Synthesis and Characterization of Phenolic Resole Resins for Composite Applications

J. E. SHAFIZADEH, S. GUIONNET, M. S. TILLMAN, J. C. SEFERIS

Polymeric Composites Laboratory, Department of Chemical Engineering, University of Washington, Seattle, Washington 98195–1750, USA

ABSTRACT: In this study, phenol–formaldehyde resins catalyzed with sodium hydroxide, triethylamine, and ammonium hydroxide were investigated and characterized in terms of their degradation behavior, flammability, mechanical properties, and chemical structure. All three resins displayed similar degradative mechanisms, and their degradation behavior was broken down into three distinct stages. These stages were attributed to the evolution of water, the volatilization of species loosely bound to the phenolic backbone, and bulk degradation of the phenolic matrix. Flammability studies were also performed on glass fiber laminates manufactured from these resins. The sodium-hydroxide- and ammonium-hydroxide-catalyzed resins were found relatively inflammable, while the triethylamine-catalyzed laminates burned readily. The mechanical properties of the resins were found to be similar or higher than the mechanical properties of other untoughened epoxies or thermosetting resins. The various chemical properties responsible for these behaviors are discussed and analyzed in terms of the catalyst basicity, solubility, and boiling point. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 505–514, 1999

Key words: phenolic resins; composites; degradation behavior; chemical structure; mechanical properties

INTRODUCTION

Phenolic resins have been a staple product of the synthetic polymer industry for the past 90 years.[1] These resins have been used extensively in the production of molded plastics, wood products, and aerospace components.[2] In constructing aerospace components, the most important use of phenolic resins is in the manufacturing of high-performance composites.

In the production of composites, both acid-(novolak)- and base-(resole)-catalyzed phenolic materials are used. Phenolic resins and powders have found diverse applications in filament winding, sheet molding compounds, honeycomb structures, prepregs, and resin transfer molding.[3] In these applications, phenolic resins are used as matrices to protect and reinforce the fibers contained within the composite structure. Phenolics have found wide utilization in these fields due to their high strength retention at elevated temperatures and low fire, smoke, and toxicity properties. However, the use of phenolics has historically also been limited due to a lack of understanding regarding their mechanical properties and fracture mechanics, as well as health concerns.[4,5]

Although a great deal of work has been done specifically in the fields of kinetic characterization,[6,7] reaction modeling,[8–10] flammability,[11–13] thermal analysis,[14–16] degradation,[17–20] mechanical performance,[4,21] and chemical analysis,[22,23]

complete investigations of these phenolic resole materials from synthesis to final performance have been limited. In this study, phenol–formaldehyde model resins catalyzed with sodium hydroxide, triethylamine, and ammonium hydroxide were synthesized and characterized in terms of their degradation behavior, flammability, chemical structures, and mechanical properties in both neat resins and fiber-reinforced composites. Ultimately, this work can be used to develop a fundamental understanding of the complex design decisions in developing phenolic resins for composite structures.

EXPERIMENTAL PROCEDURE

Resin Synthesis and Processing

The phenolic resins studied in this article were synthesized using phenol, formaldehyde, and one of three basic catalysts. The phenol (99%+), formaldehyde (37% formaldehyde in water with 7–8% methyl alcohol), triethylamine (TEA) (99%+), aqueous ammonium hydroxide (28% NH_3), and sodium hydroxide (98.6%) used were obtained from Aldrich Chemicals. The resole phenol–formaldehyde resins investigated were prepared with a catalyst-to-formaldehyde-to-phenol molar ratio of 0.2 to 1.5 to 1.0, respectively.

In synthesizing each resin, phenol crystals were dissolved in formaldehyde at room temperature. One of the three catalysts was then added to the solution of phenol formaldehyde. The phenol formaldehyde solution was charged into a three-neck flask equipped with a reflux condenser and mixed. The phenol formaldehyde solution was stirred and heated to 80°C. The solution was held at 80°C for 60 min. Following the 80°C hold, the phenol–formaldehyde resin was cooled to room temperature and placed in a vacuum oven at 50°C with an absolute pressure of 4.8 kPa for 8 h to remove any water present in the resins.

Neat resin plaques and laminates were fabricated in an autoclave. During processing, the autoclave temperature was ramped at 2.7°C/min from 27 to 150°C, held for 2 h, ramped to 177°C at 2.7°C/min, held for 2 h, then ramped back down to 27°C at 2.7°C/min. The total compaction pressure used during cure was 1.4 MPa, and a nitrogen atmosphere was employed in all cure cycles. All plaques and laminates were postcured at 130°C for 4 h at a pressure of 4.8 kPa.

Chemical Analysis

Chemical analysis was performed on neat resin plaques using gas chromatography–mass spectroscopy (GS–MS) after thermal desorption. This analysis was performed on a Scientific Instruments short path thermal desorber accessory unit TD-1 interfaced into a Varian 3400 capillary gas chromatographer. Specimens were heated at a rate of 2°C/min to 400°C. The GC analysis was coupled with a Finnigan MAT 90/95 high-resolution magnetic sector mass spectrometer, which scanned from 10 to 450 amu at a rate of 1 s per decade.

Thermal Analysis

High-resolution thermal gravimetric analysis (TGA) was performed with a TA Instruments 2950 Hi-Res® TGA interfaced to a TA 3100 Thermal Analyst System. Hi-Res® TGA specimens were ramped at 5°C/min to 1000°C in both air and nitrogen environments at a level seven resolution.

Flammability

All flammability specimens were manufactured with four plies of 7781 style fiberglass fabric with a soft A1100 finish. All laminate specimens had a resin content of 39–40%.

In determining the flammability properties of aerospace materials, flame spread, heat release, and smoke evolution are critical properties for evaluation. Measurements for flame spread were done in accordance with Boeing Specification Standard (BSS) 7230.[24] Specimens measuring 7.6 by 30.5 cm were conditioned in a chamber at 21°C with 50% relative humidity for 48 h, then placed vertically in a test cabinet. The specimens were mounted such that the bottom edge of the specimen was 1.9 cm above the top of the burner orifice, and the tip of the flame was in contact with the specimen throughout the course of the test. At the beginning of the test, a Bunsen burner with a flame temperature of no less than 843°C was placed under the specimen. After 60 s, the flame was removed from the specimen. The burn length, or flame spread, and the time for the specimen to self-extinguish was recorded. Six specimens were tested for every value and standard deviation reported.

Heat release tests were conducted in an Ohio State University (OSU) calorimeter. Specimens measuring 15.0 by 15.0 cm were conditioned in a chamber at 21°C with 50% relative humidity for

48 h. Following the conditioning, the backs of the specimens were wrapped in aluminum foil and placed in the calorimeter. The specimens were held in this chamber for 60 s with the radiation doors closed before being inserted into the main chamber of the OSU calorimeter. During the final 20 s of the 60 s hold, the thermopile readings were collected and averaged for the thermopile baseline. The specimen was then inserted into the main OSU chamber where a radiant heat flux of 3.50 W/cm^2 was impinged upon the center of the face of the sample. The specimen was held in the chamber for 5 min. From the OSU heat release test, the maximum heat release and total heat release in the first two min of the test were reported. Each heat release value and standard deviation reported represents the average of six tests, and all tests were performed in accordance with BSS 7322.[25]

Smoke evolution from the phenolic laminates was determined using a National Bureau of Standards (NBS) smoke density chamber. Specimens measuring 7.5 by 7.5 cm were conditioned in a chamber at 21°C with 50% relative humidity for 48 h. Following the conditioning, the backs of the specimens were wrapped in aluminum foil and placed in the smoke chamber. The specimen was then pushed in front of a furnace with a radiant heat flux of 2.50 W/cm^2. The percentage of light transmission through the chamber was measured with a microphotometer and recorded for 5 min. Each smoke density value and standard deviation reported represents the average of six tests, and all tests were performed in accordance with BSS 7238.[26]

Mechanical Testing

Specimens for measuring the critical stress intensity factor K_{IC} and the critical plane–strain energy release rate G_{IC} were prepared from 5.1 square cm neat resin plaques. Compact tension specimens were prepared and tested in accordance with ASTM method D5045. Each specimen was sawed with a fresh razor to provide a sharp crack tip before testing. The compact tension specimens were pulled apart in tension in an Instron 4505 mechanical tester at a rate of 0.10 cm/min until failure. Each critical stress intensity factor and standard deviation reported represents the average of seven tests.

Laminates were also fabricated to measure the interlaminar critical plane–strain and plane–shear energy release rates (G_{IC} and G_{IIC}, respec-

tively). The laminates were 18 plies thick and 33-cm long and had a 5.1-cm crack started in the midplane of the sample. The laminates were cut into 1.3-cm wide samples for testing. The critical plane–strain energy release rate was measured using the double cantilever beam (DCB) method.[27] Each specimen was precracked in the mechanical tester to provide a sharp crack tip before testing. The fracture specimen was pulled apart at 2.5 cm/min until a displacement of 6.3 cm was reached. Each G_{IC} value and standard deviation reported represents the average of four tests.

The critical plane–shear energy release rate was measured using the end notch flexure (ENF) test.[27] The same laminate preparation was used for the DCB specimens. A three-point bending apparatus with stationary posts was used to create shear fracture down the midplane of the specimen. The crack front was set 2.5 cm from the stationary post, and the loading point was set 5.1 cm from the post. A displacement rate of 0.25 cm/min was used to load the specimen in flexure until the crack propagated. An optical microscope fixture was used to locate the crack front, and the specimen was then moved back to the 2.5-cm stationary post. This was repeated until the specimen was cracked down its entire length. Each G_{IIC} value and standard deviation reported represents the average of six tests.

RESULTS AND DISCUSSION

TGA Analysis

Initial characterization of the different phenol–formaldehyde resins was conducted through high-resolution TGA analysis on neat resin plaques. The Hi-Res® TGA analysis of the three resins is shown in Figures 1 through 3. In Figure 1, the percentage of weight retained is plotted against temperature. In this figure, it can be seen that the TEA-catalyzed resin began to dramatically lose weight near 300°C and only retained 40% of its original weight at 1000°C. The resins catalyzed with sodium hydroxide and ammonium hydroxide retained approximately 70% their original weight at 1000°C.

In Figure 2, the degradation of the NH$_3$ resin in both air and nitrogen is presented. The degradation behavior of the NH$_3$ resin in air and nitrogen is indistinguishable until 450°C. At 450°C, the ammonia-catalyzed resin undergoes a more vigorous oxidation and completely burns in air.

Figure 1 Hi-Res® TGA thermal curve of NaOH-, NH$_3$-, and TEA-catalyzed phenolic resins in nitrogen.

Figure 3 The derivative of weight with respect to temperature of a Hi-Res® TGA for NaOH, NH$_3$, and TEA phenolic resins in nitrogen.

(Comparable behavior was observed in all resins.) The similar degradation behavior and peak temperatures in air and nitrogen indicate that degradation pathways in the phenolic resins are the same in nitrogen and oxygen, as shown earlier by Conley.[19,28,29] The similar mechanisms of degradation permit the correlation of different characterization techniques in a variety of environments.

In Figure 3, the derivative of the weight loss with respect to temperature is plotted. Each resin displayed three distinct weight loss regions. In Table I, the mass spectra peaks of the phenolic resins catalyzed with TEA, NaOH, and NH$_3$ are correlated with the TGA transitions shown in Figure 3.

Figure 2 Hi-Res® TGA thermal curve of NH$_3$-catalyzed phenolic resins in air and nitrogen.

TEA Chemical Analysis

For the TEA-catalyzed resin, the first weight loss transition ranged from 23 to 200°C. This transition represents water ($m/e = 18$) trapped in the matrix, as shown in Table I. Water is trapped in the matrix during the initial cure of the resin. During postcure, some of this water is removed. This transition represents the 6 wt % water that could not be removed due to continued crosslinking and diffusion limitations.

The second TEA transition represents a partial degradation of the phenolic backbone with the evolution of phenol ($m/e = 94$) from the matrix. The gases evolved in this transition are almost entirely phenol. The main mass to charge ratios for phenol are 94, 66, 65, 39, and 40 with intensities of 100, 29, 23, 20, and 13, respectively. These peaks and intensities closely match the analysis of the second TEA TGA transition. The phenol evolved in this transition represents phenol that is lightly bound to the backbone of the resin. This phenol is not free phenol due to the relatively high temperatures (260–300°C) of this transition.

The third triethylamine transition, which starts near 300°C, consists mainly of methyl phenol ($m/e = 107$), water, phenol, phenol fragments ($m/e = 39, 66, 27$), and methyl phenol fragments ($m/e = 77$ and 51). The evolution of methyl phenol in this transition represents the bulk degradation of the phenolic matrix. The 121 m/e molecular ion is attributed to dimethyl phenol. This third mass loss accounts for 45 wt % of the TEA specimen.

Table I   Eight Peak Mass Spectra of Phenolic TGA Transitions as Determined through GC–MS Analysis

Neat Resin Plaque	Transition 1			Transition 2			Transition 3		
	Peak	m/e	Intensity	Peak	m/e	Intensity	Peak	m/e	Intensity
TEA	1	18	100	1	94	100	1	107	100
TEA	2	17	28	2	66	32	2	18	58
TEA	3	16	3	3	39	30	3	39/94	56
TEA	4	44	<1	4	65	26	4	77	36
TEA	5	—	—	5	107	12	5	66/27	28
TEA	6	—	—	6	38	10	6	108	27
TEA	7	—	—	7	40	9	7	51/200	22
TEA	8	—	—	8	213/63	8	8	121	12
NH_3	1	18	100	1	94	100	1	107	100
NH_3	2	17	28	2	39	33	2	94	70
NH_3	3	16	3	3	66	30	3	18	52
NH_3	4	44	<1	4	65	22	4	39/108	36
NH_3	5	—	—	5	40/39	10	5	200	30
NH_3	6	—	—	6	107	9	6	77	23
NH_3	7	—	—	7	55	8	7	65/51	18
NH_3	8	—	—	8	200	7	8	121	16
NaOH	1	18	100	1	30	100	1	107	100
NaOH	2	17	28	2	44	34	2	122	82
NaOH	3	16	3	3	58	25	3	39	42
NaOH	4	28	<1	4	42	16	4	94/121	39
NaOH	5	—	—	5	45	15	5	91	37
NaOH	6	—	—	6	93	12	6	50	26
NaOH	7	—	—	7	29	10	7	66	22
NaOH	8	—	—	8	18	9	8	135	14

NH_3 Chemical Analysis

The first weight loss seen in the TGA is again the result of water loss. In this region of the TGA thermal curve, only 5 wt % is lost from the sample. The second NH_3 transition is very similar in composition and weight percent to the evolved gases from the second TGA transition of the TEA resin. This transition is ascribed to phenol evolution from the plaque.

The last transition accounts for a 20% weight loss from the sample. The mass spectrum analysis of this material again closely corresponds to the third transition seen in the TEA specimen, but there are two main differences between the TEA transition and the NH_3-catalyzed TGA transition. The intensity of the dimethyl phenol ion is larger in the NH_3 specimen that in the TEA specimen. This indicates that the NH_3 resin catalyzed contains slightly more dimethyl phenol linkages. The second main difference is the temperature and the quantity of mass represented by the third transition. In the TEA specimen, the bulk of the

third transition takes place before the beginning of the second transition in the other two resins and represents approximately twice the weight loss. The bulk of the third transition in the TEA-catalyzed resin occurs 175°C before bulk degradation of the resin catalyzed with NH_3. This difference can also be attributed to the degree of crosslinking. In the NH_3 resin system, the phenol chains are more tightly bound to the main backbone of the resin, thus requiring more thermal energy to break the bonds and liberate the phenol.

NaOH Chemical Analysis

The first TGA transition of the sodium-hydroxide-catalyzed resin is again a result of water being liberated from the neat resin plaque. The liberation of water accounts for a 4% weight loss from the sample.

The next TGA transition is attributed to formaldehyde (m/e = 30) evolution. Molecular ion 44 is attributed to formaldehyde fragments of mass

Table II   Summary of Phenolic Flammability Results

Phenolic Resin Catalyst	Burn Length (cm)	Maximum Smoke Density after 4 min (Ds)	OSU Rate of Heat Release (RHR)[a]
TEA	9.4 ± 1.5	23.5 ± 2.1	Peak RHR: 110.0 ± 5.3 2-min total: 95.0 ± 5.1
NH$_3$	4.6 ± 0.5	11.9 ± 2.5	Peak RHR: 24.1 ± 3.4 2-min total: 26.3 ± 2.8
NaOH	2.3 ± 0.3	0.3 ± 0.1	Peak RHR: 52.6 ± 1.5 2-min total: 19.0 ± 3.5

[a] 2 min total has units of kW min^{-1} m^{-2} and peak RHR has units of kW/m^2.

14 (CH$_2$) recombining with formaldehyde to produce ethanal (CH$_3$CHO). Mass fragment 58 is a result of another formaldehyde of mass 14 combining with ethanal in the ionization chamber to produce propanal (CH$_3$CH$_2$CHO). The evolved formaldehyde is most likely from hydroxymethyl termination of crosslinked phenol molecules. This lightly bound hydroxymethyl species only accounts for 5% by weight of the matrix. This is not believed to be free formaldehyde because of the high temperature of this transition (350 to 400°C). Any free formaldehyde (normal boiling point = −19°C) would have evolved before or with any water present in the system.

In the last transition observed for the phenolic resin catalyzed with NaOH, bulk degradation of the phenolic matrix and backbone takes place. In this transition, the evolution of methyl phenol, dimethyl phenol, and trimethyl phenol (m/e = 135) can be observed. Mass 91 can be attributed to dehydroxylation of methyl phenol to give methyl benzene, and all other peaks can be attributed to fragmentation of phenol or methyl phenol. The relative abundance of mono, di-, and trisubstituted phenol ions indicates that the cured sodium-hydroxide-catalyzed resin is a very highly crosslinked structure. From a comparison of the Table I, it can be concluded that that the NaOH resin system is more crosslinked than the other phenolic resins synthesized in this study due to the presence of these ions.

Flammability

In an effort to further characterize the various phenolic resins, a series of flammability experiments was performed. In all experiments, the NaOH- and NH$_3$-catalyzed resin displayed the best flammability properties, while the TEA resin displayed the worst properties. In terms of burn length, the TEA resin burned twice a far as NH$_3$ resin, which burned twice as far as the NaOH resin, as shown in Table II. All of the resins were selfextinguishing after the flame was removed from the specimen. The amount of smoke released from the specimens followed the same general trend as the burn length. A great deal of smoke evolved off of the TEA sample within the first 4 min of applying heat (23.5 Ds), while the amount of smoke released from the NaOH resin was scarcely detectable (0.3 Ds). In the OSU chamber, similar results were witnessed.

In Figure 4, the OSU heat release curves for the NaOH-, NH$_3$-, and TEA-catalyzed resins are presented. The TEA-catalyzed laminate was found to burn very quickly and release a great deal of heat. Due to the extensive and rapid release of heat, the TEA laminate failed to meet the FAA 65 : 65 heat release requirements for aerospace interior materials. The 65 : 65 rule states

Figure 4   OSU heat release curves for NaOH-, NH$_3$-, and TEA-catalyzed phenolic resins.

Table III   Summary of Mechanical Testing Results on Phenolic Laminates and Neat Resin Plaques

Phenolic Resin Catalyst	Laminates		Neat Resin Plaques	
	G_{IC} (J/m^2)	G_{IIC} (J/m^2)	K_{IC} (MPa m$^{1/2}$)	G_{IC} (J/m^2)
TEA	196 ± 24	1355 ± 163	0.61 ± 0.07	4.3 ± 1.7
NH$_3$	823 ± 52	2040 ± 250	1.05 ± 0.10	12.2 ± 2.3
NaOH	194 ± 28	874 ± 115	0.69 ± 0.05	6.0 ± 2.3

that the peak rate of heat release must be less than 65 kW/m^2, and the total amount of heat released after the first 2 min must be less than 65 kW min^{-1} m^{-2}. Although the TEA resin exceeded these limits, results from the NaOH and NH$_3$ resins were found to be below these limits. The rapid heat release from the TEA specimen in Figure 4 may be the result of phenol evolving and burning in the OSU chamber. The release of phenol and methyl phenol (40 to 50% by weight) from the specimen during the second and third TGA transitions is responsible for the large exotherm shown in Figure 4. The NH$_3$-catalyzed resin has also been shown to release phenol and methyl phenol during degradation, but less phenol and methyl phenol are evolved from this resin system (20% by weight evolved). The ammonia-catalyzed resin also degrades at a higher temperature. With the higher degradation temperature, the phenol and methyl phenol require a longer time to evolve from the laminate. The longer evolution time in the NH$_3$ prevents the methyl phenol from being completely liberated shortly after heating. The OSU curve of NH$_3$ presented in Figure 4 represents the slow burning of phenol and methyl phenol over an extended period of time, while the TEA laminate represents the almost immediate combustion of the same products.

In the NaOH-catalyzed resin, an exotherm can be seen 100 s after the specimen is heated. This exotherm is ascribed to the release of formaldehyde from the sample. Although the NH$_3$- and NaOH-catalyzed resins lose approximately the same weight percent from 500 to 1000°C, the combustion of the evolved gases is extremely different. The enthalpy of combustion for formaldehyde is a factor of 1.7 times greater than the enthalpy of combustion of phenol. It is this high heat content of formaldehyde, which is responsible for the heat release differences between NaOH- and NH$_3$-catalyzed resins, depicted in Figure 4 and Table II.

Mechanical Properties

Mechanical testing was conducted on laminates and neat resin plaques. The results of the mechanical tests are summarized in Table III. The mechanical properties of the phenolic resins investigated were found to be on the same order or higher than the mechanical properties of other untoughened epoxies and thermosetting resins, which have average K_{IC} and G_{IC} values near 0.6 MPa m$^{1/2}$ and 200 J/m^2, respectively.[30] The ammonia-catalyzed resin had the highest mechanical properties of all the resins synthesized. The plane–strain (G_{IC}) and plane–shear (G_{IIC}) energy release rates and the critical stress intensity factor (K_{IC}) of the NH$_3$ phenolic resin were two to four times greater than the TEA- and NaOH-catalyzed resins. These differences in fracture energy and toughness are a result of the different mechanisms of crack propagation through the materials. During fracture, the crack growth of the NH$_3$-catalyzed samples was observed to be partially stable after crack initiation. In Figure 5(A), an optical photomicrograph of the interlaminar fracture path for the NH$_3$-catalyzed resin is shown. In this figure, the effects of partially stable crack growth through the laminate can be observed. In partially stable crack propagation, a plastic deformation zone is created in the crack tip. The plastic deformation zone distributes the stresses in the crack tip to the fiber tows or other tougheners in the matrix. The fiber tows or tougheners then cavitate, or debond, to relieve these stresses.[31] The distribution of stresses through cavitation of the fiber tow, as depicted in Figure 5, is responsible for the high fracture energy of the NH$_3$ resin.

Unlike the NH$_3$-catalyzed resin, the crack propagation through the NaOH resin was noticed to be fully unstable after crack initiation. In Figure 5(B), the interlaminar fracture path of laminates manufactured from this resin system is shown. In this resin, the unstable crack growth

(A)

(B)

(C)

Figure 5 Optical photomicrographs of the plane strain (G_{IC}) fracture path for (A) NH_3-, (B) NaOH, and (C) TEA-catalyzed phenolic laminates at 25× magnification.

did not involve a plastic deformation zone, and the high stresses created in the crack tip during crack propagation could not be delocalized. When the crack tip encountered a fiber tow, the matrix fractured and the crack propagated through, or around, the fiber tow without debonding or cavitating the fiber tow. This behavior is responsible for the low fracture energy and toughness of the NaOH resin.

It has been shown from Table I that the NaOH resin is more crosslinked than the other resins synthesized in this study. The high degree of crosslinking in the NaOH-catalyzed resin resulted in a very brittle matrix. The NaOH resin was cured for 2 h at 150°C, followed by another 2 h cure at 177°C. It is at these cure temperatures where most of the dimethyl phenol and trimethyl phenol bonds are formed. When these bonds are formed, the crosslinked structure is in its most relaxed state. As the material cools, residual thermal stresses accumulate in the cured matrix. When a crack is initiated and propagated through the matrix, the resin cannot deform or distribute the stress due to the high concentration of thermal stresses. The inability of the resin to accommodate the stresses at the crack tip makes the material brittle and is ultimately responsible for the low fracture energy and toughness of the resin.

The NaOH- and TEA-catalyzed resins displayed similar toughness and fracture energies, even though the TEA has less crosslinks than the NaOH resin. With fewer crosslinks, it is expected that a laminate or neat resin plaque manufactured from the TEA would be more ductile and, therefore, have a higher toughness than the other resins studied. Along with being less crosslinked, the TEA specimens are also highly voided. Voids decrease the mechanical properties of composite matrices, but can also increase the toughness and fracture energy of the composite in tensile mode. Voids can increase the toughness of a material by delocalizing the stresses in the crack tip throughout the void. However, this phenomenon was not observed in the TEA resin. The differences in toughness and fracture energies between the other resins and the TEA are attributed to the shape of the void. The voids in the TEA matrix are oblong-shaped with sharp corners, as shown in Figure 6. When the crack tip encounters a void, the stresses at the crack tip are not evenly distributed around the entire void, as would be seen with a spherical void. Instead, the stresses in the crack tip are redirected and concentrated in the

Figure 6 Optical photomicrograph of TEA-catalyzed phenolic laminate voids at 200× magnification.

sharp corner of the void. The stresses in the crack tip are not relieved by the void, and the crack continues to propagate.

The high concentration of voids in the matrix allowed the crack to transfer from one void to another.[32] In Figure 5(C), it can be seen that the crack propagated exclusively through the flaws (voids) in the matrix. The crack propagated through the voids because they provide the path of least resistance through the composite. By not transferring the crack stresses to the fiber tows in the laminates, the matrix was not able to delocalize the stresses in the crack tip.

Ultimately, the differences in the thermal and mechanical properties of the three resins can be linked to chemical differences of the catalysts during phenol–formaldehyde addition and condensation. Sodium hydroxide ($pK_b = 0$) is a strong base. In degassing the NaOH-catalyzed resin, all of the sodium hydroxide remains in the resin due to the high boiling point of NaOH (normal boiling point = 1390°C). The high concentration of hydroxide ions in the final resin catalyzes the condensation reaction of the phenolic resin and is responsible for the high degree of crosslinking observed in this resin.[2]

Ammonia ($pK_b = 4.75$) is a weaker base than NaOH. In the NH_3-catalyzed resin, there is a smaller concentration of free hydroxide ions in the initial reaction mixture. In degassing the NH_3-catalyzed resin, a large concentration of catalyst is volatilized due to the high vapor pressure of the NH_3 (normal boiling point = −33°C). This results in a much smaller concentration of cata-

lyst in the resin during the cure. Both the lower basicity and high vapor pressure of the NH_3 contribute to a lower degree of crosslinking in the NH_3-catalyzed resin when compared to the NaOH-catalyzed resin.

In the case of the triethylamine-catalyzed resins, additional factors influence the final chemical structure of the plaques or laminates. The basicity of TEA is similar to that of NH_3 ($pK_b = 3.35$), but the solubility of TEA is considerably lower than either NaOH or NH_3, which are completely soluble in water. In 80°C water, a maximum 1.2 g of TEA can dissolve in 100 g of water. Consequently, there is a low concentration of hydroxide ions in the TEA-catalyzed aqueous mixture. This lower concentration produces a smaller number of di- and trisubstituted phenol species during the condensation reaction, as is shown by the missing trimethyl phenol peak in the mass spectra. The lightly crosslinked TEA resin system is a result of catalyst solubility and the hydroxide ion concentration.

CONCLUSIONS

In this study, three different resole phenolic resins were characterized from synthesis to degradation. The effects of sodium hydroxide, triethylamine, and ammonia catalysis on the fracture toughness, flammability, chemical structure, and degradative properties of phenolic resins were investigated. All three resins displayed similar degradative mechanisms; and during degradation, each resin exhibited three distinct weight loss regions. The first weight loss region was due to the evolution of water. The second degradation was attributed to the volatilization of species loosely bound to the phenolic backbone, and the final region represented the bulk degradation of the phenolic matrix. Flammability studies were also performed on laminates manufactured from these resins. The NaOH- and NH_3-catalyzed resins were found to be relatively inflammable, while the TEA laminates burned readily. Lastly, mechanical tests measuring the plane–strain and plane–shear energy release rates and the critical stress intensity factor were performed on the neat resin plaques and laminates. The mechanical properties of the phenolic resins investigated were found to be on the same order or higher than the mechanical properties of other untoughened epoxies or thermosetting resins. The various chemistries that exhibited the properties dis-

cussed were understood in terms of catalyst basicity, solubility, and boiling point. From this study, it can be concluded that the thermal degradation, flammability, and mechanical performance of phenolic resole resins is strongly dependent on the nature of the catalyst used in their synthesis.

REFERENCES

1. Dailey, Jr., T. H. 29th International SAMPE Technical Conference, Vol. 29; SAMPE: 1997; p. 800.
2. Knop, A.; Pilato, L. A. Phenolic Resins—Chemistry, Applications and Performance; Springer-Verlag: Berlin, Germany, 1985.
3. Böttcher, A.; Pilato, L. A. SAMPE J 1997, 33, 35.
4. Redjel, B. Plast, Rubber Compos Process Appl 1995, 24, 221.
5. Orpin, M. R. Proceedings of the Institution of Mechanical Engineers, Part F, Vol. 209; 1995; p. 19.
6. Sebnik, A.; Vizovisek, I.; Lapanje, S. Eur Polym Sci 1973, 10, 273.
7. Sprung, M. M.; Gladstone, M. T. J Am Chem Soc 1949, 71, 2907.
8. Pal, P. K.; Kumar, A.; Gupta, S. K. Polymer 1981, 22, 1699.
9. Martin, P. R. H. AlChE—1984 Spring National Meeting, 1984, ATChE: 1984; p. 1.
10. Grenier–Loustalot, M.; Laroque, S.; Grenier, P.; Leca, J.; Bedel, D. Polymer 1994, 35, 3346.
11. Nyden, M. R.; Brown, J. E.; Lomakin, S. M. Polym Mater Sci Eng 1994, 71, 301.
12. Kourtides, D. A. Polym Compos 1984, 5, 143.
13. Kourtides, D. A.; Parker, J. A.; Gilwee, Jr., W. G.; Lerner, N. A. J Fire Flammab 1976, 7, 401.
14. Follensbee, R. A.; Koutsky, J. A.; Christiansen, A. W.; Myers, G. E.; Geimer, R. L. J Appl Polym Sci 1993, 47, 1481.
15. Pizzi, A.; Garcia, R.; Wang, S. J Appl Polym Sci 1997, 66, 255.
16. Kim, M. G.; Nieh, W. L. S.; Meacham, R. M. Ind Eng Chem Res 1991, 30, 798.
17. Landi, V. R.; Fitts, B. B.; Mersereau, J. M. Mod Plast 1984, 61, 66.
18. Antony, R.; Pillai, C. K. S. J Appl Polym Sci 1994, 54, 429.
19. Conley, R. T.; Bieron, J. F. J Appl Polym Sci 1963, 7, 103.
20. Nam, J. D.; Seferis, J. C. Carbon 1992, 30, 751.
21. Charalambides, M. N.; Williams, J. G. Polym Compos 1995, 16, 17.
22. King, P. W.; Mitchell, R. H.; Westwood, A. R. J Appl Polym Sci 1974, 18, 1117.
23. Martin, P. The Chemistry of Phenolic Resins; John Wiley and Sons: New York, 1956.
24. Boeing Specification Standard BSS 7230, Determination of Flammability Properties of Aircraft Materials; Boeing Commercial Airplane Group: Seattle, WA, 1994.
25. Boeing Specification Standard BSS 7322, Ohio State University (OSU) Calorimeter Determination of Heat Release; Boeing Commercial Airplane Group: Seattle, WA, 1994.
26. Boeing Specification Standard BSS 7238, Test Method for Smoke Generation by Materials on Combustion; Boeing Commercial Airplane Group: Seattle, WA, 1997.
27. Whitney, J. M., in Composite Material Series; Pagano, N. J. Ed.; Elsevier: New York, 1989.
28. Conley, R. T.; Bieron, J. F. J Appl Polym Sci 1963, 7, 171.
29. Conley, R. T.; Bieron, J. F. J Appl Polym Sci 1965, 9, 1117.
30. Williams, J. G. Fracture Mechanics of Polymers; Ellis Horwood: Chichester, UK, 1984.
31. Julien, O.; Beguelin, P.; Monnerie, L.; Kausch, H. H. in Toughened Plastics II: Novel Approaches in Science and Engineering; Riew, C. K.; Kinloch, A. J., Eds.; American Chemical Society: Washington DC, 1996; p. 233.
32. Huang, Y.; Hunston, D. L.; Kinloch, A. L.; Riew, C. K. in Toughened Plastics I: Science and Engineering; Riew, C. K.; Kinloch, A. J., Eds.; American Chemical Society: Washington DC, 1993; p. 1.