

Enhancement of Phenolic Polymer Properties by Use of Ethylene Glycol as Diluent

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ABSTRACT: One application of phenolic resins is for the inner lining of multilayered composites in fire critical applications. Typically such resins contain water as a diluent to facilitate injection and mold filling. Although water is effective in controlling the viscosity, its evaporation from the resin during cure has been found to cause microvoids in the cured resin that are 8–10 μm in size. These voids are believed to affect the properties of the final product. In addition to the initial water content, evolution of water also takes place as a result of cure. In this study, we investigated the effects of processing parameters such as cure temperature, postcure temperature, catalyst concentration, and the use of ethylene glycol as a replacement diluent on water loss, microvoid distribution, and consequently, the mechanical properties. Weight loss during cure was followed by using a thermogravimetric analyzer (TGA). Scanning electron microscopy (SEM) was used to obtain images of cured resin

showing the microvoids. The properties that have been obtained for comparison are density, flexural modulus and strength, and fracture toughness. It has been shown that modification of the resin by removing the initial water of a commercial resin system and adding ethylene glycol as a replacement has the most significant effect on the microvoids as well as the properties of the polymer. A decrease in void content and increase in density along with a significant improvement in flexural modulus and fracture toughness have been observed upon replacement of water with ethylene glycol. This is significant because of the importance of the phenolic layer to the overall mechanical performance of a hybrid composite. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3096–3106, 2004

Key words: resins; voids; curing of polymers

INTRODUCTION

Glass fiber reinforced polymer (GRP) composites based on thermosetting resins, such as vinyl-esters and epoxies, have been in use for many years for their strength and lightweight properties. Traditionally, fire resistance has been imparted to these composites by the use of halogenated polyesters, vinyl-esters, or epoxies with or without fire-retardant additives. Phenolic resins, however, are inherently fire retardant because of the aromatic ring structure of phenol. They yield low levels of smoke and combustion products under both flaming and smoldering fire conditions. It is for this reason that they constitute the lining of GRP-composites in aircraft, armored tanks, and other applications where fire resistance is critical.

Several commercial phenol formaldehyde resins that are amenable to liquid molding techniques, such as resin transfer molding (RTM) and vacuum-assisted resin transfer molding (VARTM), are commercially available. An important requirement for a resin to be

used for liquid molding is that the viscosity of the resin is low enough to facilitate injection and mold filling. One of the most common methods of reducing the viscosity of phenolic resins is to add water as a diluent. In addition to the initial water content, evolution of water also takes place as a result of the cure process. Although effective in controlling the viscosity, evaporation of water from the resin during cure has been found to cause microvoids 8–10 μm in size in the cured resin. The presence of microvoids is believed to adversely affect the properties of the final product.

This study is directed toward investigating the effects of cure parameters such as cure temperature, postcure temperature, catalyst concentration, and diluent on water loss, microvoid distribution, and consequently, the properties of phenolic resin. Water loss, which is the principal cause of void formation, has been followed with the help of a thermogravimetric analyzer (TGA). Scanning electron microscopy (SEM) has been used to obtain images of cured resin showing the microvoids. The properties that have been determined for comparison are density, flexural modulus and strength, and fracture toughness.

Diluents other than water can be used to reduce the viscosity of the phenolic resins. Because loss of water in the phenolic resins causes void formation, replacing the initial water with ethylene glycol should have a

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significant effect on the microvoids and other polymer properties, while still giving the resin a low viscosity. The results of this work show that of the parameters investigated, modification of the resin by replacing the initial water with ethylene glycol has the most significant effect on the microvoids as well as the properties of the polymer. Ethylene glycol is believed not only to plasticize the resin system but also to become a chemically connected part of the polymer network, thus decreasing the crosslink density. A consequent decrease in void content and increase in density along with a significant improvement in the mechanical properties such as flexural modulus and fracture toughness of the modified resin have been observed. This is significant because of the importance of the phenolic layer to the overall mechanical performance of hybrid composite.

CHEMISTRY OF PHENOLIC RESINS

Phenolic resins are polycondensation products of phenol and formaldehyde. Phenol and formaldehyde can combine to give substituted phenols under different conditions and in different ratios. Based on this, the resins are characterized into novolacs and resols. Novolacs are prepared by reacting excess phenol with formaldehyde in the presence of an acid catalyst to yield high-melting oligomers. These oligomers are compounded with fillers and hexamethylene tetramine, which decomposes at high temperatures to form ammonia and formaldehyde as a crosslinking source. However, the resins of interest for liquid molding are the resols that are prepared by reacting a molar excess of formaldehyde with phenol under basic conditions. These are isolated as viscous liquids or low-melting solids after neutralization. The resols cure via condensation of hydroxymethyl groups with the evolution of water to form a crosslinked structure. Before delving into the cure chemistry, it is important to discuss the chemistry of the resol formation to provide insight into the initial composition of the resin as well as the nature of reactions that the constituent species undergo during cure.

Chemistry of resol resin synthesis

Numerous articles can be found in literature on the chemistry and reactions of resols. Saunders¹ and Knop and Scheib² give a detailed compilation of the chemistry of phenolic resins. The reactions listed in Figure 1 broadly represent the reactions taking place in the phenol formaldehyde system. The main reaction under basic conditions is the substitution of hydrogen with methylol groups at para and ortho positions of phenols.¹⁻³ Substitutions can take place at any or all of the three positions shown in the figure. In addition, there are a large number of possible reactions with

different combinations of unsubstituted and substituted phenols. The probability of dimer formation, although low under basic conditions, is not negligible. Various substituted dimers could be formed by condensation of the substituted phenols with another molecule of the same type (self-condensation) or by condensation with a differently substituted or even unsubstituted phenol (cross-condensation). Moreover, the presence of oxymethylene species are formed from formaldehyde in solution,³ which could form long straight chains before substitution at ortho and para positions of phenols. The linkages between the phenols (substituted or unsubstituted) can therefore be of different lengths.

Chemistry of cure

The cure of phenol formaldehyde resins takes place either at elevated temperatures (~ 150 – 200°C) or at lower temperatures ($\sim 60^\circ\text{C}$) with the aid of a strong acid catalyst. The chemistry of cure has been proposed on the basis of work done with simpler systems. In particular, pure mononuclear methylol phenols have been used in place of the complex mixtures that make up the resin.⁴ Fundamentally, this approach is justified because the functional groups generally undergo the same reactions in both monomeric and polymeric species.

The cure proceeds through polycondensation reactions of the variously substituted phenols. As illustrated in Figure 2, there are two possible routes for the condensation reactions (I and II). The reaction is believed to proceed through carbenium ions formed at the substituent methylol groups.¹ An ether linkage is formed when a carbenium ion reacts with a methylol group of a substituted phenol, while a methylene linkage is formed if it reacts with an unsubstituted position of a substituted or unsubstituted phenol. Preferential ether linkage is expected when there are few unsubstituted ortho and para positions available for attack by the carbenium ions.

Thus, ether and methylene bridges arise out of competitive reactions. It has been found that while the methylene bridges are generally stable, the ether bridges undergo a number of ill-defined reactions at temperatures above 150°C . One of the reactions is the breakdown of ether bridges to form methylene bridges with the loss of formaldehyde (reaction III in Fig. 2). The temperatures at which these reactions occur are not well known. Some report it as $\sim 150^\circ\text{C}$,¹⁻³ while others quote temperatures as high as 220°C .^{5,6} The formaldehyde, formed as a result of reaction III in Figure 2 and that are already present in the resin, causes further substitution at the active positions of phenols. Crosslinking takes place when the phenols undergo condensation reactions at more than two positions. The mechanisms and specific rates of

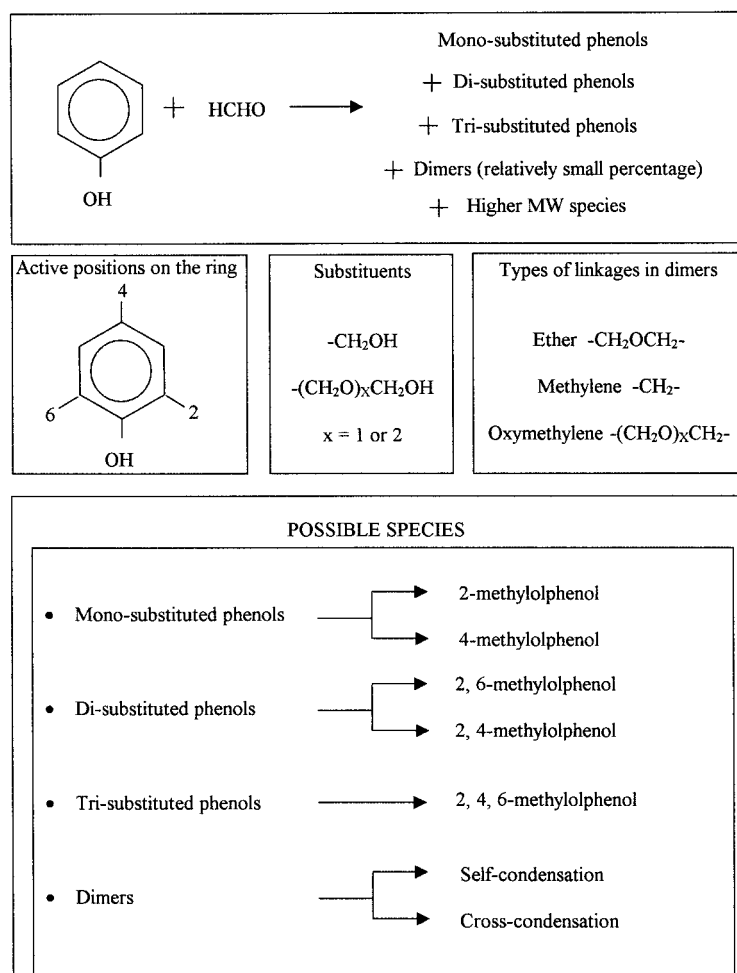


Figure 1 Chemistry of resol resin systems starting from phenol and formaldehyde.

many of the above reactions are known to markedly depend on factors such as pH, type of catalyst, and temperature.

MATERIALS

The system chosen for study was BPJ2027L, supplied by FRP Services (White Plains, NY). This was chosen because it contained no diluents other than water and it lent itself most easily to VARTM processing. A delayed action catalyst, BP Phencat 381, was used in this study. Its major constituent is *p*-toluenesulfonic acid. The delayed action of this catalyst affords enough time after mixing for injection into the mold, making it ideal for use in resin-transfer molding. Concentration of the catalyst was maintained at 4 wt % of the resin as recommended by the manufacturers except in studies with varying catalyst concentrations. The original resin contains about 10–12% water as a diluent. To investigate the effect of using a different diluent on the polymer properties and morphology, the resin was modified in the following manner: Water

was removed from the resin by applying continuous vacuum on it for approximately 12 h; ¹³C-NMR spectrum of the desiccated resin was obtained to verify that the composition of the resin remained the same; therefore, the weight loss of 10–12% can be safely attributed to loss of water. Ethylene glycol was added to the desiccated resin in a ratio of 20% by weight of resin to bring the viscosity down to the level of the original resin.⁷ The resin, thus obtained, will be referred to as modified resin in further discussions.

RESIN CHARACTERIZATION

High-resolution ¹³C₁ nuclear magnetic resonance spectroscopy (NMR) has been widely used to study the formation of phenol-formaldehyde prepolymer.^{4,8–10} A Bruker DRX400 spectrometer (400 MHz) was used to characterize phenolic resin BPJ2027L in solution (~20 mg/mL) in DMSO-d₆.

The ¹³C₁-NMR spectrum of BPJ2027L along with the band assignments is presented in Figure 3. The band assignments for the resin have been made on the basis

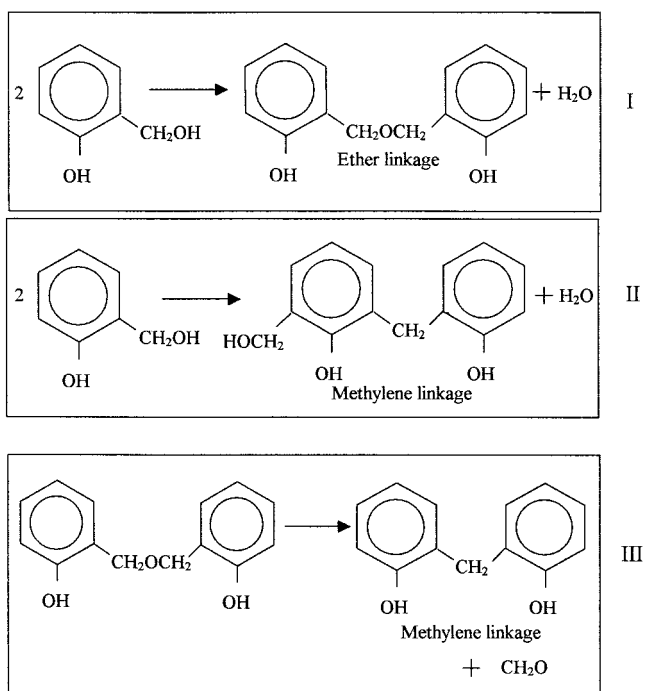


Figure 2 Chemistry of cure of resol resins.

of previous work.^{4,10} Peaks from 55 to 67 ppm are due to various kinds of ether and methyloxy carbons, and it is not possible to accurately integrate these individual peak areas. Nevertheless, it is possible to calculate the amount of substituted methylols through the well-resolved free-ortho- and para-aromatic carbon peaks according to the following method described by So and Rudin⁴:

The extent of para substituted methylols
 per phenol unit = $1 - \frac{\text{free para aromatic carbons}}{\text{phenol unit}}$ (1)

The extent of ortho substituted methylols
 per phenol unit = $2 - \frac{\text{free ortho aromatic carbons}}{\text{phenol unit}}$ (2)

Total percentage of methylation
 per phenol unit

$$= \frac{3 - (\text{free ortho and para aromatic carbons per phenol unit})}{3} \times 100$$
 (3)

The above calculation assumes that the amount of methylene bridges formed by coupling one methylol-phenol to a phenol is very small. For the result of this study, this is a valid assumption because resols are synthesized by adding an excess of formaldehyde and therefore the probability of having free phenol in the system is very low.

Values of the ratio of ortho/para-substituted methylol carbons greater than, less than, and equal to 2 indicate preferential methylation at ortho position, para position, and both ortho and para positions, respectively. Furthermore, the number of oxymethylene carbons per phenol unit, which is indicative of the polyoxymethylene oligomers (trimers to pentamers), can be measured with accuracy through ¹³C₁-NMR.

When DMSO-d₆ is used as the solvent, one of the methylene bridge carbon peaks (~ 41 ppm) is partially overlapped with the solvent peaks. To check this, acetone-d₆ was used and it was found that there was no significant peak at 41 ppm, illustrating that there was a very small amount of methylene bridges, if any, in the examined resin. Both acetone-d₆ and DMSO-d₆ do not interfere with the aromatic carbon peaks, enabling the measurement of the peak areas per unit

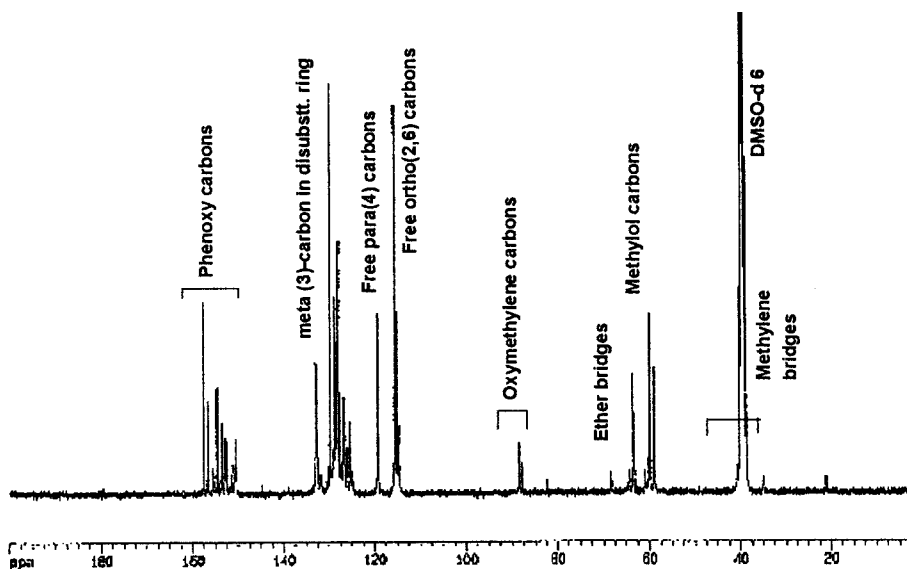


Figure 3 High-resolution ¹³C₁-NMR spectrum of BPJ2027L in DMSO-d₆.

TABLE I
Quantitative Information from $^{13}\text{C}_1$ -NMR of BPJ2027L

Chemical species	Chemical shift (ppm)	Peak area	Concentration (ppu ^a)
Phenoxy carbons	150–157	1.08	1
Free para carbons	119	0.36	0.33
Free ortho carbons	117.5–118	1.15	1.06
Ether bridge carbons	66–70	0.07	0.06
Methylene bridge carbons	31, 36, 41	~0.00	~0.00
Oxymethylenes	87–88	0.17	0.15
Para substituted methylol carbons	124–132.5	Peak not resolved	0.67 (calculated)
Ortho substituted carbons	124–132.5	Peak not resolved	0.94 (calculated)
Total concentration of methylol carbons = 52.64%			

^a ppu, per phenol unit.

phenol. Thus, in the case of BPJ2027L, either one of these could be used to make quantitative measurements. All peak intensities were measured relative to that of aromatic carbons attached to the hydroxyl group of phenol. In other words, the intensities measured are values per unit phenol (ppu). The results obtained from the calculations mentioned above are presented in Table I.

The major constituents of this resin are substituted phenols. The ratio of ortho/para-substituted carbons is 1.395, which indicates preferential methylation at the para position. At first glance, this does not seem correct as the number of ortho-substituted carbons is greater than the para-substituted carbons, but the point to be kept in mind is that the values are per phenol unit. Because there are two ortho positions and only one para position on one phenol unit, the numbers 0.935 and 0.67 actually become $0.935/2$ ($=0.467$) and 0.67. Therefore, the degree of para substitution is higher than the degree of ortho substitution, as expected. Another point that comes out of the results is that the percentage of dimers in the resin was small ($\sim 6\%$). Information regarding free phenol could not be found because the peaks were very close to the peaks of the substituted phenols and were not well resolved. However, the manufacturers have estimated the free phenol content to be 7–10% by weight. The free formaldehyde content of the resin according to the manufacturers is as much as 2.5% by weight. However, the signal representing formaldehyde did not appear in the ^{13}C spectrum, indicating that its content was low (<1 wt %). Formaldehyde exists in the form of oxymethylene oligomers $[\text{CH}_2\text{O}(\text{CH}_2\text{O})_x\text{CH}_2\text{OH}]$, as discussed earlier in the chemistry section, which manifest as oxymethylene peaks at 87–88 ppm in the spectrum. The concentration of these groups is very small (~ 0.15 ppu), as expected.

A simple representation of the resin composition can be arrived at based on the results from $^{13}\text{C}_1$ -NMR. If we assume a basis of 100 phenol units in the resin,

67 of them would have hydroxymethyl substitutions at the para position. The following scenarios are possible in this case:

1. Of the 67 para-substituted phenols units, the maximum number of trisubstituted phenol units is 46 because the total number of ortho substitutions calculated is 93. This would mean that the remaining 21 para-substituted phenol units are monosubstituted. However, the probability of mono(para)-substituted phenol units in the resin is very low because it is known that once the para position is substituted it becomes highly ortho directing.
2. If we start with one ortho position of each of the 67 para-substituted phenol units being hydroxymethylated, the number of remaining ortho substitutions is 26. There are two possibilities for these 26 remaining ortho substitutions; they are either (a) attached to the second ortho position of the 67 disubstituted phenols to form trisubstituted phenols, or (b) formed mono(ortho)-substituted phenol units. In case (a), the number of free phenol units would be 33 and in case (b), it would be 7.

The actual resin composition would, however, lie between 2(a) and 2(b) [i.e., a mixture of mono(para), diortho, and di(ortho and para)-substituted phenols along with some trisubstituted units and free phenols]. This analysis is only approximate, and there are trace amounts of other substituted phenols, as shown in Figure 4, as well as dimers and oligomers present in the resin.

EXPERIMENTAL

Thermogravimetric analysis

A DuPont 951 TGA was used to follow the weight loss in the phenolic resin during cure. DuPont 9900 ther-

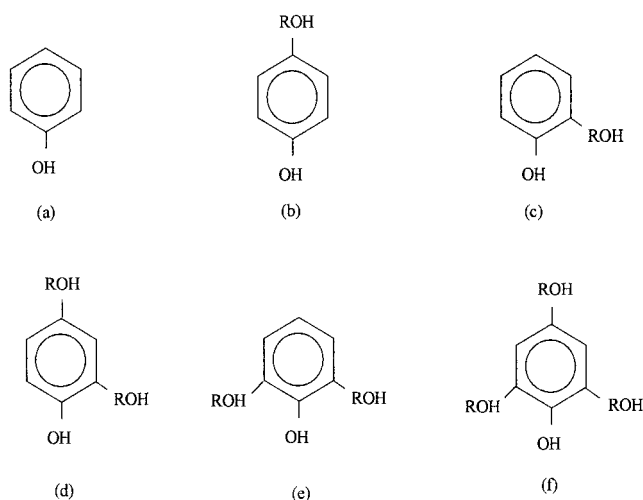


Figure 4 Various phenol units present in BPJ2027L: (a) free phenol, monosubstituted phenols, (b) at para position, and (c) ortho position, disubstituted phenols (d), at para and one of the ortho positions, (e) at both ortho positions, and trisubstituted phenols (f).

mal analyzer (TA) software interfaces with the TGA to automate control of experimental parameters and data acquisition. This instrument measures the weight loss relative to the original weight of a sample and can be subjected to a user-defined temperature program. After mixing the resin with the required amount of catalyst, the resin was poured into a quartz pan. The pan can be maintained under desired atmosphere in the heating chamber. In these experiments, it was allowed to cure under oxygen. The initial weight was measured and recorded before the run was started. The TA module recorded the change in weight with time.

Thermogravimetric analysis was conducted based on the assumption that weight loss during cure can be attributed solely to the evaporation of water. This assumption is justified because the only other substances present in the resin are phenol and formaldehyde. Phenol has a very high boiling point ($\sim 180^\circ\text{C}$), while formaldehyde is not present in its free form. Formaldehyde exists in the form of oxymethylenes in the resin and is more likely to be incorporated into the system to increase the crosslinking and thus would not escape during cure.

Density measurement

Density measurements were conducted on cured samples by using a density gradient column. The column was prepared by using sodium chloride dissolved in distilled water, such that there is a positive gradient of density with increasing depth of the column. Once the column was configured, it was allowed to stand for 24 h to stabilize, after which it was calibrated by using glass bead standards of known density. The polymer

samples used for measurement were approximately 3 mm in diameter. They were cut from cured resin plaques and filed to make them smooth and round to reduce drag and eliminate air entrapment when the samples were dropped into the column. All the samples were allowed to attain equilibrium position before recording the height. The height was then converted to density values according to the calibration curve.

Scanning electron microscopy

A JEOL 840 microscope with an accelerating voltage of 8 kV was used. The instrument was interfaced with the NIH image software to acquire digital images along with the ones on Polaroid film. Small pieces, approximately $0.5 \times 0.5 \times 0.2$ cm, were cut and glued onto aluminum studs used as holders to insert into the sample chamber of the microscope. Carbon glue was used for this purpose. These holders were then placed in a vacuum chamber and sputtered with gold to form a thin conducting layer on each sample. A conducting layer is required to observe the surface of nonconducting substances such as polymers under an electron microscope.

Testing of flexural properties

The flexural modulus of plaques of cured phenolic resin was determined according to ASTM D790-92 Standard Test Methods of Unreinforced and Reinforced Plastics and Electrical Insulating Materials, Test Method One, Procedure B. As per the ASTM standard, five specimens were tested for each condition. Samples were cut from a sheet fabricated in an aluminum mold covered with Teflon. Each specimen had a strain gauge bonded, using M-Bond 200 adhesive, on the tool surface at the center of the span. The strain gauges, of type CEA-06-125UN-350, were supplied by Micro Instruments. These were general-purpose strain gauges with fully encapsulated grid and exposed integral solder tabs with a temperature range of -75 to 200°C . There is one grid on this type of gauges to measure longitudinal strain. The strain gauge factor of $2.095 \pm 0.5\%$ with a transverse sensitivity of $0.3 \pm 0.2\%$ was entered into the LabView strain gauge module used in these experiments for data acquisition during testing with a sampling rate of 1 point per second.

An Instron 4484 testing machine equipped with a 1000-lb load cell was used with a crosshead speed of 0.05 in./min to conduct these experiments. The Instron testing machine is controlled by using the Series IX Instron data acquisition software. The sampling rate for this data acquisition was also one point per second. The ASTM-approved three-point bend fixture was used for the testing of specimens. An L/D ratio of

16 was used for all the specimens. Samples were not preconditioned prior to testing and all the tests were carried out at room temperature. The Series IX software reports the maximum load and stress once the specimen has broken. This data were recorded along with the data taken from the LabView strain acquisition software for each test. The sample dimensions were $2.65 \times 0.55 \times 0.14$ in. A span of 2.3 in. was used for all the tests.

Fracture toughness testing

The fracture toughness of cured phenolic resin was determined according to ASTM D5045-93 Standard Test Methods for Fracture Toughness and Strain Energy Release Rate of Plastic Materials, using single-edge notched bend specimen (SENB) configuration. A total of five samples was tested for each set. The ASTM standard recommends that at least three specimens be tested for each condition. Samples were cut from a sheet fabricated in an aluminum mold covered with Teflon. The specimens were first notched by machining and then a crack was initiated by sliding a sharp new razor blade across the notch root. The test method involves loading a precracked specimen in either three-point bending or tension. The standard three-point bending setup as mentioned in the section on flexural modulus testing was used for this particular set of experiments. The same 1000-lb load cell was used as well, and the crosshead speed was 0.05 in./s. All experiments were conducted at room temperature and no preconditioning was done. Load versus displacement data was obtained for each specimen. The value of the critical strain energy release rate, G_{IC} , which is a measure of the toughness of a material based on the energy required to fracture, was calcu-

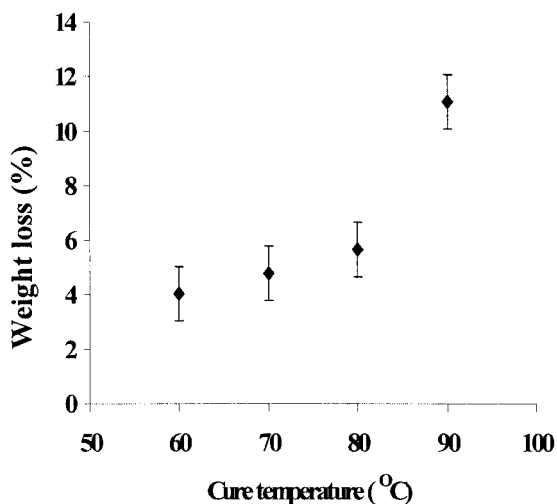


Figure 5 Effect of cure temperature on weight loss in fully cured BPJ2027L with 4% Phencat 381.

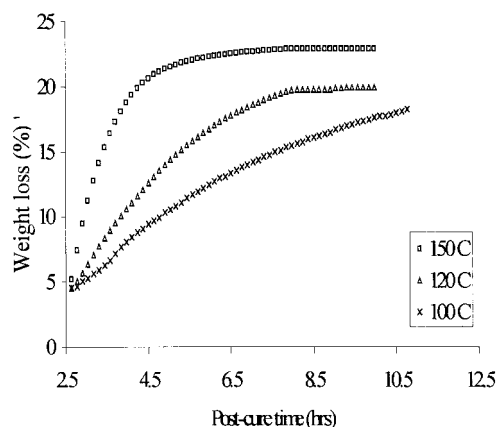


Figure 6 Effect of postcure temperature on weight loss for BPJ2027L cured at 60°C with 4% Phencat 381.

lated by using the method given in the annexes A1.5 and A1.6 in the standard ASTM D5045-93. The sample dimensions were approximately $2.75 \times 0.55 \times 0.25$ in. The crack length was about 0.24 in.

RESULTS AND DISCUSSION

Thermogravimetric analysis

There was an almost linear increase in weight loss from 60 to 80°C as seen in Figure 5, meaning that more water is eliminated during cure as the cure temperature increased. Because water is produced in each condensation step, the increase in percentage weight loss could be explained by an increase in water formation as a result of an increase in the extent of reaction, as well as an increase in evaporation with an increase in temperature. A sharp increase in the percentage weight loss was observed at 90°C. This could be attributed to the proximity to the boiling temperature of water in this case.

Figure 6 illustrates the effect of postcure temperature on the weight loss for samples cured at 60°C before beginning postcure. The rate of weight loss increased as the temperature increased. This increase was probably due to a higher rate of reaction and a consequent increase in water evolution and evaporation rate at higher temperatures. At the postcure temperature of 150°C, the ultimate weight loss (~23%) was attained after about 2.5 h of cure, whereas the curve at 120°C approached its final value in almost double that time, and its ultimate weight loss was lower than that at 150°C. When the sample was postcured at 100°C, the weight loss curve asymptotically approached 18.5%, suggesting that the final weight loss was lower than that at 120°C in this case. It can be seen from Figure 7 that although there is a slight increase in the rate during postcure with 8 wt % catalyst, the difference between catalyst concentra-

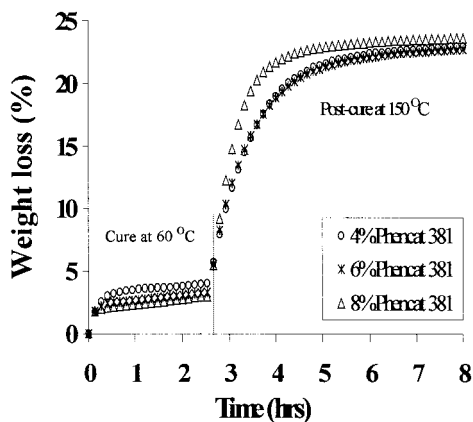


Figure 7 Effect of catalyst concentration on weight loss in BPJ2027L cured at 60°C.

tions of 4 and 8 wt % in overall weight loss during both cure and postcure is negligible.

In Figure 8(a, b), the effect of varying the diluent can be observed. This factor was found to produce the most significant change in the weight loss pattern. It was observed that there is more weight loss during cure in the case of the modified resin than the original resin. It was observed that a much higher percentage weight loss occurred during cure in the case of the modified resin in comparison to the original resin. During postcure, however, there was a very small weight loss in this resin than the original one. It may also be noted that the final value of weight loss for the modified resin was lower than the original resin.

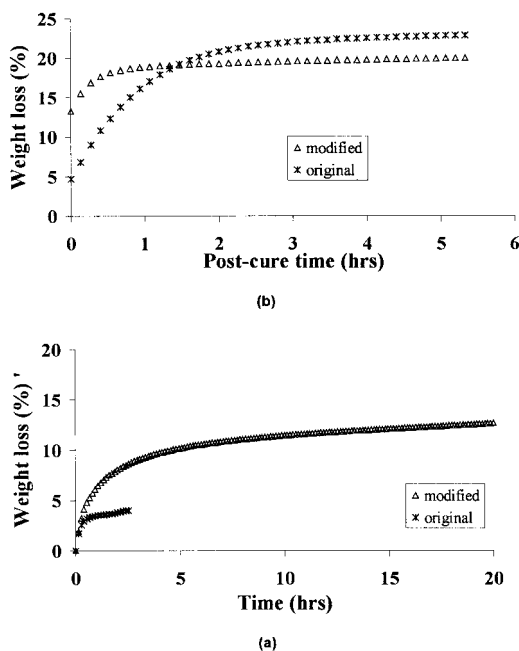


Figure 8 Effect of Ethylene glycol of BPJ2027L with 4% Phencat on weight loss during (a) cure at 60°C, and (b) postcure at 150°C.

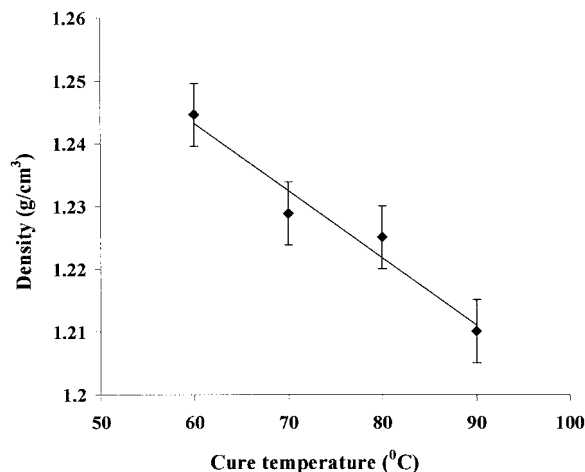


Figure 9 Effect of cure temperature on density of fully cured BPJ2027L with 4% Phencat 381.

Density trends

The density decreased from 1.244 to 1.210 g/cm³, as cure temperature increased from 60 to 90°C, as seen in Figure 9. A similar trend was observed in the weight loss results. It is shown in Figure 6 that the weight loss increases with cure temperature. Because weight loss corresponds to water loss, which is supposed to cause microvoids, a consequent decrease in density was expected. Although the trend was as expected, the point to note is that there was no sharp decrease in density at 90°C corresponding to the sharp increase in weight loss. This is probably due to the fact that along with the effect of voids there are other factors, such as cure shrinkage and extent of reaction, that affect the density. With increasing extent of cure at 90°C, an increase in crosslinking is also expected, which would lead to shrinking of the polymer. Therefore, as the void space increases due to loss of more water, the total volume shrinks due to increased crosslinking. The two compensatory effects possibly caused the density decrease to be less sharp than that expected from TGA results.

Figure 10 shows how density changes with respect to time as the postcure temperature is varied. The final density decreased with temperature, while the rate of change increased with temperature. These results are in agreement with the weight loss results, which also showed an increase in rate with postcure temperature. The values of weight loss at 150°C at all times were higher than the values at 120°C, which would translate into a lower density at 150°C. An important observation from the density results is that the time scales of the changes in density do not correspond to those of the changes in weight. Weight loss continued for approximately 8 h, while there was no further change in density after a little more than an hour of postcure. A possible reason for this behavior could be

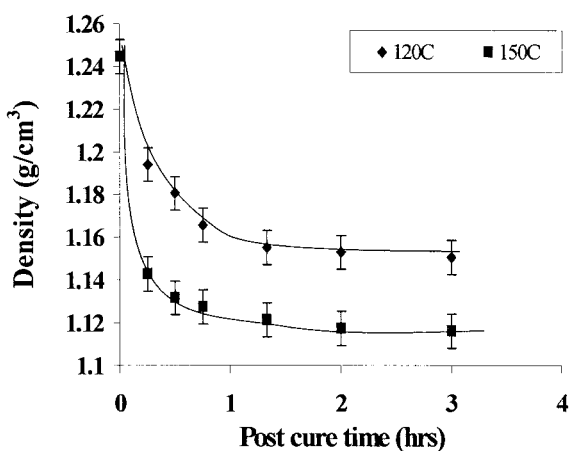


Figure 10 Effect of postcure temperature on density for BPJ2027 cured at 60°C with 4% BP Phencat 381.

that there is an extent of crosslinking beyond which the effect of cure shrinkage becomes large enough to compensate for the loss in weight, stabilizing the density values.

As was the case in weight loss experiments, it was found that changing the catalyst concentration did not have a significant effect on the behavior of the material, as seen in Figure 11. Again, the most significant effects were observed when the diluent was changed from water to ethylene glycol. A comparison of the density change with time for the original and modified resins is presented in Figure 12. There was a large difference in the densities of the final product for the two cases. Another observation that is worth pointing out is that there was almost no change in the density of the modified resin during postcure. Following in line with the thermogravimetric data, these results also show that most of the changes due to water loss in the modified resin occurred in the cure stage before

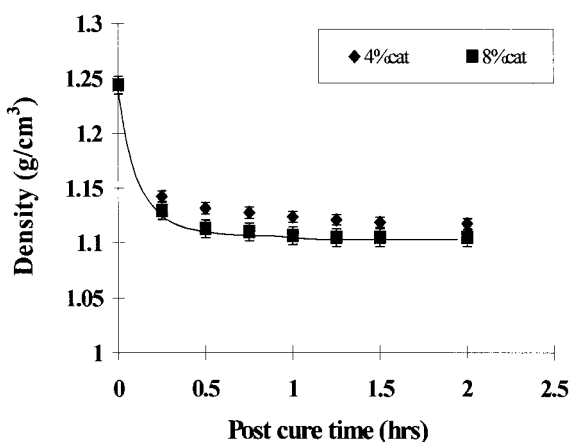


Figure 11 Effect of catalyst concentration on BPJ2027L cured at 60°C and postcured at 150°C.

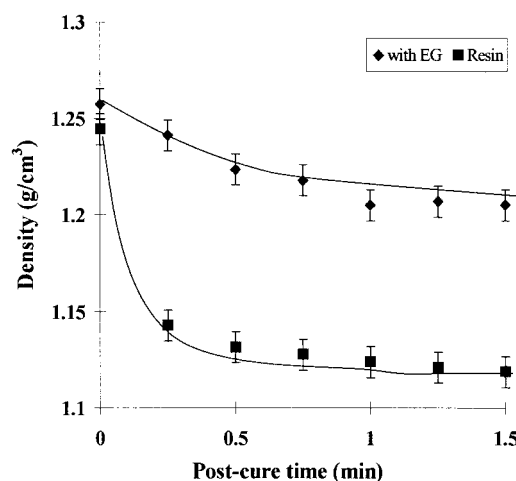


Figure 12 Effect of ethylene glycol on density resin cure at 60°C and during postcure at 150°C.

the resin had hardened. The SEM images presented in the next section shed more light on this effect.

SEM

The micrographs obtained for varying the cure/postcure temperature, catalyst concentration, and diluent are presented in Figure 13. These pictures corroborate the results of earlier experiments for weight loss and density. It has been shown that there was an increase in weight loss accompanied by a decrease in density for the resin cured at higher temperatures. These results point toward an increase in void content at higher cure temperatures. The micrographs of the original resin cured at 60 and 90°C in Figure 13(a, b), respectively, show that the content of voids was greater at 90°C. Figure 13(d, e) shows the micrographs of the original resin fully postcured at 120 and 150°C, respectively, and there appears to be a slight increase in the void content at the higher postcure temperature. The catalyst was found to have no visible effect on the void content, as seen in Figure 13(c, e). There is, however, a significant difference in the void content between the original resin and the modified resin, both cured at 60°C and postcured at 150°C, as seen in Figure 13(e, f). This agrees very well with the experimental results presented earlier where it was found that the decrease in density as well as the increase in weight loss during postcure were much lower for the modified resin than the original resin. It may be concluded that in the case of the modified resin there was more loss of water during the cure stage when the surrounding material can flow into the space left by water, resulting in a reduction in void content of the modified resin sample.

Mechanical properties

It would be reasonable to expect, at this point, that the replacement of diluent, which had a significant effect

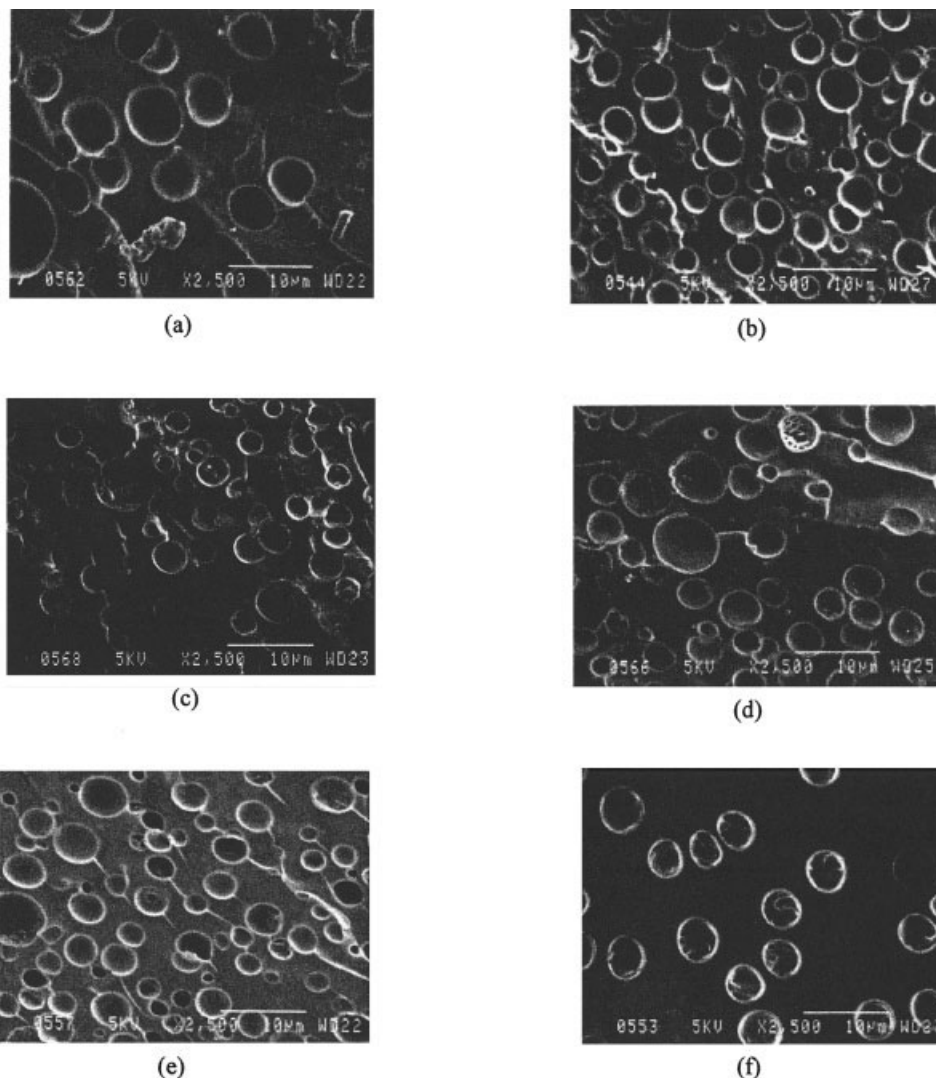


Figure 13 SEM micrographs of original and modified BPJ2027L cured under different conditions. (a) Original resin cured at 60°C; (b) original resin cured at 90°C; (c) original resin cured at 60°C postcured at 150°C with 8% Phencat 381; (d) original resin cured at 60°C and postcured at 120°C; (e) original resin cured at 60°C postcured at 150°C; and (f) modified resin cured at 60°C and postcured at 150°C (4% Phencat 381 used unless otherwise stated).

on water loss pattern and physical properties of the resin, would also manifest as an overall improvement in the mechanical properties of the final product. Therefore, flexural properties and fracture toughness were measured for the fully cured and postcured specimens of the original and modified resin systems.

Flexural properties

Flexural modulus values were measured for two sets of samples made from the original resin and the modified resin cured at 60°C and two sets that were further postcured at 150°C. The results are presented in Table II. The results show that while the flexural modulus values for the non-post-cured original and modified resin specimens were within standard deviation, there

was a definite increase in the modulus of the modified resin sample over the original one after postcure.

Fracture toughness

G_{IC} values were found for the fully postcured samples for the modified as well as the original resin. The samples were cured at 60°C and postcured at 150°C. The results are presented in Table III. It was observed that addition of ethylene glycol increased the fracture toughness more than four times with respect to the original resin. This means that a much higher energy is required for a crack to propagate in the modified resin sample relative to the original resin sample. This result is significant in light of observations made in all the experiments discussed before. Propagation of

TABLE II
Flexural Modulus Values for the Original and Modified Resin

Type of resin (BPJ2027)	Cure temperature (°C)	Post-cure temperature (°C)	Flexural modulus (MPsi)
Original	60	No postcure	0.24 ± 0.02
Original	60	150	0.37 ± 0.02
Modified	60	No postcure	0.27 ± 0.02
Modified	60	150	0.44 ± 0.03

cracks is known to be easier if there are more voids in the system and it has been shown through SEM micrographs that there are indeed a higher number of voids per unit area in the original resin, accounting for the lower G_{IC} value. Apart from the consideration of void content, another factor that would serve to make the resin tougher is the plasticization of the resin upon addition of ethylene glycol.

CONCLUSION

Experiments have shown that varying catalyst concentration had no effect on either the weight loss pattern or the density changes during cure/postcure of the polymer. Varying the cure and postcure temperature had some effect, but the most significant effects were observed when the diluent was changed to ethylene glycol instead of water. The weight loss pattern observed in the thermogravimetric analysis pointed toward the fact that most of the water evaporated during cure of the modified resin. Along with the variation in weight loss pattern, there was also a decrease in the final weight loss values from the original to the modified resin. This indicates a possibility of plasticization due to addition of ethylene glycol and also explains the large reduction of visible void content seen in the SEM micrographs.

TABLE III
Critical Strain Energy Release Rate for Modified and Original BPJ2027L

Type of resin (BPJ2027)	Cure temperature (°C)	Postcure temperature (°C)	G_{IC} (J/m ²)
Original	60	150	69 ± 6
Modified	60	150	284 ± 52

A remarkable improvement in the flexural strength and fracture toughness was observed with the addition of ethylene glycol in place of water with little effect on the molecular level. This could be attributed to the fact that ethylene glycol acts as a plasticizer by elongating the polymer chains and delaying crosslinking reactions until higher temperatures are attained. This affords more time for water to escape from the resin during cure without deleterious effects on the mechanical properties. Although the curing time was longer, the samples manufactured by using the modified resin exhibited superior mechanical properties as compared to the original resin, while still maintaining a resin viscosity low enough to facilitate injection.

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