# CHARACTERIZATION OF PHENOLIC RESINS FOR COMPOSITE HONEYCOMB APPLICATIONS

J. E. Shafizadeh and J. C. Seferis

Polymeric Composites Laboratory, Department of Chemical Engineering, University of Washington Box 351750, Seattle, Washington, United States of America

**SUMMARY**: In this study, phenol-formaldehyde resins catalyzed with sodium hydroxide, triethylamine and ammonium hydroxide were characterized and compared to a commercial honeycomb dip. All four resins displayed similar degradative mechanisms, and their degradation behavior was understood through GS/MS analysis. 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 flammability of the commercial system was linked to ethanol volatization. The various chemical properties responsible for these behaviors are discussed and analyzed in terms of the catalyst basicity, solubility and boiling point. Lastly honeycomb ring specimens were fabricated and resin fracture toughness was found to be more significant than the flexural strength in honeycomb ring compression tests.

**KEYWORDS**: Phenolic resins, Honeycomb Dip Resins, Honeycomb Ring Test, Degradation Behavior, Mechanical Properties and Flammability.

## **INTRODUCTION**

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. 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 health concerns as well as to a lack of information regarding their mechanical properties and fracture mechanics.[1]

Although a great deal of work has been done specifically in the fields of kinetic characterization, reaction modeling, flammability, thermal analysis, degradation, mechanical performance and chemical analysis, complete investigations of phenolic materials from synthesis to final performance have been limited. In this paper, three model phenolic resins

were be characterized in terms of their degradation, flammability and mechanical performance in honeycomb and laminate structures. Through comparison with a commercial honeycomb resin, the significant properties which define the honeycomb core and phenolic resin were investigated.

#### EXPERIMENTAL PROCEDURE

# **Resin Synthesis and Processing**

The model phenolic resins studied were synthesized using phenol, formaldehyde and one of three basic catalysts: triethylamine (TEA), aqueous ammonium hydroxide (28 wt. % NH<sub>3</sub>) and sodium hydroxide. The resole phenol-formaldehyde resins investigated were prepared with a catalyst/formaldehyde/phenol molar ratio of 0.2 to 1.5 to 1.0, respectively. A commercial honeycomb dip resin was also investigated in this study. The resole phenolic resin was GP5236 Redi-Lam Resin. This resin was manufactured by Georgia Pacific and sold for honeycomb production. The resin was sold in 40%-60% ethanol. To remove the solvent, the resin was placed in a vacuum oven at 50°C with an absolute pressure of 4.8 kPa for twelve hours.

In synthesizing each resin, phenol crystals were dissolved in formaldehyde and one of the three catalysts was then added to the solution. The phenol-formaldehyde solution was stirred and heated at 80°C for 60 minutes. The phenol-formaldehyde resin was then placed in a vacuum oven at 50°C with an absolute pressure of 4.8 kPa for eight hours.

All laminates were fabricated in an autoclave and ramped at 2.7°C/min from 27°C to 150°C, held for two hours, ramped to 177°C at 2.7°C/min, held for two hours, then ramped back down to 27°C at 2.7°C/min. The total compaction pressure used during cure was 1.4 MPa. All specimens were post-cured at 130°C for four hours at an absolute pressure of 4.8 kPa.

## **Chemical and Thermal Analysis**

Chemical analysis was performed on neat resin plaques using gas chromatography/mass spectroscopy 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 heat at a rate of 2°C/min to 400°C. The gas chromatography analysis was coupled with a Finnigan MAT 90/95 high-resolution magnetic sector mass spectrometer which scanned at a rate of 1 second per decade.

Hi-resolution thermogravimetric analysis (TGA) was performed with a TA Instruments 2950 Hi-Res<sup>®</sup> TGA. Specimens were ramped at 5°C/min to 1000°C in both air and nitrogen environments at a level seven resolution.

## Flammability and Layered Mechanical Testing

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% and were cured as described above.

In determining the flammability properties of aerospace materials, flame spread and heat release are critical properties for evaluation. Measurements for flame spread were done in accordance with Boeing Specification Standard (BSS) 7230.[2] At the beginning of the test, a Bunsen burner, with a flame temperature of no less that 843°C, was placed under the specimen. After 60 seconds, the flame was removed from the specimen. The burn length, or flame spread, and the time for the specimen to self-extinguish was recorded.

Heat release tests were conducted in an Ohio State University (OSU) calorimeter. Specimens measuring 15 cm by 15 cm were conditioned in a chamber at 21°C with 50% relative humidity for 48 hours. Before testing, the backs of the specimens were wrapped in aluminum foil and placed in the calorimeter. The specimens were held for 60 seconds with the radiation doors closed before being inserted into the main chamber of the OSU calorimeter. After this time, the specimens were inserted into the main OSU chamber where a radiant heat flux of 3.50 W/cm² was impinged upon the center of the sample. The specimen was held in the chamber for five minutes. From the OSU heat release test, the maximum heat release and total heat release in the first two minutes of the test were reported. All tests were performed in accordance with BSS 7322.[3]

Specimen preparation and mechanical testing procedures for measuring the flexural yield stress and modulus, the critical plane-strain energy release rate,  $G_{IC}$ , and plane-shear energy release rates,  $G_{IIC}$ , are reported elsewhere.[4]

# **Honeycomb Ring and Peel Testing**

Honeycomb core fails under compressive loads in a predictable manner. In the out-of-plane direction, the honeycomb core first deforms in a linear-elastically manner. During this deformation, the walls of the honeycomb core axially compress. When the honeycomb reaches its maximum compressive stress, the core buckles elastically in a periodic manner and looses all structural integrity.[5] A thin ring buckles and fails in the same phenomenological way as a honeycomb structure. The ring wall axial compresses and when the ring reaches its critical stress, it buckles.[6] Through stability and mechanical arguments, mathematical relationships can be derived directly relating the critical buckling stress of honeycomb core to the critical buckling stress of thin rings.

Based on this background, a honeycomb compression ring test was developed to compare different phenolic honeycomb dip resins and web materials. Honeycomb compression rings were constructed to evaluate the compressive properties of the model and commercial phenolic dip resins. Rings were fabricated from 2.5 cm wide, 126.0 cm long and 0.08 mm thick strips of Nomex<sup>®</sup> 410 paper. The Nomex strips were dipped in a phenolic resin diluted with 60% ethanol. After dipping, the Nomex strips were wrapped twice around a rod with a 10 mm radius. The strips were then wrapped with shrink-wrap tape and placed in an oven which had been preheated to 160°C. In the oven, the rings were held for two hours at 160°C, then cooled to room temperature at 2.7°C/min. While in the oven, the shrink-wrap tape contracted five percent. The five percent shrinkage provided the necessary compaction to consolidate the rings. To densify the rings, the rings were dipped in a phenolic resin diluted with 60% ethanol. After dipping, the phenolic resin was allowed to drip off the rings for two minutes. Once the excess resin had dripped off, the rings were then placed in an air-circulating oven at 160°C for 10 minutes. Following the cure of the phenolic resin, the rings were allowed to cool and then redipped until they had been dipped a total of 5, 10, 15, 20, 25 or 30 times. After dipping the rings were compressed at a rate of 0.25 cm/min until failure.

#### RESULTS AND DISCUSSION

# **Degradation and Chemical Analysis**

High-resolution thermogravimetric analysis was performed on neat resin plaques in an attempt to understand the degradation behavior of the resins. Hi-Res TGA analysis of the four resins is shown in Figures 1 and 2. In Figure 1, the percent weight retained is plotted against temperature.

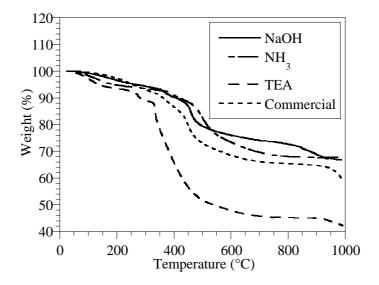


Fig. 1: Hi-Res TGA of a commercial system and the model resin systems in nitrogen

In this figure, it can be seen that the TEA model resin began to dramatically lose weight near 300°C, and only retained 40% of its original weight at 1000°C. The other three resins retained 60 - 70% their original weight at 1000°C. The commercial and NH<sub>3</sub> resins have similar degradation behaviors from 25°C to about 950°C. After 950°C, the char of the commercial resin continues to degrade while the NH<sub>3</sub> model resin char remains stable.

In Figure 2, the derivative of the weight loss with respect to temperature is plotted. Each resin displayed three distinct weight loss regions.

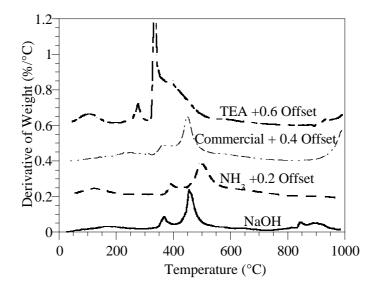


Fig. 2: Hi-Res TGA derivatives of the commercial and model resin systems in nitrogen

For the TEA catalyzed resin, the first weight loss transition ranged from 23°C to 200°C. From chemical analysis, this transition can be linked to water and other unbound species trapped in the matrix. Water was trapped in the matrix during the initial cure of the resin. During post cure, some of this water was removed. This transition represents the six weight percent water that could not be removed due to diffusion limitations. The second TEA transition represents a partial degradation of the phenolic backbone with the evolution of phenol from the matrix. The gases evolved in this transition were almost entirely phenol. The phenol evolved in this transition represents phenol that was lightly bound to the backbone of the resin. This phenol was 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, water, phenol, phenol fragments and methyl phenol fragments. The evolution of methyl phenol in this transition represents bulk degradation of the phenolic matrix. This third mass loss accounts for 45 weight percent of the TEA specimen.

The first weight loss seen in the NH<sub>3</sub> TGA was also the result of water loss. In this region of the TGA thermal curve, only five weight percent was lost from the sample. The second NH<sub>3</sub> transition shown in Figure 2 was very similar in composition and weight percent to the evolved gases from the second TGA transition of the TEA model resin. This transition is ascribed to phenol evolution from the plaque. The last transition accounts for a 20 percent weight loss from the sample. The mass spectrum analysis of this material closely corresponds to the third transition seen in the TEA specimen, but there were two main differences between the TEA transition and the NH<sub>3</sub> catalyzed TGA transition. The intensity of the dimethyl phenol ion in the GC/MS analysis was larger in the NH<sub>3</sub> specimen than that in the TEA specimen. This indicates that the NH<sub>3</sub> resin catalyzed contained slightly more dimethyl phenol linkages. The second main difference was the temperature and the quantity of mass represent by the third transition. In the TEA specimen, the bulk of the third transition took 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 occurred 175°C before bulk degradation of the resin catalyzed with NH<sub>3</sub>. This difference can also be ascribed to the degree of cross-linking. In the NH<sub>3</sub> resin system, the phenol chains were more tightly bound to the main backbone of the resin thus requiring more thermal energy to break the bonds and liberate the phenol.

The first TGA transition of the sodium hydroxide catalyzed resin is again a result of water and unbound materials being liberated from the neat resin plaque. The liberation of water accounts for a four percent weight loss from the sample. The next TGA transition is attributed to formaldehyde evolution. The evolved formaldehyde was most likely from hydroxymethyl termination of cross-linked phenol molecules. This lightly bound hydroxymethyl species only accounts for five percent by weight of the matrix. This is not believed to be free formaldehyde because of the high temperature of this transition (350°C to 400°C). Any free formaldehyde (normal boiling point = -19°C) would have evolved with, or before, any water present in the system. In the last transition, bulk degradation of the phenolic matrix and backbone took place. In this transition, the evolution of methyl phenol, dimethyl phenol, and trimethyl phenol was observed. The relative abundance of mono, di- and tri- substituted phenol ions indicated that the cured sodium hydroxide catalyzed resin was a very highly cross-linked structure. It can be concluded that that the NaOH model resin system was more cross-linked than the other phenolic resins synthesized in this study due to the presence of these ions.

As the commercial resin began to degrade, water was the first product to evolve. Along with the water, ethanol also began to volatize. Ethanol was used to lower the viscosity of the phenolic dip resin. With a low viscosity, a thin uniform phenolic film can be deposited on the honeycomb core. The bulk of the ethanol in the resin was removed in the vacuum oven, but some ethanol was still present in the resin and became trapped in the matrix during cure. In the second TGA transition ethanol continued to evolve. This ethanol was probably lightly linked to the phenolic backbone as suggested by the high temperature of evolution. How the ethanol was linked to the backbone could not be fully determined. Ethanol was also trapped in the matrix during cure and this ethanol was likely present to some extent in both the first and second TGA transitions. The first two TGA transitions account for less than ten percent the total weight of the sample. In the third transition water continued to evolve, but the presence of methyl phenol, phenol, and dimethyl phenol fragments indicates that the backbone of the resin was degrading. The absence of tri-substituted species suggests that the resin was not as densely cross-linked as the NaOH resin. The high evolution of water makes a determination of whether the commercial resin was as densely cross-linked as the NH<sub>3</sub> or TEA resins difficult. However, the commercial resin system does seem to have the same bonds and chemical groups as the model systems synthesized.

The presence of mono-, di- and tri- substituted phenolic species indicated the degree of crosslinking in the resin. From coupled TGA-GC/MS analysis, the NaOH resin was found to have the greatest cross-link density and triethylamine was found to have the lowest. The cross-link density of the commercial system was between the NH<sub>3</sub> and NaOH resin systems. In degassing the NaOH catalyzed resin, all of the sodium hydroxide remained in the resin due to the high boiling point of NaOH (b<sub>p</sub>=1390°C). The high concentration of hydroxide ions in the final resin catalyzed the reaction of the resin and was responsible for the high degree of cross-linking observed. Ammonia ( $pK_b = 4.75$ ) is a weaker base than NaOH. In the NH<sub>3</sub> catalyzed resin there was a smaller concentration of free hydroxide ions in the reaction mixture. In degassing the NH<sub>3</sub> catalyzed resin, a large concentration of catalyst was volatilized (b<sub>p</sub>=-33°C). This resulted in a much smaller concentration of catalyst in the resin during the cure. Both the lower basicity and high vapor pressure of the NH<sub>3</sub> contributed to a lower degree of cross-linking. In the case of the triethylamine catalyzed resins, additional factors influenced the final structure of the material. The basicity of TEA was similar to that of  $NH_3$  (pK<sub>b</sub> = 3.35), but the solubility of TEA is considerably lower than either NaOH or NH<sub>3</sub>. Consequently, there is a low concentration of hydroxide ions in the TEA catalyzed mixture, and a lower cross-link density.

## **Flammability**

In an effort to further characterize the various phenolic resins, a series of flammability experiments was performed. In all experiments, the NaOH 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<sub>3</sub> resin, which burned twice as far as the NaOH resin, as shown in Table 1. The burn length performance of the commercial resin was between NH<sub>3</sub> and NaOH. All of the resins were self-extinguishing after the flame was removed from the specimen.

Table 1: Summary of phenolic flammability results

Phenolic Resin System	Burn Length (cm)	OSU Rate of Heat Release (RHR)*	
TEA	9.4+1.5	Peak RHR: 110.0±5.3	
	9.4±1.3	2 min Total: 95.0±5.1	
NH <sub>3</sub>	4.6±0.5	Peak RHR: 24.1±3.4	
		2 min Total: 26.3±2.8	

NaOH	2.3±0.3	Peak RHR: 52.6±1.5		
		2 min Total: 19.0±3.5		
Commercial	3.1±0.3	Peak RHR: 61.4±5.47		
		2 min Total: 48.4±1.5		

\* - Peak RHR has units of kW/m² and the 2 min total has units of (kW min)/m²

In the OSU chamber, similar results were witnessed. In Figure 3, the OSU heat release curves for the commercial and NaOH, NH<sub>3</sub> 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 that the peak rate of heat release must be less than 65 kW/m<sup>2</sup> and the total amount of heat released after the first two minutes must be less than 65 (kW min)/m<sup>2</sup>. Although the TEA resin exceeded these limits, results from the other resins were found to be below these limits. The rapid heat release from the TEA specimen in Figure 3 may be the result of phenol evolving and burning in the OSU chamber. The release of phenol and methyl phenol (40 to 50 percent by weight) from the specimen during the second and third TGA transitions was responsible for the large exotherm shown in Figure 3. The NH<sub>3</sub> 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 percent 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. The longer evolution time in the NH<sub>3</sub> prevents the methyl phenol from being completely liberated shortly after heating. The OSU curve of NH<sub>3</sub> presented in Figure 3 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 seconds after the specimen is heated. This exotherm is ascribed to the release of formaldehyde from the sample. Although the NH<sub>3</sub> and NaOH catalyzed resins lose approximately the same weight percent from 500°C to 1000°C, the combustion of the evolved gases was 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 was responsible for the heat release differences between NaOH and NH<sub>3</sub> catalyzed resins depicted in Figure 3 and Table 1.

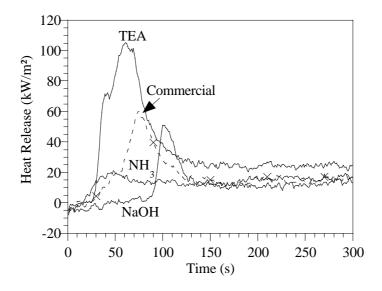


Figure 3: OSU heat release curves for the commercial and model resin systems.

From the OSU curve of the commercial resin, a great deal can be learned about the flammability of honeycomb materials. The flammability of the commercial system was just under the FAA 65:65 limitations for interior materials. As shown in the TGA and GS/MS analysis, ethanol evolves readily from the specimen during the first and second TGA transitions. The large exotherm observed in Figure 3 was the result of ethanol volatilization from the specimen. In honeycomb manufacturing, ethanol is added to the phenolic resin after synthesis to lower the viscosity of the resin. The resin viscosity must be sufficiently low to coat the honeycomb core with a thin even phenolic film. The ethanol added to the commercial system could not be completely removed from the commercial resin due to diffusion and kinetic limitations. As a result, the rate of heat release from the commercial laminates was greater than the heat that would have been released from laminates fabricated from the neat resin before the addition of ethanol.

## **Mechanical Testing**

Mechanical testing was conducted on laminates and neat resin plaques, and the results are summarized in Table 2. The differences in fracture energy and toughness are a result of the different mechanisms of crack propagation through the materials.

TD 11 A C	C 1 1	1 1 .		1 1 1	•
Table 7: Summary	zot machanical	l tacting reculte o	n commercial an	d modal	racin exictance
Table 2: Summary	OI INCCHAINCAI	FIGURIES FERRITOR	II COHIIIEICIAI AII	(1 1110/05	TESTIL SYSTEMS
10010 = 0011111111111111111111111111111	01 1110 01100111001	1 000001115 0			100111 0 , 0001110

Phenolic Resin	Laminates			Neat Resin Plaques	
Catalyst	$G_{IC}(J/m^2)$	$G_{IIC}(J/m^2)$	E <sub>F</sub> (GPa)	$K_{IC}$ (MPa m <sup>1/2</sup> )	$G_{IC}(J/m^2)$
TEA	196±24	1355±163	21.0±0.5	0.61±0.07	4.3±1.7
NH <sub>3</sub>	833±52	2040±250	17.5±0.6	1.05±0.10	12.2±2.3
NaOH	194±28	874±115	17.0±0.6	0.69±0.05	6.0±2.3
Commercial	798±40	1343±88	23.5±0.8	N/A*	N/A*

<sup>\*-</sup> K<sub>IC</sub> specimens could not be fabricated from the commercial system due to ethanol volatilization

The crack growth of the NH<sub>3</sub> catalyzed samples was observed to be partially stable after crack initiation. 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. Unlike the NH<sub>3</sub> catalyzed resin, the crack propagation through the NaOH, TEA, and commercial resin systems was noticed to be fully unstable after crack initiation. In these resins, the unstable crack growth did not involve a plastic deformation zone, and 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 linked to the crosslink density of the matrix. The high degree of cross-linking found in the NaOH catalyzed resin resulted in a very brittle matrix. The NaOH resin was cured for two hours at 150°C followed by another two hours cure at 177°C. At these cure temperatures, the dimethyl and trimethyl phenol bonds were formed. When these bonds were formed, the cross-linked structure was in its most relaxed state, and residual thermal stresses accumulated in the cured matrix during cooling. When a crack was initiated and propagated through the matrix, the resin could not deform or distribute the stress due to the high concentration of thermal stresses. The end result was a very brittle material. The NaOH and TEA catalyzed resins displayed similar toughness and fracture energies even though the TEA has less cross-links than the NaOH resin. With fewer cross-links, it is expected that a laminate or neat resin plaque manufactured from the TEA would be more ductile, and therefore have a higher toughness. However, the TEA specimens were also highly voided which resulted in decreased mechanical properties. The G<sub>IC</sub> fracture energy of the commercial system was comparable to the  $NH_3$  model system, but the  $G_{IIC}$  value was much lower. This behavior is most likely the result of fully unstable crack growth after crack initiation. Crack growth in the commercial system occured along the fiber/matrix interface. The crack path is longer in the commercial system than in the TEA and NaOH resin systems, and is most likely responsible for the differences in  $G_{IC}$  between the unstable crack growth systems. The matrix interface failure may be due to poor compatibility between the fiber sizing and resin system. However, the crack propagates around the entire fiber bundle, instead of being limited to one side of the fiber bundle. This indicates that the matrix may be deforming plastically around the fiber bundle, but the matrix may not be able to fully relieve the stresses at the crack tip.

Although the NH<sub>3</sub> system displayed the best fracture mechanics it did not display the best flexural properties. The flexural properties of the resin are extremely important because during compression the honeycomb core walls bend and deform. Any resin coating a honeycomb structure must have a high flexural modulus to resist the bending of the cell wall. If the flexural modulus of the resin is low, the resin will reach its ultimate yield strain at low compression loads. When the resin yields, the reinforcement around the web yields, and the honeycomb fails. The commercial resin had the highest flexural modulus, E<sub>F</sub>, as shown earlier in Table 2. The flexural properties of the TEA resin were very close to the properties of the commercial resin. The voids contained within the TEA laminate helped distribute the stresses away from the loading point. The flexural modulus of the NH<sub>3</sub> and NaOH laminates were about 25% less than the flexural modulus of the commercial system. The NaOH resin is "over cross-linked" and could not distribute the high flexural stresses without yielding. The lower elastic modulus of the NH<sub>3</sub> model resin system is likely due to the cross-link density of the model system.

## **Honeycomb Ring and Peel Testing**

Due to surface wetting and flammability constraints, ring specimens were only fabricated from the  $NH_3$  and commercial resin systems. Before fabricating ring specimens, the phenolic resins were diluted to 60 weight percent solvent with ethanol. At  $40^{\circ}$ C, the model and commercial resins systems had kinematic viscosities of 2.35 and 2.9 centistokes, respectively.

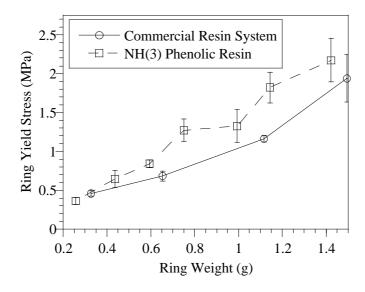


Fig. 4: Honeycomb ring yield stress for the commercial and NH<sub>3</sub> model resin systems

As shown in Figure 4, the model system performed as well or better than the commercial system in compression. The results of the compression tests suggest that the fracture mechanics of the dip resin may have a larger influence on the ultimate yield stress of

honeycomb core than the flexural properties of the resin. This conclusion may be drawn because the model resin system has better fracture toughness than the commercial system, but the commercial system has better flexural properties than the model system.

#### CONCLUSIONS

In this study, three different model phenolic resins were characterized from synthesis to degradation and compared to a commercial honeycomb dip resin. All of the phenolic resins investigated 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 and unbound species. The second degradation transition was attributed to the volatilization of species loosely bound to the phenolic backbone, and the final region represented bulk degradation of the phenolic matrix. Flammability studies were also performed on laminates manufactured from these resins. The flammability of all resins investigated was correlated to bound and unbound materials in the matrix. Mechanical tests were performed on the neat resin plaques and laminates. The various chemistries that exhibited the properties discussed were understood in terms of catalyst basicity, solubility and boiling point and crosslink density. Honeycomb fracture testing was also performed on the commercial and model systems and the fracture toughness of the resin was found to have a larger influence on the compressive properties of the honeycomb than on the flexural strength of the resin. From this study it can also be concluded that the performance of phenolic resins is strongly dependent on the nature of the catalyst used in their synthesis.

## **ACKLOWLEDGEMENTS**

The authors express their appreciation to Boeing Materials Technology and the Boeing/Steiner Professorship.

## **REFERENCES**

- 1. Redjel B., "Mechanical properties and fracture toughness of phenolic resin", *Plastic, Rubber and Composite Processing and Applications*, Vol. 24, 1995, pp. 221-228.
- 2. Determination of Flammability Properties of Aircraft Materials, Boeing Commercial Airplane Group, Seattle, WA, 1994.
- 3. Ohio State University (OSU) Calorimeter Determination of Heat Release, Boeing Commercial Airplane Group, Seattle, WA, 1994.
- 4. J. M. Whitney, Interlaminar response of composite materials, in *Composite Material Series*, N.J. Pagano, ed., New York, Elsevier, 1989.
- 5. L. J. Gibson and M. F. Ashby, *Cellular Solids: Structure and Properties*, Cambridge, Cambridge University, 1997.
- 6. S. P. Timoshenko and J. M. Gere, *Theory of Elastic Stability*, New York, McGraw Hill, 1961.