

Impact Performance of Phenolic Composites Following Thermal Exposure

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ABSTRACT: The notched and unnotched Izod impact properties of a series of phenolic-glass composites following thermal exposure at 180°C, 300°C, and 800°C have been investigated. Four phenolic resins; a resol, a novolac, a resol/novolac blend, and a furan-novolac/resol copolymer were used to prepare the composites. The notched and unnotched impact properties of all S-glass composites improved following thermal exposure at 180°C for times up to 28 days. The best results at 180°C were obtained for the copolymer-based composite. However, thermal exposure at 300°C for times greater than 1 day led to significant reduction in the performance of this composite. The best retention of impact properties following exposure at 300°C and 800°C was found for the composite made with the resol/novolac blend. The results indicate that the impact properties of phenolic composites made with modified resins, that is, a blended resol/novolac or a furan-novolac/resol copolymer resin, improve significantly. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 349–361, 1998

Key words: phenolic; composite; impact strength

INTRODUCTION

Polymeric composites are finding wider application in the construction industry. They are of particular interest to the shipbuilding industry, largely because their high specific strength and modulus provide an opportunity for significant reductions in topside weight. Their resistance to corrosion by the marine environment is but one of the additional advantages offered by these materials.

The use of polymers in construction always raises concerns about flammability. One method of dealing with this problem has been to add fire

retardants and smoke suppressants to the resin. While this may work well in certain applications, there are some potential drawbacks with this approach. Some additives may degrade the mechanical properties of the resin. Perhaps more importantly, flame retardants designed to raise the ignition temperature and reduce the flame spread rate of a resin may increase the rate of release of smoke and toxic gases once the fire is underway.

A somewhat different approach to the problem of flammability involves the use of resins that are more resistant to heat and flame because of their particular chemical structure. Phenolic resins exhibit superior fire resistance compared to other thermoset resins such as polyesters and epoxies. They are also considerably cheaper than many high performance resins such as PEEK, making

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them more attractive for high volume applications. The fire resistance of phenolics is directly related to the structure and thermal degradation mechanisms of these polymers. The thermal degradation of phenolic resins leads to the production of a structural char which results in extremely low flame spread rates compared to polyester resins. Phenolics have a very high critical oxygen index (45–70%) and therefore are difficult to ignite and maintain in a burning condition.¹ Phenolics are also among the lowest smoke producing plastics known. In addition, phenolics produce smoke that is less toxic than most flame retardant plastics. For instance, one study has shown that, compared to a flame retardant polyester resin, a standard phenolic resin produced four times less carbon monoxide, six times less hydrogen chloride, and levels of hydrogen bromide an order of magnitude lower.² The fire resistance of phenolics can be improved even further by introducing flame retardant elements such as phosphorous or bromine. The addition of phosphorous at the monomer stage enhances significantly both the thermal stability and the limiting oxygen index of the resin compared to that obtained by the addition of phosphorous at the polymer stage.³ The addition of bromine does increase the limiting oxygen index, but at the expense of the thermal stability and the char yield.³

Phenolics also exhibit excellent dimensional stability, thermal stability, chemical resistance, and load-bearing capability at elevated temperatures. Design engineers routinely specify phenolics for close tolerance precision moldings that must function in hostile environments. The superior thermomechanical properties are directly related to the high crosslink density that results from the cure of these resins. However, the high crosslink density also results in low strains-to-failure (0.4–0.8%), which prevent the resin from yielding and which make phenolics more brittle compared to many other plastics.⁴ Impact strength is also compromised because of the evolution of water during cure and, in the case of novolacs, the formation of gas, largely ammonia. This can lead to microcracking or molded-in stresses in the final product.

The notched Izod impact strength of most commercially available phenolic resins falls in the range of 0.15 to 0.6 J/cm.⁵ Although the polymer is inherently brittle, reinforcing phenolic resins with glass fibers produces composites with impact resistance comparable to some reinforced thermoplastics.⁴ Notched Izod impact strengths for com-

posites made from impact-modified phenolic resins and short glass fibers have been reported as high as 5 J/cm.⁶ Notched Izod impact strengths of up to 8 J/cm have been reported for phenolic composites made with continuous glass fibers⁵ but the high-end impact strengths of similarly reinforced epoxies and polyesters are about double this value. Improving the relatively low impact resistance of phenolic composites has become the subject of several research and development efforts.^{6–8}

This article examines the notched and unnotched Izod impact strength of a resol and a novolac resin and two modified phenolic resins. The modified resins are a reactive blend of a resol and a novolac, and a graft copolymer made from a resol and a furan-based novolac. These types of blends and copolymers are known to have an excellent degree of molding plasticity⁹ and appeared to have good potential for increased impact strength. This is especially true because the resol is used to cure the novolac, meaning that no curing agent is needed. This reduces the amount of gas evolved during cure, and reduces the occurrence of microcracking and molded-in stresses. The literature is relatively sparse on the subject of such resins, although the toughness of phenolic resins has been shown to be improved by copolymerization with a *p*-hydroxyphenylmaleimide/acrylic ester copolymer¹⁰ and with a 4-hydroxyphenylmaleimide/*n*-butylacrylate copolymer.¹¹

Glass reinforced composites made with each of the four phenolic resins were exposed to three temperatures, 180°C, 300°C, and 800°C for different periods of time. The composites were exposed to 180°C in order to determine the effects of post-curing and to assess the impact performance of these materials after they are exposed to temperatures similar to those seen in automotive “under the hood” applications. The materials were exposed to 300°C in order to assess their performance in hostile environments for extended periods. These composites were also exposed to 800°C for one minute to give some idea of the effect of a flash fire condition on impact performance. Dynamic mechanical analysis and scanning electron microscopy were also used in an attempt to relate impact strength to structure.

EXPERIMENTAL

Materials

Resins

The four phenolic resins used in this study were supplied by Plastics Engineering Company, She-

boygan, Wisconsin. These were a resol resin (Plenco 11956), a novolac resin (Plenco 21483), a 70/30 blend of the resol and novolac resins, and a graft copolymer made from the resol and a furan-based novolac.

The resol resin was a heat curable resin produced from formaldehyde and phenol in the ratio 1.266 : 1.0. It had a number average molecular weight of 139 and a weight average molecular weight of 173.

The novolac resin was produced from phenol and formaldehyde in the ratio 1.393 : 1.0. The novolac resin had a number average molecular weight of ~ 1000 and a weight average molecular weight of $\sim 15,000$. It was a noncuring novolac upon production, but was cured by adding 10% hexamethylenetetramine (HMTA) and heating.

The phenolic blend was a heat-curable resin produced from the resol and the novolac described above. To prepare the blend, the resol and the novolac were ground separately in a laboratory Wiley mill and passed through a 0.05-in. (1.27 mm) screen. The blend was made on a small ribbon blender using 600 g of novolac and 1400 g of resol. This blended mixture was then fine-ground through an impact grinder to yield an intimate mixture having a maximum particle diameter of $\sim 10 \mu\text{m}$. This mixture was compounded on a differential two-roll heated mill. The front roll of the mill was maintained at 104°–110°C and the back roll at 26.7°–37.8°C. The milling was continued for 1.5 min after sheet formation, and then the sheet was removed, cooled, and ground.

The phenolic-furan graft copolymer was made from a resol and a furfural-based novolac. To prepare the furfural-based novolac, a mixture of phenol and furfural in the ratio 1.395 : 1.0 was placed in a flask with a mechanical stirrer, distillation condenser, and heating mantle. The mixture was heated to 66°C and sodium carbonate was added. The charge was then slowly heated to 121°C and the heating mantle removed. The reaction became exothermic and increased to 135°C where boiling commenced. The distillate was collected in a separating device and the furfural layer was periodically drawn off and returned to the batch during the course of the reaction. Distillation was continued for 3 h 40 min with the batch temperature maintained between 133° and 139°C. The resin was then discharged from the vessel and allowed to cool. The phenolic-furan novolac resin had a number average molecular weight of ~ 600 and a weight average molecular weight of ~ 2000 .

The graft copolymer was formed by adding the

furfural-based novolac to a aqueous solution of a resol made from formaldehyde and phenol in the ratio 1.14 : 1.0. The formaldehyde/phenol mixture was placed in a flask equipped with a reflux condenser and a mechanical stirrer and heated to 39°C. Sodium hydroxide and a small amount of HMTA were added and the temperature increased to 90°C over a period of 30 min. After 30 min, the reflux condenser was replaced with a vacuum distillation apparatus and the batch was rapidly cooled to 63°C under vacuum. The fine-ground phenol-furfural novolac was then added to the mixture over a period of eight minutes. During the addition, the temperature was allowed to rise slowly to 68°C. When the addition was complete, the vessel was closed and a vacuum distillation was carried out to 92°C. The graft copolymer was discharged from the vessel, cooled, and ground to pass through a 60-mesh screen. Following compounding on a differential two-roll compounding mill (front roll 121°C, back roll 27°C), it was cooled and reground.

Composites

The S-glass mats (Hexcel 4533-60-F-72) and E-glass mats (Hexcel 7533-60-S-72) were treated with a silane-based coupling agent (Dow Corning Z-6020 coupling agent). The resins were combined with methanol (10%) and blended in a high speed mixer prior to the application to the 0/90 glass fiber mats. After each treatment, the excess resin was wiped repeatedly over the surface with a rubber wiper blade to assure good penetration, and the excess wiped off. The resin-impregnated mats were heated at 90°C in an oven for 45 min. The mats were then stacked between two polished steel plates (23" \times 37") and put into the compression mold. Seventeen mats were then stacked up in the press and molded for 5 min at 145°C and 4.9 MPa. The molded composite sheets were $\sim \frac{1}{8}$ " thick. Burnout tests indicated that the glass fiber loading ranged from 64% to 68% by weight.

Thermal Aging

Thermal aging of the phenolic composites was carried out in an oven at 180°C, 300°C, and 800°C. Samples were aged at 180°C for 1 day, 2 days, 7 days, 14 days, and 28 days, at 300°C for 1 day and 7 days, and at 800°C for 1 min prior to Izod testing.

Izod Impact Tests (ASTM D-256)

Both the notched and unnotched tests were carried out according to ASTM D-256 on a 16 ft lb Izod pendulum tester made by Satec Industries. Notched specimens were cut according to ASTM D-256. The impact values were obtained by dividing the height difference indicated by the dial by the thickness of the specimen. The resulting value was then converted from ft lb in.⁻¹ to J/cm. Five replicates were obtained for each data point.

Dynamic Mechanical Analysis

The dynamic mechanical analysis was performed using a TA Instruments Model 983 Dynamic Mechanical Analyzer. The tests were carried out in the fixed frequency mode (2 Hz), and the temperature was ramped from room temperature (~ 20°C) to 350°C, at a rate of 10°C/min. The data were collected and analyzed using TA Instruments Thermal Analyst 2100 System on an IBM PC.

The samples were cut at a rate of 0.65 cm/min using a liquid-cooled cut-off saw. This saw was used to minimize the effect of frictional heating on the thermal history of the specimen.

Scanning Electron Microscopy

The electron micrographs were produced using an ISI Model DS130 Scanning Electron Microscope, with a PGTIMIX-XD X-ray and imaging microanalysis system. Specimens were sputter-coated with gold palladium to prevent charging.

RESULTS AND DISCUSSION

Phenolic Resins

Phenolic resins are produced by a condensation reaction between phenol and formaldehyde. Phenolics are divided into two broad classes, resols and novolacs.

Resols are referred to as one-step resins because they can be cured by heat alone and require no crosslinking agent. These resins are formed by reacting phenol with an excess of formaldehyde under alkaline conditions. Typical ratios of formaldehyde to phenol used in the preparation of resol resins are between 1.5 : 1.0 and 3.0 : 1.0. The reaction involves formation and addition of a quinone-type carbanion to formaldehyde [Fig.

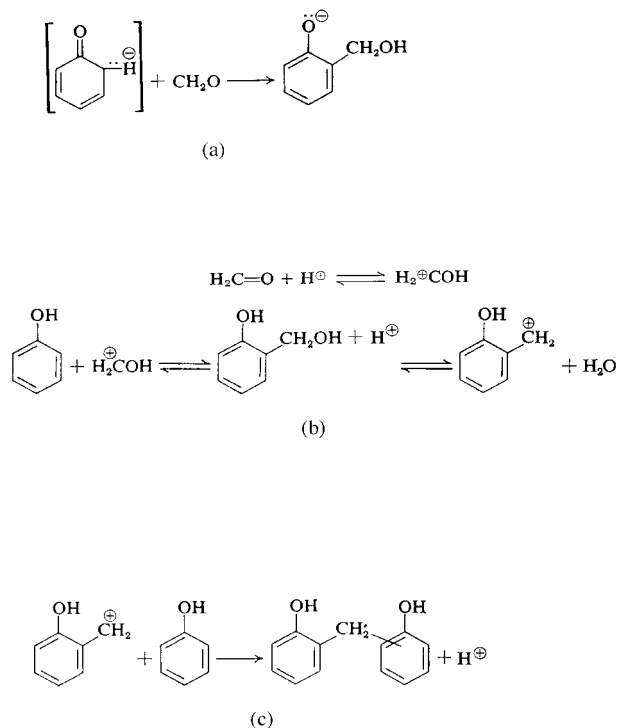


Figure 1 (a) The first step in the formation of a resol; phenol and formaldehyde react under alkaline conditions; (b) the first step in the formation of a novolac; formaldehyde is protonated reacts with phenol under acidic conditions; (c) a benzylic carbonium ion reacts with phenol to form a novolac prepolymer.¹²

1(a)].¹² This results in the formation of both *ortho* and *para* methylolphenols, which react to form dimers and trimers. The reaction tends to favor *ortho*-substituted monomers and dimers.¹³ As the oligomers are formed, *para-para* methylene bridge formation is favored over *ortho-para*, and *ortho-ortho* is not observed.¹³ These monomers, dimers, and trimers are stable and isolable, and make up the bulk of a resol resin.

The condensation of two methylolphenols proceeds more quickly than the condensation of a methylolphenol and phenol.¹⁴ The two main pathways involve the formation of either an ether linkage or a methylene linkage (Fig. 2).¹⁵ The formation of ether linkages is very unlikely under alkaline conditions, but resols are generally neutralized before crosslinking takes place. Under these conditions, ether linkages tend to predominate up to ~ 130–150°C,¹⁶ after which methylene bridges become predominant. The crosslink density depends on a variety of factors, including the formaldehyde-to-phenol ratio (high F/P ratios favor crosslinking), the pH (high pH favors crosslinking), and the type of base

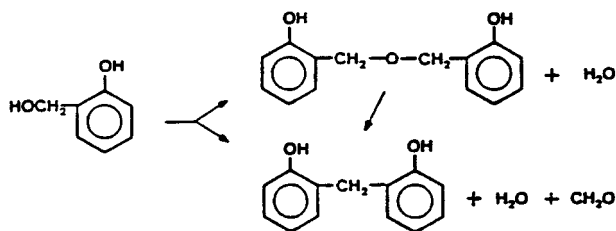


Figure 2 Condensation of methylolphenols to form dihydroxydibenzyl ether and diphenylmethane.¹⁵

used as a catalyst.¹⁷ As the temperature increases, the small size of the oligomeric prepolymers means that there are few steric barriers, which accounts for the very tightly crosslinked structure of the resol once a crosslinked network is formed (Fig. 3). Likewise, the prevalence of the stable methylene linkages accounts for the thermal stability and fire resistance of the resin.

Novolacs are prepared by reacting an excess of phenol with formaldehyde under acidic conditions. A typical ratio of phenol to formaldehyde is 1.25 : 1.00. Novolacs are two-step resins, in that they require the addition of a crosslinking agent and heat to achieve cure. Hexamethylenetetramine (HMTA), the most common crosslinking agent, is added at levels between 8% and 15%. The reaction involves the attack of a carbonium ion on an aromatic ring [Fig. 1(b)].¹² Once again this results in the formation of both *ortho* and *para* methylolphenols. The difference in this case is that the monomeric methylol derivatives are present only transiently in very small concentrations.¹² Under acidic conditions, methylol groups are converted to benzylic carbonium ions, which react quickly with other phenolic nuclei by electrophilic substitution

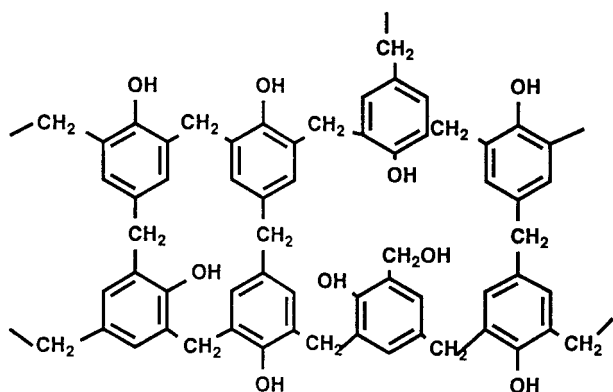


Figure 3 Structure of a cured resol phenolic resin.

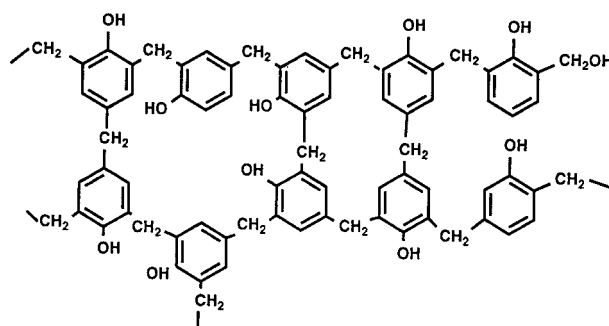


Figure 4 Structure of a cured novolac resin.

reactions to form dihydroxydiphenyl methanes [Fig. 1(c)].¹² Methylene bridge formation takes place at both the *ortho* and *para* positions, but the *para* linkages are favored.¹² The slight excess of phenol prevents uncontrolled crosslinking, resulting in relatively linear prepolymers that are much larger than those of the resol.

Cure is achieved via the methylene groups provided by a crosslinking agent. The use of HMTA results in the formation of both methylene linkages and benzylamine linkages, and the release of ammonia. At temperatures above 140°C, the benzylamine groups largely decompose, but even at temperatures up to 190°C, the nitrogen content of the products may still be above 6%.¹² The HMTA cure results in a highly crosslinked structure (Fig. 4).

Although the resol/novolac blend contained 30% novolac, no curing agent was added to this resin. The *ortho* and *para* positions of the novolac are active with respect to the methylol groups of the resol resin and are positions where crosslinking takes place during the cure of the blend.

Similarly, the copolymer was without the addition of curing agent. As was the case with the resol/novolac blend, the *ortho* and *para* positions of the novolac resin are active with respect to the methylol groups of the resol. Crosslinking at these sites leads to the cure of the copolymer.

One of the goals of preparing the blend and the copolymer was to produce resins with modified structures, for instance, less highly crosslinked than the resol or novolac phenolic resins. If a less highly crosslinked structure results, then the resins might exhibit higher strains to failure and higher impact strength, while maintaining most of their high temperature properties. In addition, the absence of added curing agents, such as HMTA, means that less gas would be released

Table I Effect of Thermal Exposure at 180°C on Notched and Unnotched Izod Impact Energy

Resin (Glass Type)	Notched Izod Energy (J/cm)					
	0 Days	1 Day	2 Days	7 Days	14 Days	28 Days
Resol (S)	9.4 ± 0.9	9.6 ± 0.5	10.1 ± 0.7	9.3 ± 1.0	10.4 ± 1.1	10.7 ± 1.4
Resol (E)	7.7 ± 0.5	5.9 ± 1.0	5.8 ± 0.4	5.0 ± 0.5	6.6 ± 0.6	5.3 ± 0.9
Novolac (S)	10.6 ± 1.1	10.7 ± 0.4	11.1 ± 1.9	10.3 ± 1.1	9.6 ± 0.9	10.1 ± 1.1
Blend (S)	7.7 ± 0.2	8.3 ± 0.5	9.3 ± 1.1	9.6 ± 0.7	8.4 ± 2.6	9.1 ± 0.9
Copolymer (S)	7.5 ± 0.6	8.8 ± 0.6	9.1 ± 0.8	10.1 ± 0.6	10.1 ± 1.9	13.6 ± 1.3
	Unnotched Izod Energy (J/cm)					
	0 Days	1 Day	2 Days	7 Days	14 Days	28 Days
Resol (S)	10.9 ± 2.6	10.5 ± 1.0	11.3 ± 0.6	12.5 ± 0.4	10.8 ± 0.9	11.5 ± 0.7
Resol (E)	11.8 ± 1.0	12.0 ± 0.7	11.4 ± 1.4	14.0 ± 1.6	10.5 ± 1.1	12.2 ± 2.4
Novolac (S)	12.1 ± 1.1	13.6 ± 5.2	11.2 ± 0.8	11.5 ± 3.1	9.8 ± 1.3	10.6 ± 3.4
Blend (S)	11.0 ± 0.6	14.7 ± 2.2	14.5 ± 1.6	13.7 ± 1.8	13.7 ± 1.2	16.7 ± 2.2
Copolymer (S)	13.1 ± 3.4	15.6 ± 2.2	19.9 ± 1.6	20.5 ± 2.1	15.5 ± 2.3	19.9 ± 1.7

during cure, thereby reducing microcracking and molded-in stresses.

Izod Impact Test Results

The notched and unnotched Izod impact strengths of the five phenolic composites, resol/E-glass, and resol, novolac, blend, and copolymer with S-glass, before and after aging at 1, 2, 7, 14, and 28 days at 180°C, are shown in Table I. The notched and unnotched Izod impact strengths of the five phenolic composites after aging for 1 and 7 days at 300°C, and for 1 min. at 800°C are shown in Table II. The notched Izod test gives some idea of the energy required to propagate a standardized crack through a material, while the unnotched Izod test is a measure of the energy required to both initiate and propagate a crack. Although Izod test data cannot be used by designers directly, it is a good first step in characterizing the impact resistance of a material. The effect of thermal exposure on the impact strength of the composites will be discussed in the following sections.

Exposure to 180°C

All of the composites, with the exception of the blend, had initial notched Izod impact strengths of at least 8 J/cm with the novolac/S-glass composite having the highest (10.6 J/cm). After exposure at 180°C for 1 day, the notched Izod strengths decreased for the resol/E-glass compos-

ite, varied little for the resol/S-glass and novolac S-glass composites, and increased for the blend/S-glass and copolymer/S-glass composites. These notched Izod impact strengths put the S-glass composites at or above the high-end published values for phenolic composites.

The unnotched Izod impact strengths of the unaged composites were between 11 and 13 J/cm. Two of the composites, the blend/S-glass and the copolymer/S-glass, showed considerable improvement in impact strength following exposure for 1 day at 180°C. Comparison of the unnotched and notched Izod impact strengths of the phenolic composites indicated that the unnotched strengths were higher than the notched strengths before and after 1 day at 180°C. This was expected, as the impact strengths of the unnotched samples represent the energy required for both crack initiation and propagation.¹⁸

The notched impact strengths of the five composites are plotted against exposure time at 180°C in Figure 5. Exposure times varied from 1 day to 28 days. It can be seen in Figure 5 that the notched impact strengths of the composites vary little for aging times between 1 day and 14 days. After 28 days at 180°C, the copolymer/S-glass composite had the highest notched Izod impact strength (13.6 J/cm). This value was more than 50% higher than the best published notched Izod impact strength for a phenolic composite⁵ and is in the range of many glass-reinforced polyester and epoxy resins.

The unnotched impact strengths of the five

Table II Effect of Thermal Exposure at 300°C and 800°C on Notched and Unnotched Izod Impact Energy

Resin (Glass Type)	Notched Izod Energy (J/cm)		
	1 Day at 300°C	7 Days at 300°C	1 min at 800°C
Resol (S)	8.1 ± 0.4	3.2 ± 0.4	3.4 ± 0.6
Resol (E)	4.1 ± 0.6	2.4 ± 0.3	1.3 ± 0.5
Novolac (S)	10.0 ± 1.8	3.7 ± 1.2	4.8 ± 0.6
Blend (S)	6.4 ± 0.6	6.2 ± 0.9	4.9 ± 0.4
Copolymer (S)	10.1 ± 1.1	0.4 ± 0.1	2.6 ± 0.6

Resin (Glass Type)	Unnotched Izod Energy (J/cm)		
	1 Day at 300°C	7 Days at 300°C	1 min at 800°C
Resol (S)	8.9 ± 0.9	5.7 ± 0.3	5.8 ± 1.3
Resol (E)	6.6 ± 1.0	6.9 ± 0.7	2.4 ± 0.7
Novolac (S)	10.5 ± 1.7	5.8 ± 0.9	5.4 ± 0.7
Blend (S)	10.2 ± 1.2	11.2 ± 1.2	9.8 ± 1.5
Copolymer (S)	18.6 ± 1.7	0.7 ± 0.2	4.9 ± 0.9

composites are plotted against exposure time at 180°C in Figure 6. Time of exposure at 180°C had very little effect on the unnotched Izod impact strength of the resol/S-glass and novolac/S-glass composites, while the unnotched Izod impact strengths of the blend/S-glass and copolymer/S-glass increased relative to their unaged values.

The results for the resol/S-glass and the resol/E-glass composites illustrated the fact that the strength of the reinforcing fiber has a greater effect on notched Izod impact strength than on unnotched Izod impact strength. The unnotched Izod performances of the two resol composites were similar, but the resol reinforced with S-glass per-

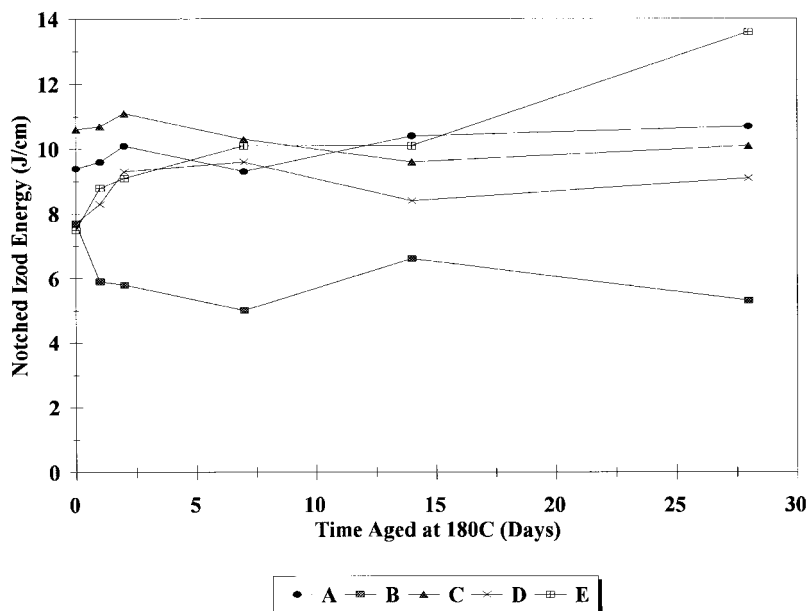


Figure 5 Notched Izod energy of phenolic composites exposed to 180°C; (A) resol (S-glass), (B) resol (E-glass), (C) novolac (S-glass), (D) blend (S-glass), (E) copolymer (S-glass).

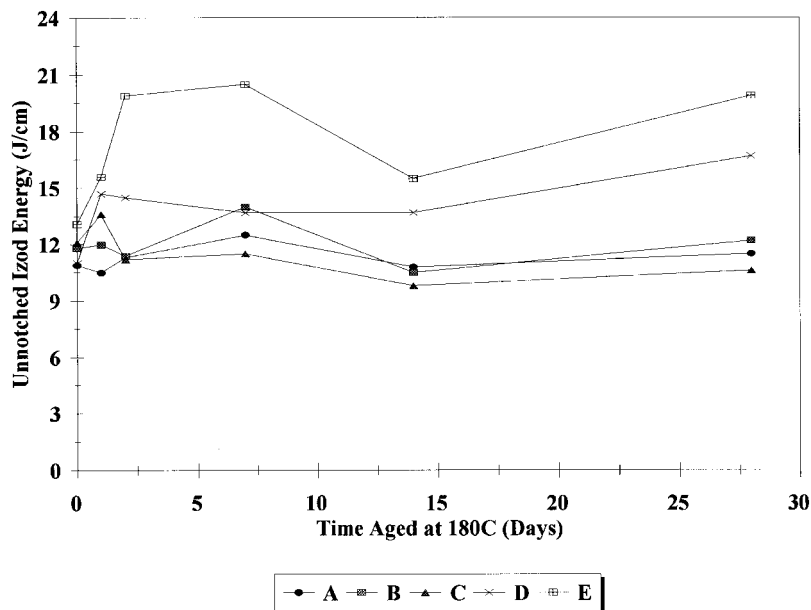


Figure 6 Unnotched Izod energy of phenolic composites exposed to 180°C; (A) resol (S-glass), (B) resol (E-glass), (C) novolac (S-glass), (D) blend (S-glass), (E) copolymer (S-glass).

formed significantly better than that reinforced with E-glass in the notched Izod test. The superior performance in the notched Izod test was due in part to the higher strength of the S-glass fibers (85.5 MPa vs. 72.4 MPa).¹⁹ Since the crack was already in place, matrix cracking took place more readily and fiber failure became the chief mode of energy absorption. Several researchers^{20,21} working with carbon fibers have demonstrated that materials made with fibers having a higher failure strength will offer better notched impact resistance. Similar results have been observed following low-velocity impact tests on E- and S-glass fiber composites.²² The results of this study confirmed these findings. The lack of a significant difference in the unnotched Izod impact strengths of these materials, in spite of the higher strength of the S-glass, underlined the significance of the matrix properties in the unnotched test.

Figures 7–9 show plots of $\tan \delta$ versus temperature for the five phenolic composites prior to aging, after aging for 1 day at 180°C, and after aging for 14 days at 180°C. $\tan \delta$ is the ratio of the loss modulus to the storage modulus of a material, and gives an indication of the relative contributions of the elastic and viscous characteristics of that material to its dynamic properties. Its maximum occurs in the area of the glass transition of a polymeric material, that is, the temperature at which the material changes from a hard,

glasslike material to a softer, rubberlike material. It has been used to evaluate the effects of post-curing and heat aging²³ on the dynamic response of materials.

For the unaged materials, the blend had the highest $\tan \delta$ peak, the two resols the lowest, and the novolac and the copolymer intermediate values. The multiple peaks in the $\tan \delta$ versus temperature plots for the novolac composite is indicative of an undercured material.²⁴ The multiple peaks are thought to arise from the continuing cure of the material. As the material is heated through its glass transition, mobility within the polymer increases and cure (crosslinking) of the resin continues. This increases the glass transition temperature of the polymer and $\tan \delta$ goes through another maximum.

For thermosetting polymers, the maximum in the $\tan \delta$ versus temperature plot moves to higher temperatures and the magnitude of $\tan \delta$ decreases as cure proceeds. Comparison of the Figures 7–9 indicated that the temperature of the maximum value of $\tan \delta$ increased with aging time and the magnitude of $\tan \delta$ decreased with aging time for each of the composites. This change in the dynamic response of the composites is consistent with the post-cure, that is, increased crosslinking of the resin. In general, increased crosslinking is associated with an increase in brittleness of a thermosetting resin. For a resin with no

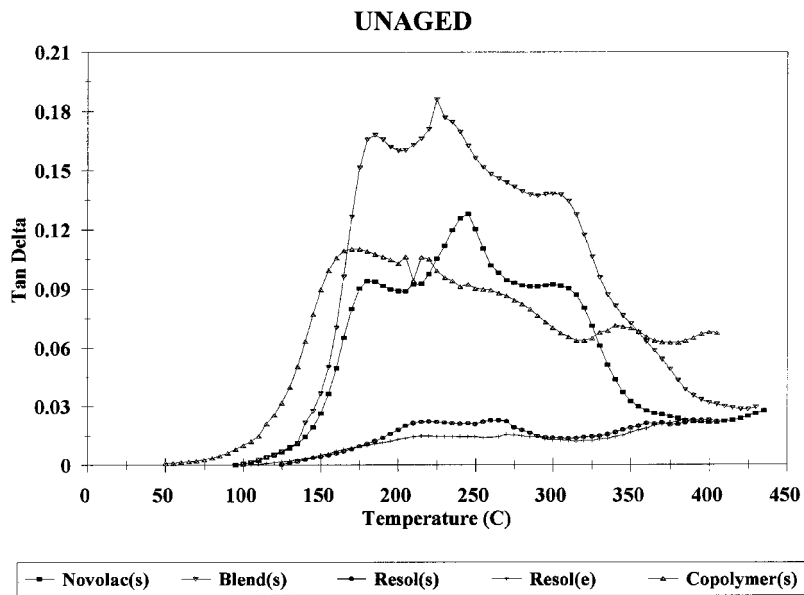


Figure 7 $\tan \delta$ versus temperature data for unaged phenolic composites, as measured by dynamic mechanical analysis.

reinforcing fibers this might also be expected to lead to a reduction in impact strength. However, in a composite the interaction between the resin and the reinforcing fiber must also be considered, and the results in Table I indicate that the impact strength of the S-glass composites improved following thermal aging at 180°C.

It has been observed¹⁸ that if an impact load is

applied perpendicular to the fibers, good adhesion is required for even moderate impact strength. By contrast, if an impact load is applied parallel to the fibers, the highest impact strengths are obtained if the adhesion is relatively poor and the fibers are short, so that maximum energy can be dissipated by mechanical friction during the pull-out process and by debonding of the fibers. Since

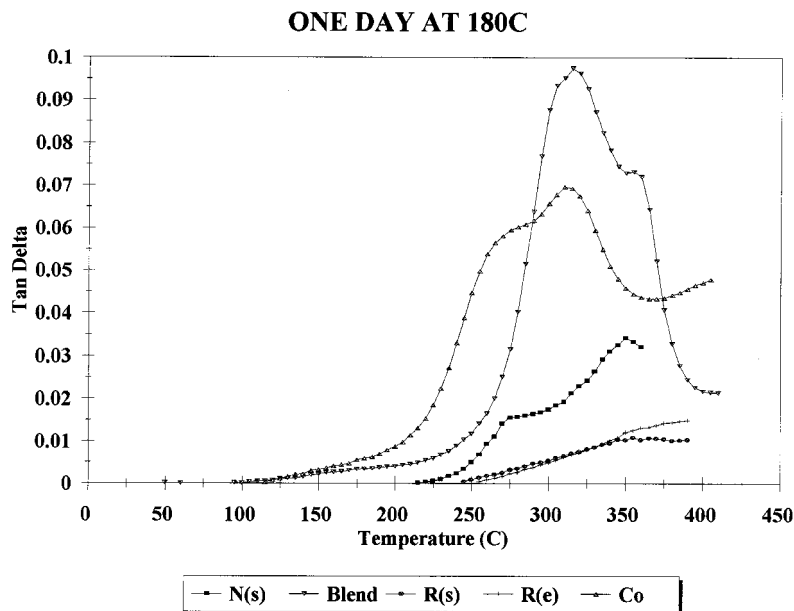


Figure 8 $\tan \delta$ versus temperature data for phenolic composites aged for 1 day at 180°C, as measured by dynamic mechanical analysis.

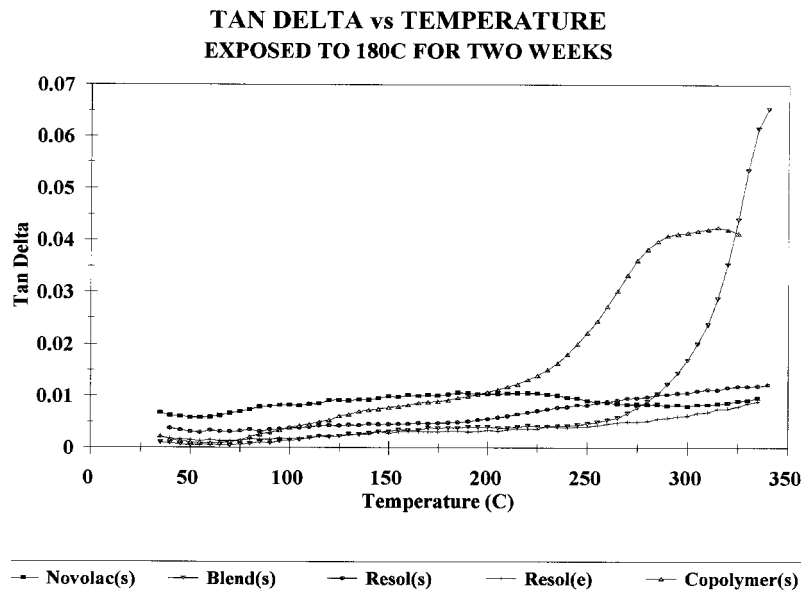


Figure 9 Tan δ versus temperature data for phenolic composites aged for 14 days at 180°C, as measured by dynamic mechanical analysis.

the fibers perpendicular to the application of the load bear most of the load in an Izod test, the improvement of the interfacial bond is the best explanation of the improvement in notched Izod strength of the postcured in spite of the increased crosslinking of the resins.

Exposure to 300°C and 800°C

Resol and novolac resins have been found to be stable up to $\sim 300^\circ\text{C}$.¹⁵ Very little decomposition is observed and weight loss is relatively small (1–2%). Most of that consisted of water and unreacted phenol and formaldehyde which was entrapped during cure. Decomposition starts around 300°C, mainly by random chain scission; no depolymerization takes place.¹⁵ Aging at 300°C therefore gives some idea of the impact performance of these materials following exposure to a temperature where degradation can take place.

The notched and unnotched Izod impact strengths of the novolac/S-glass composite decreased slightly, while those of the two resol composites decreased substantially after one day of exposure at 300°C. For instance, the notched and unnotched impact strengths of resol/E-glass composite decreased by $\sim 50\%$ following 1 day at 300°C. The impact strength of the blend/S-glass composite varied little after one day, while the impact strengths of the copolymer/S-glass composite increased, particularly the unnotched Izod impact strength.

After a week at 300°C, the notched and unnotched impact strengths of the resol composites and the novolac/S-glass composite decreased by 50–75% of the values for the unaged composites. Exposure of the copolymer/S-glass composite for 7 days at 300°C led to a large reduction in impact strength. This was in contrast to the effect of 1 day at 300°C, where the copolymer/S-glass composite had the highest impact strength.

The decline in performance of all of the composites is most likely related to thermal decomposition and the breakdown of the bonds at the fiber/resin interface of the composites. The precipitous decline in the impact strengths of the copolymer/S-glass composite has been attributed to the breakdown of the furan rings of the furan-based novolac portion of the resin. The ether linkage in these rings would be expected to be more thermally labile than other bonds in the resol and novolac resins and cleavage would lead to degradation of the copolymer structure. This would account for the highly accelerated degradation of the impact properties of the copolymer composite following extended exposure at 300°C.

The blend/S-glass composite had the highest notched and unnotched impact strengths following exposure at 300°C. As the resin used in this composite was a 70/30 blend of a resol and the novolac resin, the improved retention of impact strength implies that this is due to differences in the structure relative to either the resol or the novolac resin.

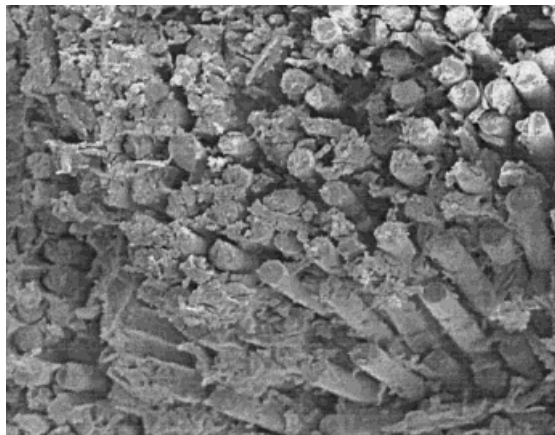


Figure 10 Fracture surface of unaged resol reinforced with S-glass. Magnification $\times 500$.

Researchers have found that reactive blending of novolacs with resols substantially increases the flame leaching time for materials subjected to the oxyacetylene torch test (ASTM E-285-65T).²⁵ In this test, one side of a panel is exposed to the flame of an oxyacetylene torch (heat flux ~ 835 W/cm²) and the time is measured until flame seeps through the material (leaching) and until a hole is made through the material (burn-through). It was postulated that the leaching of a flame through the material was due to microcrack formation in the specimen during high-temperature oxidation, and that flame burn-through was due to breakdown of the entire structure. The resol had a long burn-through time, but did not yield easily and was susceptible to a greater degree of microcrack formation. This reduced flame leaching time. As the proportion of novolac increased, the flame leaching time increased. This suggested that changes in the structure of the resin introduced by adding novolac, for instance a decrease in crosslink density, retarded microcrack formation during high-temperature treatment.

Exposure to 800°C for one minute degraded the notched Izod impact strengths of the composites. The copolymer/S-glass and the resol/S-glass composites lost approximately two-thirds of their notched Izod strength, while the resol/E-glass composite lost $\sim 80\%$. The notched impact strength of the blend/S-glass composite was only reduced by 15%, while the novolac had roughly the same notched Izod strength as the blend after exposure, but it had lost over 50% of its initial value.

The unnotched Izod strengths of the composites were also degraded by exposure at 800°C for 1

min. The best performance was exhibited by the blend/S-glass composite, which retained $\sim 90\%$ of its unnotched Izod strength. This suggests that blending led to a modified structure that lessened the effect of thermal exposure on the impact properties of the resin and composite.

Scanning Electron Microscopy

The assertion that improvement in Izod impact strength following aging at 180°C is related to improved bonding at the fiber/resin interface may be supported by the comparison of several electron micrographs of the failure surface of the Izod samples. Figure 10 and 11 show the fracture surface of the unaged resol/S-glass composite and the unaged blend/S-glass composite. These two materials exhibit comparable Izod impact performance, and they both appear to have a significant degree of adhesion between the resin and the fibers.

In contrast to the unaged case, the blend/S-glass composite had a notched Izod impact strength $\sim 50\%$ greater than that of the resol/S-glass and an unnotched Izod strength was almost twice that of the resol/S-glass composite after exposure at 800°C for 1 min. Figures 12 and 13 show the fracture surface of the blend/S-glass composite and resol/S-glass composite respectively following exposure at 800°C for 1 min. There is a considerable degree of adhesion between the resin and the fibers at the fracture surface of the blend/S-glass composite, while very little resol remains on the fibers at the fracture surface of the resol/S-glass composite after exposure to 800°C.

Figures 14 and 15 show the fracture surfaces

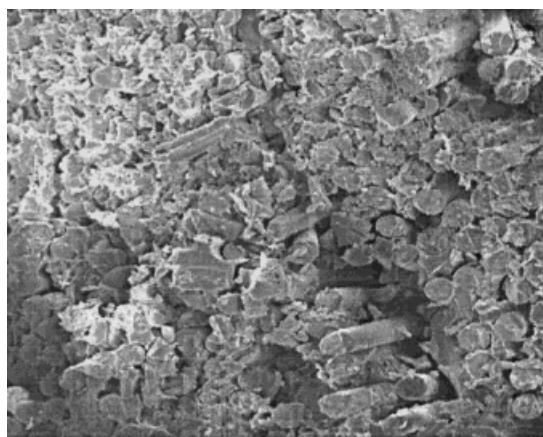


Figure 11 Fracture surface of unaged blend reinforced with S-glass. Magnification $\times 500$.

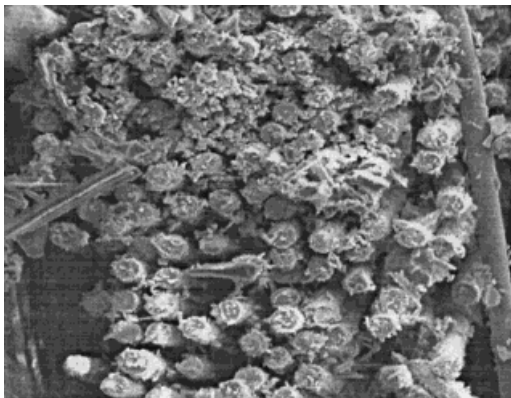


Figure 12 Fracture surface of blend reinforced with S-glass exposed to 800°C for 1 min. Magnification $\times 500$.

of blend/S-glass composite following thermal aging at 180°C for 4 weeks and 300°C for one week, respectively. More specifically, the figures show fibers exposed when the samples were split parallel to the long axis of the Izod specimens. The blend/S-glass had a higher impact strength after exposure to 180°C for 4 weeks than it did after exposure to 300°C for 1 week, that is, notched and unnotched Izod values were $\sim 50\%$ greater for the composite aged at 180°C. Again, the specimen with the higher impact strength exhibits a greater degree of resin adhesion to the glass fiber.

CONCLUSIONS

Exposure to 180°C led to improved impact properties for all composites except the resol E-glass composite. The improvements to the notched Izod

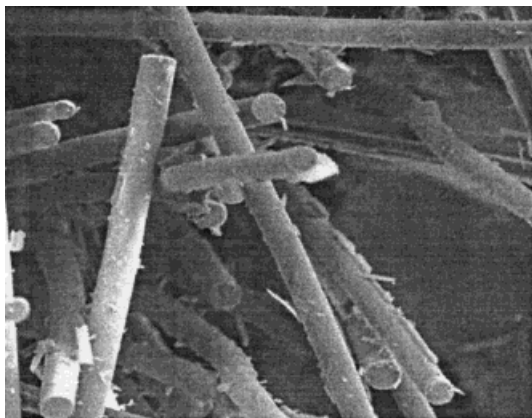


Figure 13 Fracture surface of resol reinforced with S-glass exposed to 800°C for 1 min. Magnification $\times 500$.

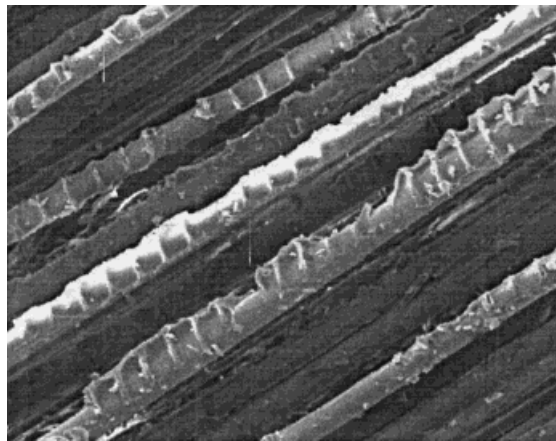


Figure 14 Exposed fibers of blend reinforced with S-glass after 4 weeks at 180°C. The specimen was split longitudinally up from the fracture surface. Magnification $\times 500$.

impact strength in most cases resulted in significantly better performance than is recorded in the literature for phenolic composites. This suggests that embrittlement of the resin that might result from thermal exposure (postcure) is more than offset by other factors, such as improved fiber/resin bonding.

The copolymer had the highest notched impact values, while the copolymer and blend had the highest unnotched impact values after exposure at 180°C. Dynamic mechanical analysis indicated that the copolymer and blend had higher $\tan \delta$ values (lossier structures) than the resol or the novolac at elevated temperatures. This suggests that the structure of the copolymer and blend

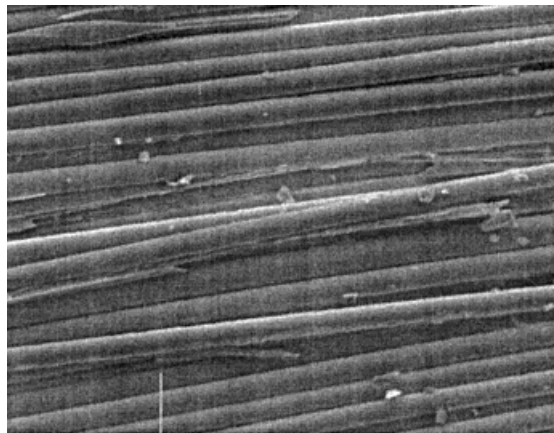


Figure 15 Exposed fibers of blend reinforced with S-glass after 1 week at 300°C. The specimen was split longitudinally up from the fracture surface. Magnification $\times 500$.

were also different from the resol and novolac resins. However, an equally important factor might be differences in the interaction between the resins and the glass fibers via the silane coupling agent. Strong interfacial bonding is a key determinant of impact resistance in composites when the load is applied perpendicular to the fibers.

Impact performance of the composites declined when the exposure temperature was increased to 300°C. The copolymer performed well after one day of aging at this temperature, but both notched and unnotched Izod strengths fell to nearly zero after one week of exposure. It is postulated that this was due to the degradation of the furan rings in the copolymer, which led to degradation of the resin structure. The resol/novolac blend exhibited the best retention of impact properties following exposure at 300°C. Dynamic mechanical analysis suggests that the blend, like the copolymer, has a less highly crosslinked (lossier) structure than the resol or novolac composites. This type of structure has been shown to resist microcracking when exposed to thermal stress.²⁵ This may also account for the 85–90% retention of impact strength by the blend after exposure to 800°C, whereas that of the other materials was degraded sharply.

FURTHER WORK

The relative contributions of changes in resin structure and the resin/fiber interface to the impact properties of phenolic composites require further experimentation. Dynamic mechanical analysis, swelling experiments, and impact studies will be carried out on the neat resin in an effort to correlate changes in resin structure to changes in impact properties. Fiber pullout tests will be conducted to gauge the effect thermal exposure on the strength of the fiber/resin bond.

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