methods were laid down by Baekeland.[11] It is 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.[12,13] 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.

A novolac resin obtained by acid-catalyzed reaction with a deficit of formaldehyde does not contain any reactive methylol groups and hence is incapable of self-condensation when heated without curing agents. On the other hand, resols contain reactive methylol groups that enable the resin to cure by itself when heated, forming a crosslinked structure without the need for hardening agents. The curing reaction of resol takes place between methylol groups or between the methylol group and a vacant o- or p- position of the phenolic ring. During this exothermic process, simple molecules like water and formaldehyde are released and a three-dimensional network structure results.

As the curing reaction advances, the resin viscosity rises and the escape of the condensation products becomes more difficult. The entrapment of the condensation products in the cured resin leads to microvoids, which adversely affects the properties of the cured resin. These problems associated with the curing of phenolics were largely solved by Baekeland,[11] who developed molding methods that employ heat and pressure to get products with less porosity. Another method to reduce the microvoids is by adding diluents such as glycols.[8,10] The addition of

diluents yields dual advantages. First, it reduces the viscosity of the resin, which helps the escape of condensation products, and second, the glycols disperse the condensed water into fine droplets of dimensions less than that of the wave length of visible light.[14] It has been reported that acid-curing agents like toluenesulfonic acid not only accelerate the curing reaction but also reduce the microvoids.[9] Most of the reported studies on improving the properties of PF resin are aimed at toughening of the cured resin.[15–21] However, only a limited number of studies have been reported on microvoid reduction in cured phenolic resin.[10,22]

Glycols and some dicarboxylic acids are effective in enhancing the mechanical properties of phenolic resin.[9,10] The quinone methide moieties present in phenolic resin prepolymers are capable of forming a ring structure with double bonds.[15] It is our experience that combining the effects of diols, dicarboxylic acids, and double bonds, low-molecular-weight unsaturated polyesters (UPs) can both reduce the microvoids and improve the properties of resol phenolic resin in general. With this possibility in mind, we have used UP as a modifier. To our knowledge, this is the first time UP has been employed to control microvoids in phenolic resin. This technique promises to be a very simple means of controlling the microvoids and thereby improving the overall properties.

UP is synthesized by the reaction of a mixture of anhydrides (at least one of which contains unsaturation) with diols. UPs from various mixtures of maleic anhydride (MA) and phthalic anhydride (PA) with 1,2-propylene glycol (PG) were synthesized in the laboratory and used as modifiers. The influence of MA/PA ratio and the acid value of the polycondensation product in controlling the microvoids in the cured phenolic resin were studied by measuring the specific gravity, the extent of total soluble content in the cured resin, and weight loss by isothermal gravimetric analysis and scanning electron microscopy (SEM). The tensile and impact strength of the cured resins were tested to confirm the effectiveness of UP for modifying resol phenolic resin. We have cast phenolic specimens without the application of pressure so that voids will not be suppressed, but be visible.

EXPERIMENTAL

Materials

1,2-PG, MA, PA, xylene, triphenyl phosphate, and glacial acetic acid were laboratory reagent (LR) grade supplied by E. Merck India, Bombay, India. Commercial resol resin in alkaline condition (solid content ∼ 50%) was obtained from M/S.Polyformalin, Thripunithura, Kerala, India.

Resol resin was neutralized with glacial acetic acid until the pH reached a value of ∼ 7.0. It was then kept overnight for phase separation and the water layer was decanted off. The resin was subsequently dried for 12 h using a vacuum oven to completely remove the water.

Synthesis of unsaturated polyester

Benny et al.[23] have observed that the optimal procedure for synthesis of UP is to initially react PA with the total stoichiometric amount of PG and subsequently react the product with MA. This procedure has been adopted for the synthesis. UPs with four different MA to PA (MA/PA) ratios (90/10, 70/30, 50/50, and 30/70) designated as UP1, UP2, UP3, and UP4, respectively, were synthesized (acid value ∼ 26 mg KOH/g). PG and PA were taken in the molar ratio 1.1 : 0.30 in a 1-L three-necked RB flask equipped with a mechanical stirrer, N_2 inlet, and a reflux condenser. A small amount of excess PG was included to allow for evaporation losses. The reaction was conducted under an inert blanket of N_2. Triphenyl phosphate (0.05%) was added to prevent decolourization. About 10 mL xylene was used to remove water of condensation azeotropically. The reaction mixture was heated at 210°C for 2 h. At this stage, 0.70 moles of MA was added. The acid value was monitored every 2 h by dissolving a definite amount of the UP in a 50 : 50 (v/v) mixture of benzene and methanol and titrated against standard alcoholic KOH solution (ASTM D-2849). When the acid value became 40, vacuum was applied to bring it below 30 by removing the water of condensation. UP with different acid values were obtained by withdrawing samples at different stages.

Sample preparation

Dried phenolic resol resin (R) was mixed with varying proportions of UP dissolved in methyl ethyl ketone using a mechanical stirrer for 20 min. The solvent was then removed by applying vacuum for about 45 min. The modified resins were designated as RUP1, RUP2, RUP3, and RUP4 corresponding to each MA/PA ratio. Since UP2 corresponding to a MA/PA ratio of 70 : 30 was observed to give the best properties when blended with phenolic resin, subsequent studies using polyesters of different acid values were limited to UP2 only. RUP2a–d represent various blends containing UP of different acid values, namely 93, 70, 60, and 50. The dried and degassed samples were then poured into a Teflon mold with 4-mm-deep rectangular cavities and cured in an air oven according to the following
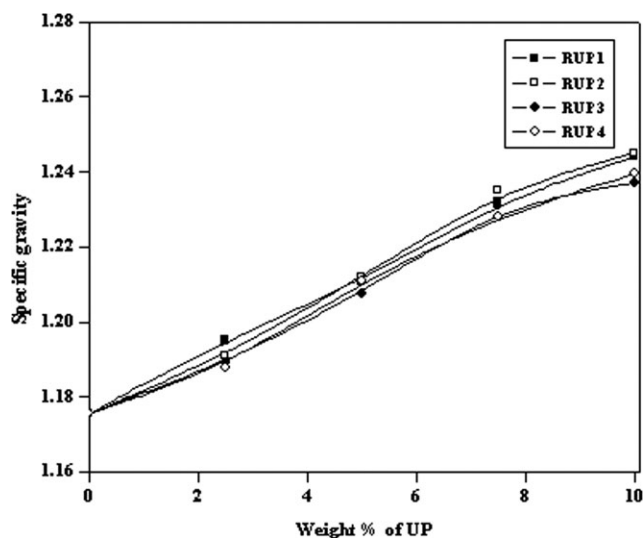
Figure 1 Variation in specific gravity of cured resol modified by UP of varying MA/PA ratio.

temperature schedules: 60°C, 2 h; 70°C, 15 h; 80°C, 2 h; 90°C, 1 h; 100°C, 1 h; 110°C, 1 h; and 120°C, 2 h. This slow cure schedule helps the water of condensation to escape as and when formed.

Specific gravity

For specific gravity measurement, cylinder-shaped specimens were cast according to the temperature schedule as mentioned earlier. Specific gravity was determined by following Archimedes' principle using water at 25°C.

Thermogravimetric analysis

Approximately 10 mg of each of the cured samples were kept at 100°C for 30 min in N_2 atmosphere to find out the amount of volatiles (particularly water) in the cured sample. A TA instrument, thermogravimetric analysis (TGA) Q 50 analyzer was used for this study.

Soxhlet extraction

The samples were ground to particles of about 1 mm diameter. About 2 g of each were wrapped in Whatman No.1 filter paper and extracted with acetone in a Soxhlet apparatus for 24 h.

FTIR studies

FTIR spectra of the samples were taken in a Bruker Tensor 27 FTIR Spectrometer to study structural changes, if any, after modification.

SEM analysis

The morphology of the tensile-fractured surface was studied using JEOL JSM 840A SEM to find the extent of microvoids in the cured phenolic resin.

Mechanical properties

Tensile strength of the cured samples was tested on a Shimadzu Autograph AGI Universal Testing Machine. Dumbbell shaped samples were cast in a Teflon mold, fabricated as per ASTM D-638-89. All samples were cured as per the time and temperature schedule given earlier. Impact strength of the cured samples was tested on a Resil Impact Analyser (Junior) as per ASTM D-256-89. The specimens were tested using a hammer with 4 J capacity at a speed of 3.46 m/s.

RESULTS AND DISCUSSION

Figure 1 shows the variation in specific gravity of cured resol resins modified by UP with different MA/PA ratios. For all MA/PA ratios, the specific gravity of the cured resin is seen to increase with the increase in the UP content. The increase in the specific gravity values indicates that the microvoids gradually disappear as the UP content in the phenolic resin increases. The curves also show that a higher amount of MA in UP has only a marginal influence on the specific gravity of the cured sample.

The amount of soluble content in the various cured resins as determined by Soxhlet extraction using acetone is shown in Figure 2. The amount of acetone-soluble content drastically decreases with the addition of UP, irrespective of the MA/PA ratio.
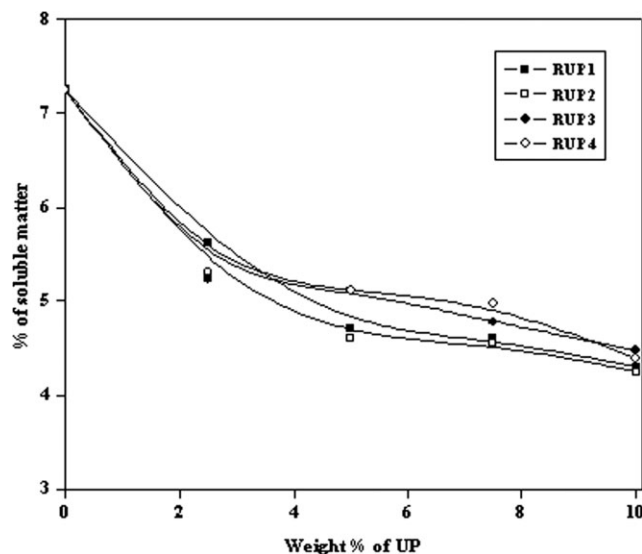

Figure 2 Variation in soluble matter of cured resol modified by UP of varying MA/PA ratio.
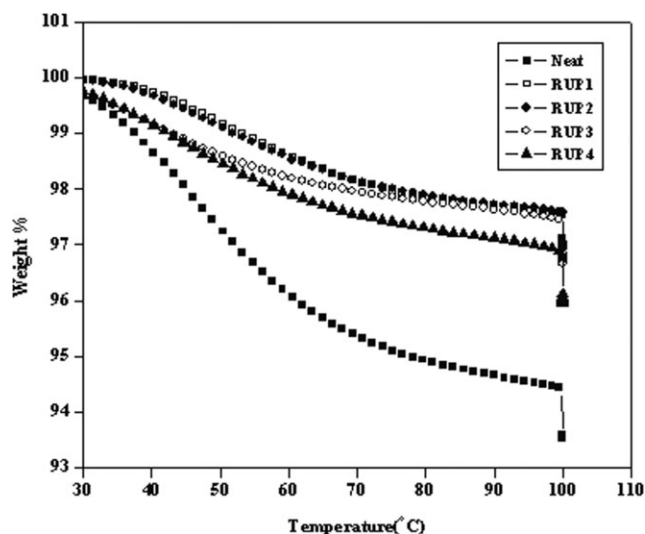
Figure 3 Isothermal TGA curve of cured resol modified with UP of varying MA/PA ratio.

Even a small amount of UP ($\sim$ 2.5%) reduces the soluble content in the cured resin by as much as 30%. The decrease in the acetone-soluble content points to the fact that monomers or oligomers are present to a lesser extent in the modified resin. Also, the added UP has, apparently, been incorporated chemically into the phenolic resin. Moreover, condensation byproducts like water are less pronounced in the modified resin.

A similar trend is also noticed in the TGA results. All the modified cured samples with 7.5% of UP were kept at 100°C for 30 min. The variation in weight loss during TGA program is shown in Figure 3. The thermogram clearly indicates that the amount of condensation byproducts is highest in the neat-cured phenolic resin. There is also a significant
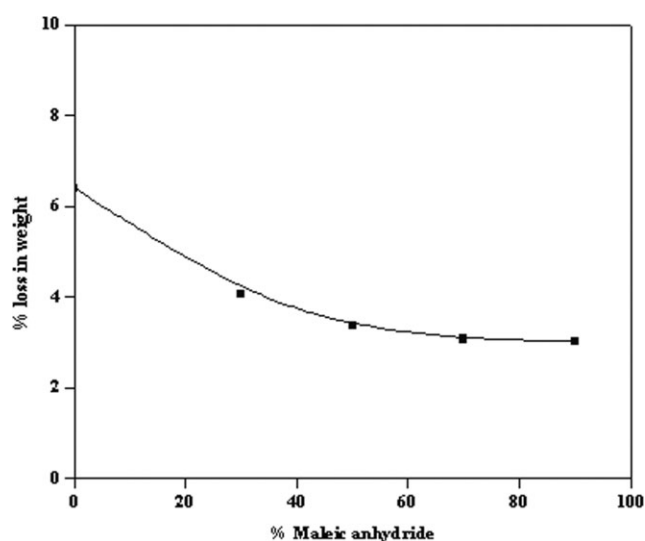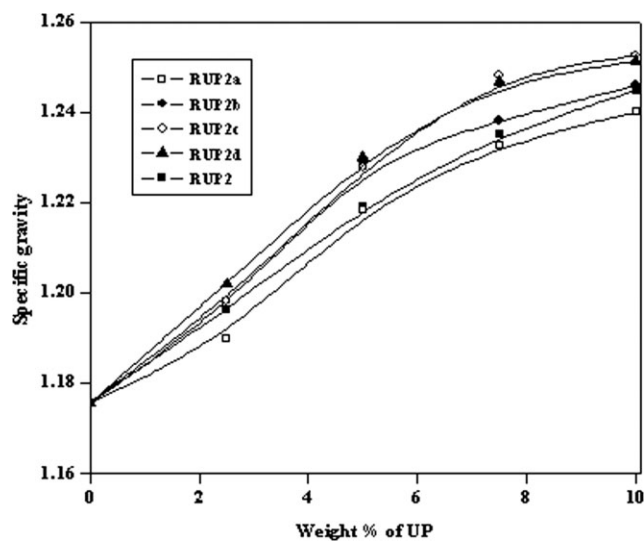

Figure 5 Variations in specific gravity of cured resin modified with UP of different acid values.

decrease in the weight loss for modified resins containing higher amounts of MA in the modifier UP. These results also support the Soxhlet extraction data. Figure 4 represents the loss in weight as a function of MA content for a constant UP content of 7.5% after isothermal study. The weight loss is less for samples with high MA content; but beyond 70% MA, the variation in weight loss is not substantial. An MA/PA ratio of 70/30 appears to be optimal, considering that a higher MA content does not lead to further improvement in the quality. Based on this finding, all samples for subsequent studies were made using a UP of MA/PA ratio = 70/30 (UP2).

The dependence of modified resol properties on acid value was investigated by employing UP of varying acid values. These are UP2-93 (UP2a), UP2-
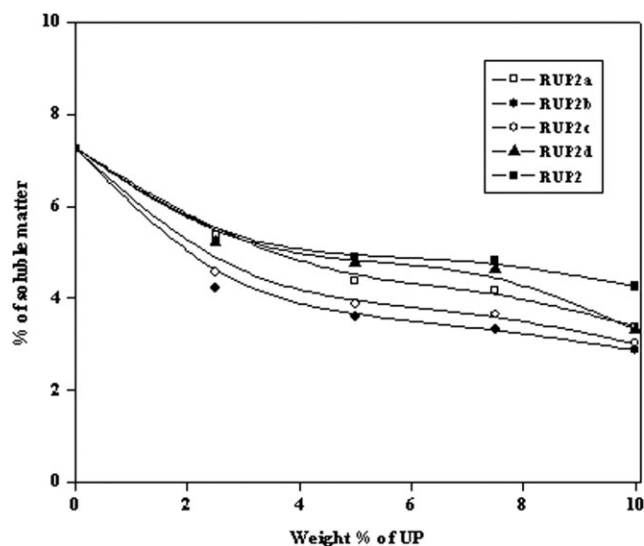

Figure 4 Variation in weight loss during isothermal TGA as a function of % of MA in the UP.

Figure 6 Variations in soluble matter in the cured resin modified with UP of different acid values.
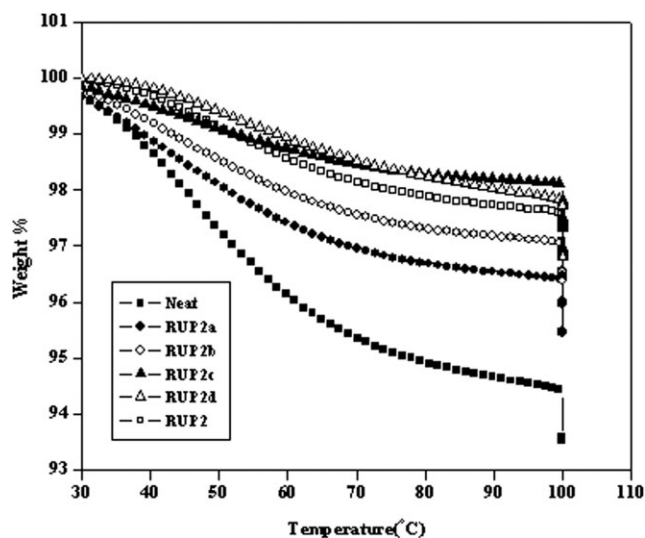
Figure 7 Isothermal TGA of modified phenolic resin containing 7.5% of UP2 of different acid values.
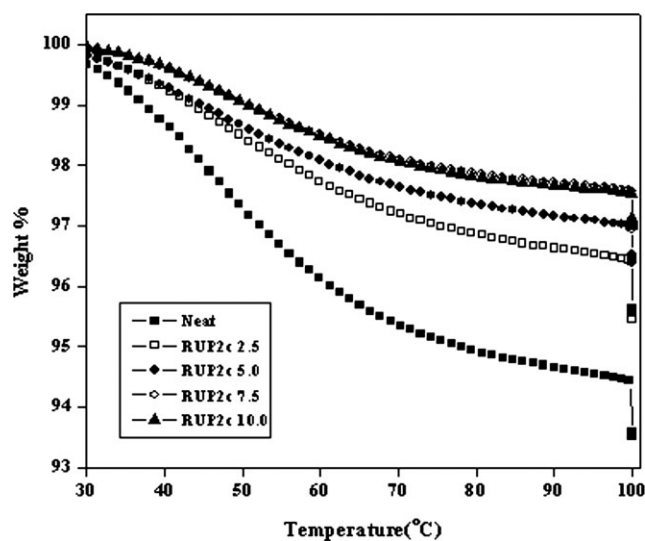

Figure 9 Isothermal TGA curve of the modified phenolic resin with varying amounts of UP2c.

70 (UP2b), UP2-60 (UP2c), and UP2-50 (UP2d), the number after hyphen denotes the acid value of the particular UP under consideration. The corresponding modified resol resins are RUP2a, RUP2b, RUP2c, and RUP2d, respectively.

Figure 5 represents the variation in specific gravity with the amount of UP in the phenolic resin. As in previous study, there is a clear dependence on the amount of UP, with the graph assuming a sigmoid shape. From the curves in Figure 5, the lowest specific gravities are exhibited by samples RUP2a and RUP2, corresponding to acid values of 93 and 26, respectively. Intermediate acid values are seen to have led to higher specific gravity for the modified cured resol resin.
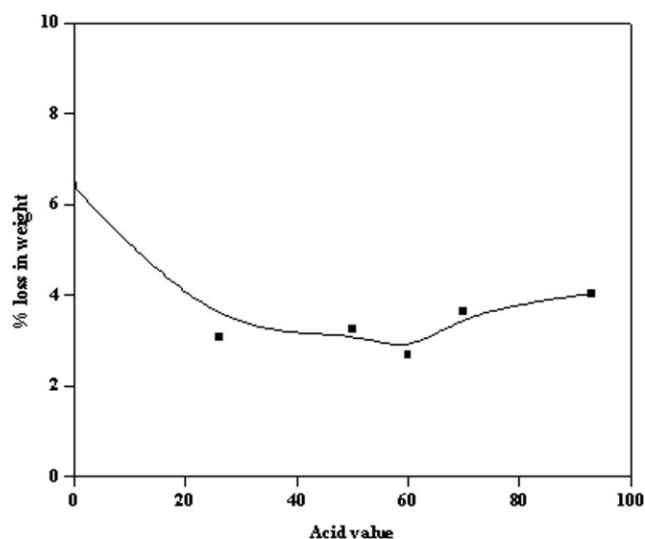
The variation of soluble content on Soxhlet extraction is shown in Figure 6. The amount of soluble content decreases initially with the increase in the UP content, irrespective of the acid value of the UP. The soluble content is minimal for cured resin modified with UP of intermediate acid value. This supports the observation from specific gravity measurements.

The isothermal TGA analysis of cured resol resin with 7.5% of UP2 having different acid values and corresponding values of loss in weight are shown in Figures 7 and 8. The dependence of acid value on the weight loss during isothermal TGA is clearly manifested. For higher and lower acid values of UP2, the amount of volatiles are higher when
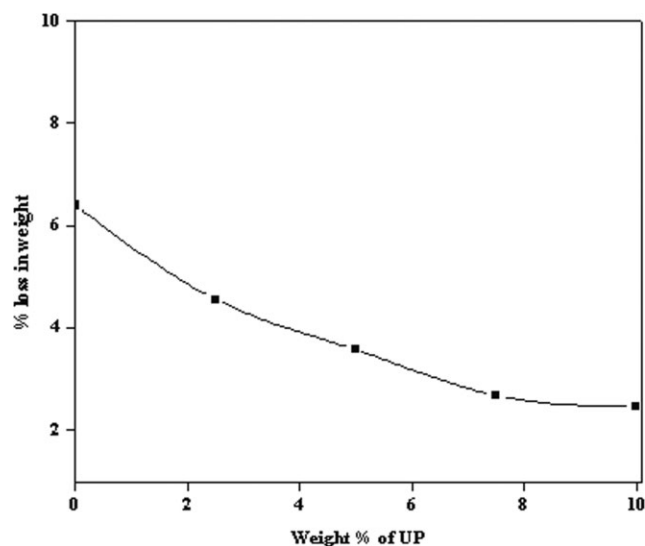

Figure 8 Variation in loss in weight on isothermal TGA of modified phenolic resin with acid value of UP2.

Figure 10 Variation in weight loss during isothermal TGA of the cured resin containing varying amounts of UP2c.

TABLE I
Tensile and Impact Strength of Modified Cured Resin

Sample	Tensile strength (MPa)	Impact strength (J/m)
Commercial phenolic resin	26.0 ± 1.8	47.4 ± 4.2
RUP1	33.2 ± 2.1	114.2 ± 3.8
RUP2	34.0 ± 2.4	117.8 ± 4.6
RUP3	31.8 ± 1.8	111.6 ± 5.0
RUP4	29.9 ± 2.2	106.2 ± 4.3
RUP2a	34.1 ± 2.4	118.8 ± 3.5
RUP2b	34.0 ± 2.2	122.0 ± 4.4
RUP2c	35.3 ± 2.0	133.8 ± 6.2
RUP2d	32.4 ± 2.4	120.0 ± 5.3

Figure 12 FTIR spectrum of the modified phenolic resin with varying amounts of UP2c in the region of 4000–2600 cm^{-1}.

compared with the intermediate acid values. This is consistent with the observations in Figure 5. Although lower acid values lead to lower volatile contents initially, further lowering of the acid values do not lead to any drastic reduction of volatile matter. Thus, UP of intermediate acid value is more efficient in controlling water and other volatile byproducts during the curing of resol phenolic resin.

Figure 9 represents the isothermal TGA of modified PF resin containing different amounts of UP2c, which gave the best overall results. The neat resin contains a higher amount of volatiles (presumably moisture) when compared with the modified resins. The amount of UP added plays an important role as seen from the figure.

The thermograms of cured phenolic resin containing 7.5% UP2c and 10% UP2c are almost identical. This indicates that 7.5% of UP is better suited for modifying the phenolic resin. The loss in weight during the isothermal TGA experiment is illustrated
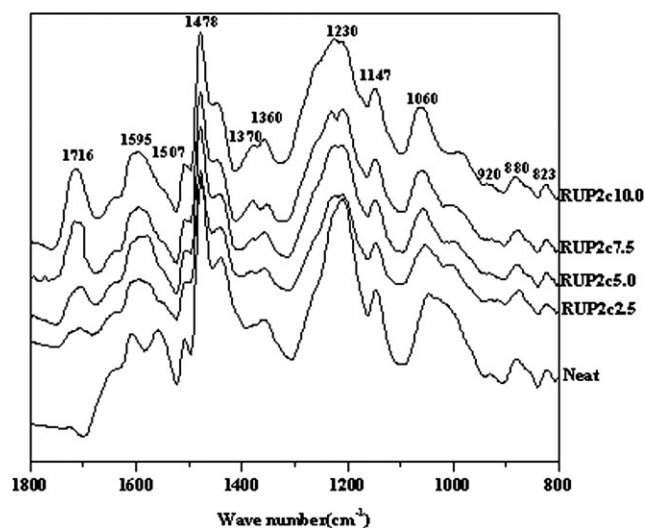
in Figure 10. The reduction in the weight loss is seen to level off at 7.5% of UP2c.

The tensile strength and impact strength values of the neat resin and the modified resins containing 7.5% of UP are given in Table I. All the modified resins show improved tensile strength and impact strength. The extent of improvement of tensile strength changes only in a narrow range for various modifications. An appreciable increase in the impact strength ($\sim$ 150–180%) is noted for all modified samples. This improvement in tensile and impact strengths can be attributed to the reduction in the extent of microvoids and greater chain flexibility resulting from the introduction of UP into the three-dimensional network structure of the resol resin.

The role played by UP in modifying the phenolic resol resin at the structural level is somewhat complex. The actual constitution of the crosslinked structure calls for more investigations. The intractable nature of the cured resin makes it difficult to resolve the chemistry of the cured structure. The reasons for the modifying action of UP may be one (or combinations) of any of the following:

1. The chemical anchoring of the UP to phenolic resol resin is possible through the quinone methide structure of phenolic resin. The double

Figure 11 FTIR spectrum of the modified phenolic resin with varying amounts of UP2c in the region of 1800–800 cm^{-1}.

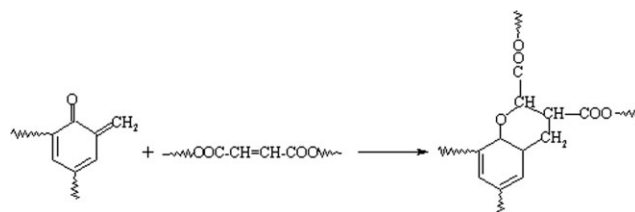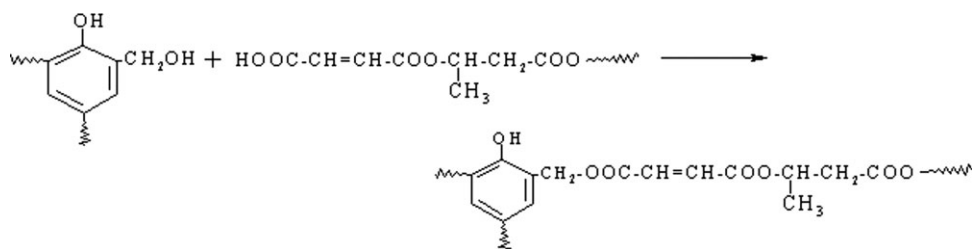**Scheme 1** Formation of cyclic ether linkages in the cured resin.

Scheme 2   Formation of ester linkages in the cured resin.

bonds present in the UP combine with the quinone methide moiety of phenolic resol resin to form a cyclic ether-like structure. The FTIR spectra (in the region of interest) of the modified cured phenolic resin using various amounts of UP2c are shown in Figures 11 and 12. The broadening at ~ 1230 cm^{-1} and the appearance of a shoulder peak at 1050 cm^{-1} are indications of the formation of cyclic ether linkages. The merging of peaks at ~ 1610 and 1550 cm^{-1} and the decrease in the intensity of the peak at ~ 1507 cm^{-1} due to the aromatic —C=C— bond stretching might have resulted from structural changes in the aromatic ring. "Diels Alder"
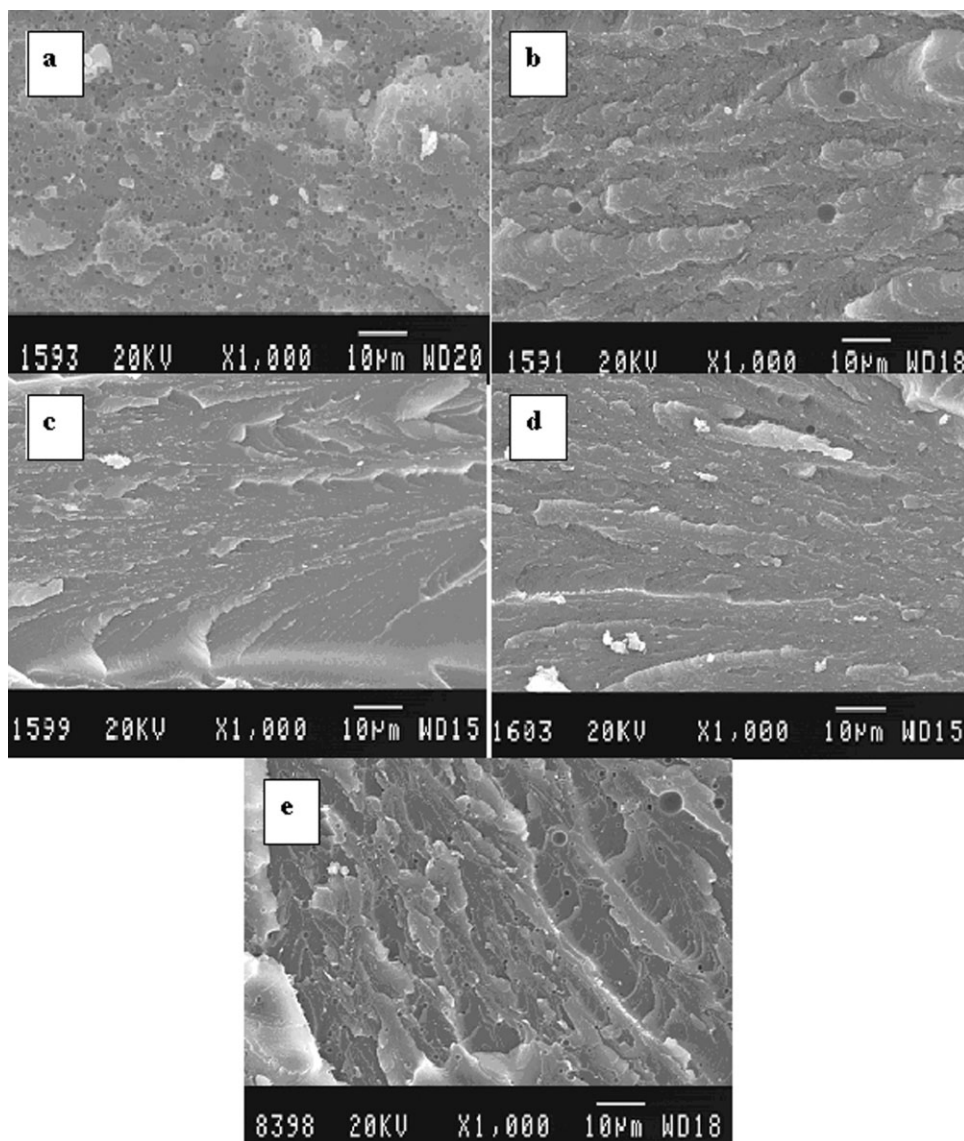

Figure 13   SEM micrographs of the fractured surface of the modified phenolic resin with 7.5% of UP2: (a) RUP2a; (b) RUP2b; (c) RUP2c; (d) RUP2d; and (e) RUP2.
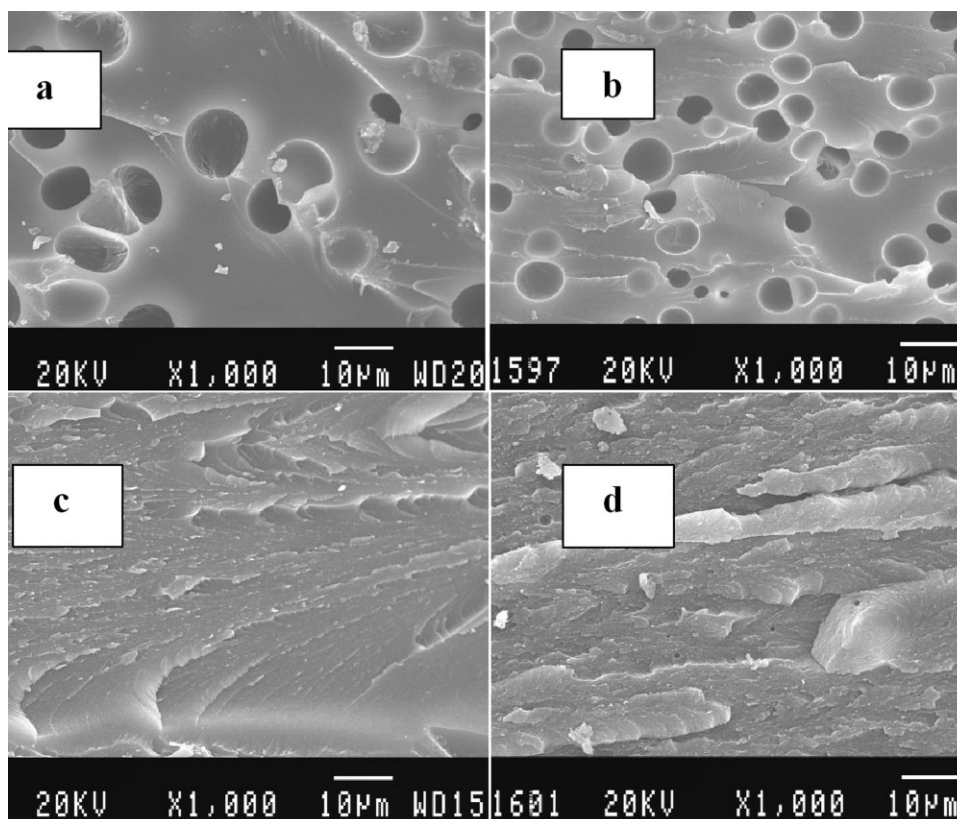
Figure 14 SEM micrographs of the fractured surface of the modified phenolic resin with various amounts of UP2c: (a) 2.5%; (b) 5.0%; (c) 7.5%; and (d) 10.0%.

type addition of —C=C— into the *o*-quinone structure of phenolic resin during the cure process (Scheme 1) may be responsible for this. The small peak at ~ 920 cm^{-1} due to the ring deformation of phenolic ring becomes broad in the modified resin. This also indicates that the phenolic ring has undergone some structural changes. The reduction in the intensity of the —OH stretching frequency at ~ 3300 cm^{-1} (Fig. 12) with the addition of UP suggests an appreciable reduction in the water content of the cured resol resin.

2. The —COOH end group of the UP can combine with methylol groups of phenolic prepolymers to form ester linkages (Scheme 2). The formation of ester linkages by the reaction of UP with the resol resin prevents the generation of dimethylene ether linkages (—CH$_2$—O—CH$_2$—). This may further reduce the amount of methylene bridges and the liberation of formaldehyde.

3. There is the possibility of the molecules of water of condensation hydrolyzing the ester linkages in UP under the curing conditions. This may lead to splitting of the ester groups and formation of still lower length chains. UPs with high acid value will have shorter chain lengths and a higher number of acid end groups. The total number of ester groups in the UP decreases with increase in the acid value. The decrease in the number of ester linkages and the resultant shorter chain lengths may cause less than complete utilization of the water of condensation and the trapping of the same inside the cured resin.

The low acid value UP contains longer chain lengths and a higher number of ester groups, which may cause excessive hydrolysis. This may, in turn, lead to recombination of the products and formation of water. However, this may happen only to a limited extent under the existing conditions. For the intermediate acid values, the UP may be of a "critical chain length" that satisfies the conditions conducive to the formation of a minimum number of voids.

4. The UP chains may have a plasticizing effect on the phenolic resin leading to a fall in viscosity of the system. This might make the physical escape of volatile matter from the resin easier.

Further proof of reduction of the volatile content by UP is provided by the SEM. Figure 13 shows the SEM micrographs of the tensile-fractured phenolic resol surfaces containing 7.5% each of UPs with different acid values, as described earlier. For high acid

value of UP-modified phenolic resol [Fig. 13(a)], a large number of microvoids <1 μm is noted on the fractured surface. The voids are almost absent in the sample modified with UP2c [Fig. 13(c)].

The reduction of void content with increasing amount of UP is clearly seen in Figure 14. These samples contain 2.5, 5.0, 7.5, and 10% of UP2c, respectively. The void size is considerably reduced by the addition of 5% UP. At 7.5%, the voids vanished completely. On this basis, coupled with the observations based on Figure 8, it can be inferred that 7.5% UP content leads to a minimum number of voids in the modified phenolic resin.

CONCLUSIONS

Phenolic resol resin can be gainfully modified with low-molecular-weight UP. Higher MA contents in the UP exert only a marginal influence on the quality of resol phenolic resin. The UP with MA/PA ratio 70 : 30 gives the best comparative overall performance. The decrease in the acetone-soluble matter on Soxhlet extraction along with structural changes noticed in the FTIR spectra of the modified resin indicate chemical anchoring of UP to the resol resin. Modification by UP of acid value ∼ 60 shows a minimum number of voids, as shown in the SEM micrograph of fractured surfaces. The higher specific gravity, lower soluble content on extraction, and lower volatile matter, as revealed by the isothermal TGA measurements of the cured resin, modified by UP with acid value ∼ 60, support the SEM evidence. The minimum quantity of UP required for the modification is ∼ 7.5%. Tensile and impact strength values of modified samples also indicate the positive results of modifying resols with UP. It can be expected that this effect will be more pronounced when the molding is done under pressure in the presence of fillers.

References

1. Knop, A.; Scheib, W. Chemistry and Application of Phenolic Resin; Springer: New York, 1979.
2. Qian, J.; Jin, Z.; Wang, J. Mater Sci Eng A 2004, 368, 71.
3. Hunter, J.; Forsdyke, K. L. Polym Compos 1989, 2, 169.
4. Yang, T. H.; Lin, C. J.; Wang, S. Y.; Tsai, M. J. Build Environ 2007, 42, 189.
5. Tyberg, C. S.; Sankarapandian, M.; Bears, K.; Shih, P.; Loos, A. C.; Dillard, D.; McGrath, J. E.; Rittle, J. S.; Sorathia, U. Construct Build Mater 1999, 13, 343.
6. Zaks, Y.; Lo, J.; Raucher, D.; Pearce, E. M. J Appl Polym Sci 1982, 27, 913.
7. Sasidharan, A. P.; Ramaswamy, R. J Appl Polym Sci 1998, 69, 1187.
8. Kaynak, C.; Tasan, C. C. Eur Polym J 2006, 42, 1908.
9. Wolfrum, J.; Ehrenstien, G. W. J Appl Polym Sci 1999, 74, 3173.
10. Singh, K. P.; Palmese, G. R. J Appl Polym Sci 2004, 91, 3096.
11. Baekeland, L. H. U.S. Pat. 942,699 (1907).
12. Bender, H. L.; Farnham, A. G.; Guyer, J. W.; Apel, F. N.; Gibb, T. B., Jr. Ind Eng Chem 1952, 44, 1619.
13. Freeman, J. H.; Lewis, C. W. J Am Chem Soc 1954, 76, 2080.
14. Brydson, J. A. Plastics Materials; Butterworth: London, 1989; p 618.
15. Nirmal, C.; Maithi, S. N.; Padmavathi, T.; Vanaja, A.; Rao, R. M. V. G. K. High Perform Polym 2006, 18, 57.
16. Choi, M. H.; Byun, H. Y.; Chung, I. J. Polymer 2002, 43, 4437.
17. Ma, H.; Wei, G.; Liu, Y.; Zhang, X.; Gao, J.; Huang, F.; Tan, B.; Song, Z.; Qiao, J. Polymer 2005, 46, 10568.
18. Cevdet, K.; Onur, C. Polym Test 2006, 25, 296.
19. Matsumoto, A.; Hasegawak, K.; Fukuda, A. Polym Int 1993, 30, 65.
20. Wu, H. D. J Appl Polym Sci 1997, 63, 911.
21. Zhan, M. S.; Xiao, W.; Li, Z. J Aeronautical Mater 2003, 23, 34.
22. Wu, H. D.; Lee, M. S.; Wu, Y. D.; Su, Y. F.; Ma, M. C. C. J Appl Polym Sci 1996, 62, 227.
23. Benny, C.; Eby, T. T. Polym Plast Technol Eng 2005, 44, 931.