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INVESTIGATION OF THE EFFECTS OF NaOH DOPANT LEVEL ON THE
PHYSICAL AND MECHANICAL PROPERTIES OF CARBON/PHENOLIC
COMPOSITE MATERIAL.

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ABSTRACT

The near-catastrophic erosion of the STS-8A solid rocket booster nozzle was the instigating factor in the recent, and on-going, intensive investigation of carbon/phenolic composite materials. Much of this effort has been focused on the effect of sodium contamination on the carbon fibers. It is known that sodium acts as a catalyst in the oxidation of the fibers at elevated temperatures. However, the effect of such contamination upon the phenolic resin and matrix-controlled mechanical properties was unknown. To this end, a study was undertaken to determine what changes were caused by variation in sodium content.

Investigations were conducted in three areas: phenolic resin, carbon/phenolic prepreg, and cured laminates. Due to the exploratory nature of the studies, a variety of tests in addition to those normally run in production facilities were considered. The experimental methodologies and results of these experiments are discussed, and recommendations for improving techniques and extending the research program are presented.

1. INTRODUCTION

Quality control, both in the constituent materials and throughout the fabrication process, is the critical factor in the production of reliable composite parts. To be assured of the reliability of the product, it is necessary to (1) have a thorough understanding of the parameters involved in each processing step, (2) have representative material property allowables, and (3) be able to nondestructively evaluate the integrity of the part.

The importance of the above requirements was underscored by the discovery that sodium contamination of carbon cloth used in the construction of the shuttle carbon/phenolic solid rocket booster nozzles was a contributing factor in the near failure of STS-8A nozzle. Results of initial studies of this anomaly indicated that sodium, known to be a catalyst in the oxidation of carbon fibers at elevated temperatures, (1-4) accelerated material erosion. However, the effect of sodium contamination on resin properties was not addressed. The research described in the following pages was undertaken to assess this effect and to examine test techniques for the qualification of carbon/phenolic materials.

Investigations were conducted to determine resin, prepreg, and cured laminate properties at specific dopant levels. The prepreg series included analyses of resin flow; resin, cloth, and carbon filler contents; volatile constituent identification and standard volatiles content; sodium content, and gel permeation chromatography. Tests conducted on the phenolic resin included gel time, differential scanning calorimetry, thermomechanical analysis, thermogravimetric analysis, gas chromatography, gel permeation chromatography, infrared spectrophotometry and viscosity. The cured laminates were subjected to a variety of NDE methods before being machined into specimens. The mechanical properties characterized were those which depended to varying degrees on matrix properties: short beam shear, compression, and flexure.

2. PHENOLIC RESIN STUDY

The phenolic resin analyzed in this part of the investigation was Borden's SC-1008. This system is presently being qualified under military specification MIL-R-9299C for the production of nozzles for the solid rocket boosters. At the outset, it will be necessary to briefly discuss basic resin chemistry, but only to the extent to which it impacts the study. For additional information, there are numerous texts written on the subject of phenolic polymerization which deal with the process in much greater detail. (5,6)

There are two kinds of phenolic resins, one stage and two stage. Ironside 9ILD (used in the prepreg) and the SC-1008 are both one stage resins. A simplified reaction for the production of a phenolic resin is shown in Figure 1. Phenol reacts with formaldehyde under neutral or slightly basic conditions to yield two major products, ortho-methylol phenol and para-methylol phenol. Ortho substitution is kinetically preferred and thus there will be a greater relative percentage of this product. As noted, the para-substituted product will react faster, thus

reducing gel times. One other feature of interest is the chromophore formed by the pendant hydroxyl group and the benzene ring. A color change will result when the hydrogen in the hydroxyl group is replaced, for example, by sodium. Such a change was noted in several trial laminates constructed from resin impregnated white bleeder paper. The matrix darkened with increased sodium content.

An elementary polymerization reaction is also shown in Figure 1. The hydroxyl groups lost in the cross-linking process form water which is the dominant constituent of volatiles given off during curing. In reality, the condensation polymerization is of much greater complexity than that shown here.

The key point is the effect of sodium hydroxide doping on these reactions. In the first reaction, Na^+ will attack the OH^- group yielding sodium phenolate. It is consistent with theory (6) that this is a more active compound and may lead to a higher incidence of para-substitution. Also sodium hydroxide will degrade resin oligomers; i.e., break down the small to medium length chains into even smaller chains. (7) The addition of sodium may promote the formation of ether linkages during polymerization (Williamson ether synthesis) (6). This linkage is weak and may start to degrade at elevated temperatures.

Finally, it is worth noting that compounds often used in the processing of two stage phenolic systems were identified in the SC-1008 and the 91LD resins. The presence of hexamethylenetetramine, which is used as an activator in the polymerization of two stage resins, was indicated by ammonia efflux noted during gel time tests. It has been suggested that hexa was introduced to control the pH (7). Furanicarboxaldehyde is added to two stage resins to control the flow rate, as these resins are often used as molding compounds. It was identified, using the gas chromatograph-mass spectrometer technique described in section 3.4.2, as a constituent of the 91LD phenolic. The role of the additive in the single stage resin is unknown at this time.

1 STAGE RESIN

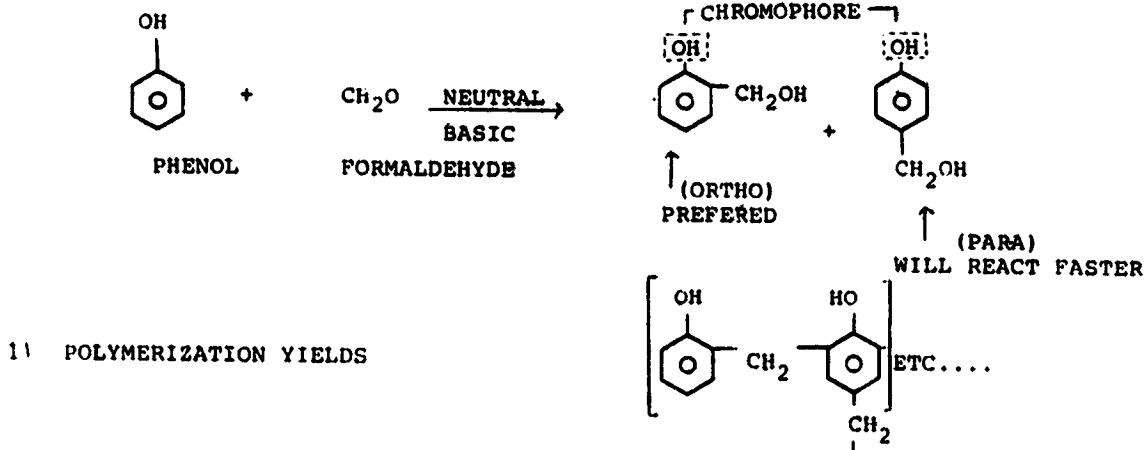


Figure 1. Simplified Reactions for Phenolic Resin Production and Polymerization

2.1 Gel Time

The effect of sodium hydroxide doping on resin gel time was determined using a Fisher-Johns Melting Point Apparatus. All tests were conducted at a constant 350° F. Two critical parameters which must be controlled to obtain repeatable results are drop size and surface area exposed to elevated temperature. Drop size was kept constant at 0.167 grams by using a micro pipette. Due to changes in viscosity with sodium content (discussed in section 2.3) it was necessary to evenly spread the drop to maintain an initially uniform surface area.

The variation in gel time with sodium content is shown graphically in Figure 2. On the semi-log scale, the relationship between the two parameters is a linear one. The fact that gel times are reduced with increasing sodium level agrees well with the hypotheses concerning the effect of NaOH addition proposed in the prior section.

2.2 Differential Scanning Calorimetry

Samples of NaOH doped resin (approximately 0.2 grams) contained in volatile pans were tested in a nitrogen atmosphere under a pressure of 225 psi. using a Dupont 910 Differential Scanning Calorimeter. The chamber was initially purged with nitrogen, and the temperature rise rate was set at 2°C/minute.

The DSC traces are presented in Figure 3. It is apparent that increasing the sodium content lowers the polymerization onset temperature and increases the reaction rate. These results are consistent with the behavior observed during gel time tests and may possibly be attributed to a higher incidence of para-substitution caused by sodium addition. However, further work is necessary to substantiate this hypothesis. Note also that the exotherm increases with sodium level.

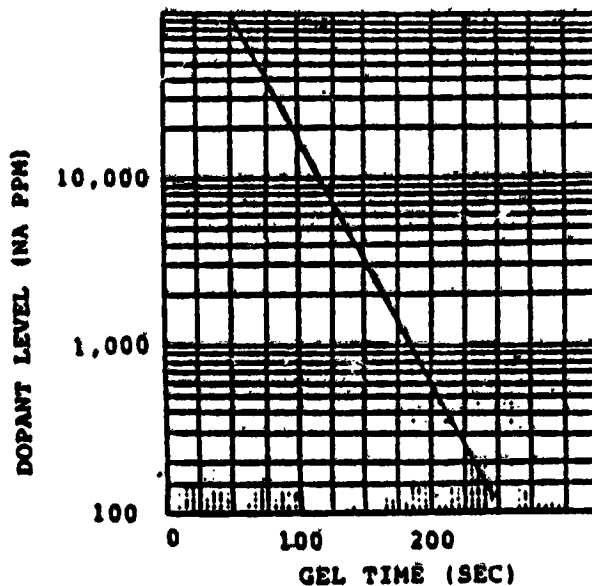


Figure 2. SC-1008 Phenolic Resin Gel Time as a Function of Sodium Content

2.3 Viscosity

Resin viscosity as a function of sodium content was measured at room temperature using a Brookfield Model LVDT Digital Viscometer. To obtain prescribed sodium levels, equal volumes of several concentrations of aqueous sodium hydroxide were added to pure resin. The viscosity of each sample was compared to that of a baseline solution which consisted of pure resin mixed with a volume of deionized water equal to that of the sodium hydroxide solutions. The viscosities of the aqueous NaOH solutions were also measured. The baseline for these measurements was pure deionized water.

The percent changes in viscosity with respect to baseline values are presented in Table 1. It is evident that the increase in viscosity at the 1000 ppm and 2000 ppm levels was due primarily to a chemical change in the resin as there was no measurable difference in the viscosities of the aqueous sodium hydroxide solutions. At a concentration of 5000 ppm, a transition had begun in which the dominant influence on the viscosity shifted from being chemical in nature to simply a "thickening" effect as evidenced by the increase in the viscosity of the aqueous NaOH solution. As the sodium level was increased, this effect became obvious.

2.4 Gel Permeation Chromatography

Gel permeation chromatography (GPC) is the separation by molecular size of molecules in solution. (8) Since the effective size of the polymer molecule is closely related to the molecular weight of the polymer, molecular-weight distributions may also be obtained. This technique was utilized to both compare the two resin systems and to evaluate sodium effects and resin advancement.

A Waters High Performance Liquid Chromatograph with Sigma data station was used with Waters Ultra Gel Permeation columns having pore sizes of 1000 Å, 500 Å, and 100 Å. Further, a flow rate of 1 ml/minute was chosen and sample size was standardized at 40 microliters.

Three solutions, 0.5% by weight, SC-1008 resin to tetrahydrofuran (THF) were examined. The first solution was pure SC-1008 phenolic resin. The second was pure SC-1008 resin which had been exposed to ambient conditions for 15 days prior to solution preparation. The third solution was SC-1008 doped with 5000 ppm sodium.

By comparing the results of the latter two solutions with those of the pure resin solution, the following conclusions were drawn:

1. Resin exposed to ambient conditions for 15 days had a higher number of higher molecular weight constituents, indicative of resin advancement, and
2. Sodium hydroxide doped samples had lost some high molecular weight constituents and gained some low molecular weight constituents. This shift in the molecular weight distribution can be attributed to the breaking down of the oligomers. This degradation is caused by sodium addition, as stated previously.

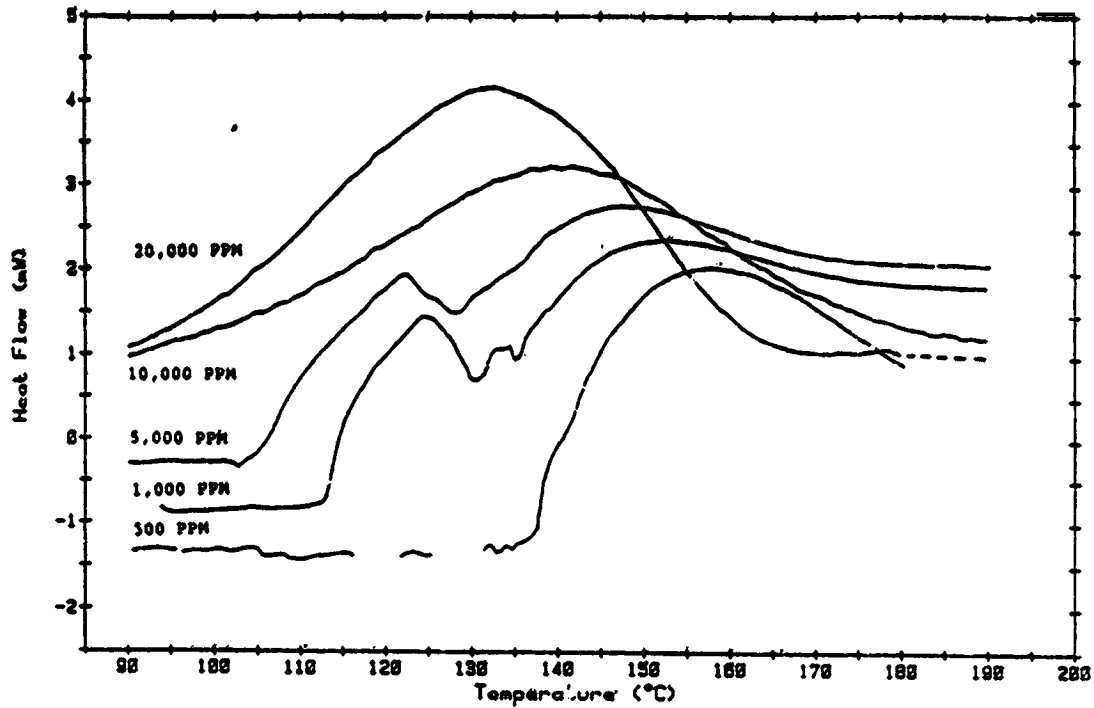


Figure 3. Differential Scanning Calorimetry Traces of Sodium Hydroxide Doped SC-1008 Phenolic Resin.

TABLE I

Viscosity Analysis

DOPANT LEVEL (Na ppm) SC-1008 + H ₂ O	% CHANGE RESIN Baseline	% CHANGE NaOH + H ₂ O Baseline
1000	9.4	0
2000	16.0	0
5000	18.9	10
10000	75.5	75
20000	132.0	175.0

2.5 Infrared Spectrophotometry

Samples of pure, and sodium hydroxide doped SC-1008 phenolic resin were studied using a Perkin-Elmer Model 137 Sodium Chloride Spectrophotometer. This analysis was conducted to determine if differences existed among the molecular structures of the pure and doped resin solutions. Several unidentified and unexpected peaks were observed, and research on the sources of these peaks is continuing. However, with the present instrumentation, it is not possible to obtain the information necessary for a proper analysis. Equipment of greater sophistication is required.

3. PREPREG ANALYSIS

The carbon/phenolic prepreg material used in this investigation was U.S. Polymeric FM 5055. The phenolic resin was Ironside 91LD, which was qualified under military Specification MIL-R-9299C. The carbon cloth, qualified under Thiokol Corporation Specification STW4-3184, was a rayon-based, eight harness satin fabric. Limits on the thread count were set at 45-55 yarns per inch in both the warp and fill directions, yielding a fabric weight range of 7.5 - 9.5 ounces per square yard. The third constituent was a carbonaceous filler, specifically P33, having a minimum carbon assay of 99%.

Before discussing the test methods and results, it is appropriate to describe the procedure used for NaOH doping of the prepreg. Four concentrations of a deionized water-sodium hydroxide solution were prepared and sprayed uniformly on one side of the test plies using a commercial air brush. The concentrations were calculated to add approximately 500, 1000, 1500, and 3000 ppm of sodium to the as-received material which served as the sodium content baseline. The amount of solutions sprayed on each ply did not vary among dopant levels. A control group (designated "water wash") which was sprayed with an equivalent amount of deionized water was also included.

Immediately after having been sprayed, materials were placed in a vacuum chamber at room temperature for one hour to remove excess moisture. It was determined that this period of time was sufficient to return the material to its weight before spraying, plus, of course, the added sodium. At this point, the doped prepreg material was ready for testing or fabricating into laminates.

Standard prepreg qualification tests required by Thiokol specification STW5-2649E were conducted. Additionally, several other tests not normally run in a production environment were incorporated, which did provide useful information. Methods for these additional tests will be explained, and standard test methods will be described in cases where it is felt that improvements can be made or potential problems exist.

3.1 Sodium Content

The prepreg content in parts per million (ppm) was determined using a Perkin-Elmer Model 5000 Atomic Absorbance Spectrophotometer. Samples weighing approximately 2 grams were placed in an oven for 16-18 hours at 1112°F to burn off the organics, thereby leaving sodium and other inorganic metals. This material was then put into solution with 5 milliliters of 12.1 N hydrochloric acid and 5 milliliters of deionized water used to rinse all matter from the crucible. The solution was diluted by a factor of 100 to 1 with deionized water before measurements were made.

The variation in the sodium level along the length of the as received prepreg can be seen in Table 2. Substantial differences in the level of sodium contamination are apparent, even in samples taken from roughly the same area, as evidenced by the values at 26 feet. These changes in concentration certainly contributed to the variation of sodium content in doped samples. Average values for each dopant level are also shown in Table 2.

3.2 Prepreg Resin, Cloth, and Filler Contents

The contents of the primary constituents of the carbon/phenolic prepreg were measured both to qualify the material with respect to Thiokol certification and to ensure that the sodium doping procedure did not alter these quantities. The following method was used to determine the percentages, by weight, of the three main constituents of the prepreg.

A room temperature sample, approximately 2 grams, was initially weighed, and then stirred in 450 milliliters of THF (tetrahydrofuran) at 95° F for 30 minutes. The solution was filtered and the fabric and separated fibers removed from the filter. This material was repeatedly washed with THF and the filtrant collected until the washing solution remained clear. Fabric and fibers, and the filter paper were then dried under vacuum at 113° F. The weight of filler was determined from the difference between initial and final filter weights. Resin weight was calculated by subtracting the cloth and filler weights from the devolatilized initial sample weight, (see section 3.4 for volatile content). The percentage was determined by dividing the weight of each constituent by the devolatilized sample weight.

Measurements were made on as received material and on samples considered to be extremes from this state, water wash and 3000 ppm added. Results of the analysis are presented in Table 3. The slight deviations of the 3000 and WW values from the as received state were within experimental error. It was concluded that the sodium doping procedure had a negligible effect on the resin, cloth, and filler content of the material.

TABLE 2

Sodium Contents of Prepreg Samples

As Received		Doped Material	
<u>Location (ft)</u>	<u>Average Na (ppm)</u>	<u>Sample Designation</u>	<u>Average Na(ppm)</u>
1	463	Waterwash	502
26	497	500	1214
26	890	1000	1358
44	385	1500	1792
75	524	3000	2708
100	462		
121	806		

TABLE 3

Resin, Cloth, and Filler Contents of Prepreg Material

	<u>Thiokol-Supplied Batch Properties (%)</u>	<u>As Received (%)</u>	<u>3000 ppm Added (%)</u>	<u>Waterwash. (%)</u>
Resin Content	32.8	31.7	31.2	32.6
Cloth Content	52.8	53.8	55.9	54.9
Filler Content	14.4	14.4	12.9	12.5
Volatile Content	4.2	5.2	5.0	5.3

3.3 Resin Flow

The standard resin flow test as specified by Thiokol involves cutting four 4" x 4" squares of prepreg across the fabric width, stacking the squares to form a four-ply laminate, and recording the weight of the stack. All plies are to be bias cut to avoid fiber loss. The specimen, sandwiched between release plies, is placed in a heated press (325° F) and 150 ± 10 psig is applied immediately. After 10 minutes, the specimen is removed; resin flash is scraped away; and the specimen is weighed. The percent resin flow is calculated from the difference between the initial and final weights.

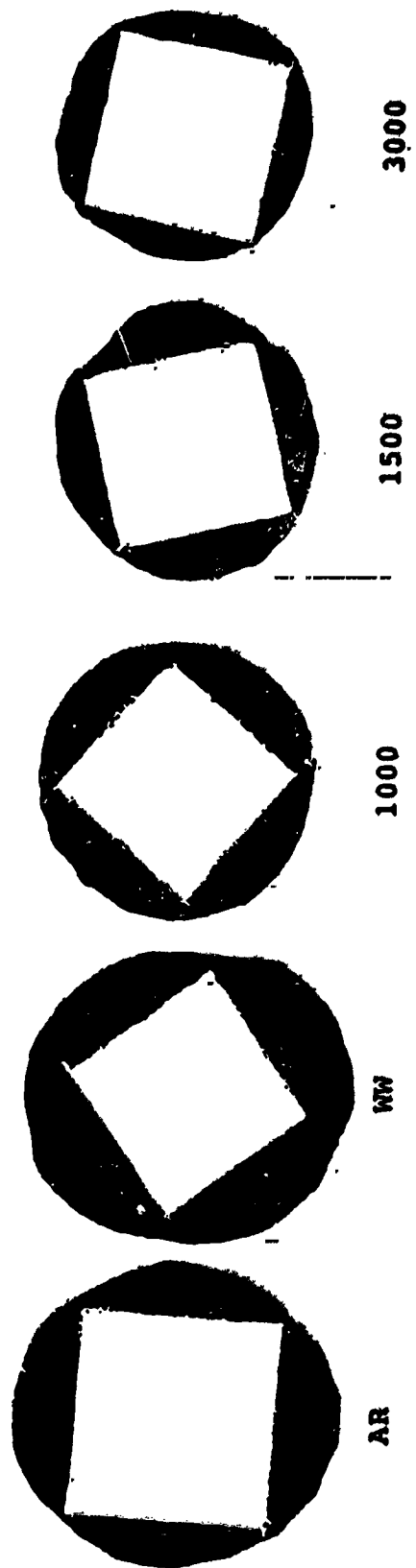
The prepreg material supplied by Thiokol was five inches wide, thus prohibiting use of a four inch square specimen cut on a 45° bias. The choice was either to piece together a four inch specimen or run a smaller three and one-half inch square bias cut specimen. Initially, there was concern that a nonlinear relationship might exist between specimen size and percent resin flow, so tests were conducted on three inch and three and one-half inch square specimens. Resin flow averaged 23.87% and 24.27% respectively. Obviously two points cannot settle a question of nonlinearity. However, since the ranges of the data sets completely overlapped and test results from pieced specimens (4", 3.5", and 3" square) were much too variable, it was decided to conduct flow tests using 3.5" square bias cut specimens.

The results of the tests are presented in Figure 4. The actual sodium contents listed are representative values based on chemical analysis described in section 3.1. The dark circles surrounding the white square are reduced reproductions of actual flow specimens. Resin flow areas are darkened, and the white square is the area from which the four-ply specimen was removed. From Figure 4, it is apparent that the flow decreases with increasing sodium content. The trend is fully supported by the experimental data, in which a nearly inverse proportionality is evident between percent resin flow and sodium content.

This behavior corroborates the results of the resin study. In the discussion of basic resin chemistry, one proposed effect of sodium addition was the tendency for a higher incidence of para-methylol phenol, which reacts more quickly and thus reduces gel time. The hypothesis was supported experimentally by the results of gel time and differential scanning calorimetry tests. The impact of increased sodium on resin flow is an obvious reduction due to faster gel.

As a final comment on the test procedure, it must be noted that the time during which the specimen is exposed to elevated temperature before the application of pressure is a critical factor. At 325° F the resin cures rapidly, and delays in pressure application will significantly influence the data. The time differential should be monitored and reported with the flow data. For all test results reported herein, this time was 19 ± 2 seconds.

FLOW TESTS



III-10

Sample Designation	Representative Sodium Level (ppm)	Resin Flow (%)
Water wash	500	26.27
As Received	600	26.68
500 PPM Doped	1200	23.10
1000 PPM Doped	1400	22.64
1500 PPM Doped	1800	20.89
3000 PPM Doped	2700	17.57

Figure 4. Visual and Quantitative Results of Prepreg Resin Flow Tests

3.4 Volatiles Analysis

3.4.1 Standard Test

The standard test for volatile content is straightforward. The weight loss of a sample of prepreg fabric (4" x 4") is measured after exposure to 323° F for 10 minutes in a recirculating oven. This value, when divided by the initial weight, yields the percent volatiles content.

Due to the excess water introduced into the material by the doping procedure, it was necessary to place the specimens under vacuum for one hour at room temperature to remove the moisture before testing. As received specimens were also vacuumed for consistency. Tests conducted on doped samples were limited to extreme states, WW and 3000, to ascertain whether differences existed and tests at intermediate levels were warranted.

Results are presented in Table 4. Although values from tests of the 3000 ppm added samples were slightly below those obtained from either of the other groups, the differences among the three groups were considered to be insignificant.

Also displayed in Table 4 are results from specimens tested without exposure to vacuum. The as received and the water wash samples were exposed to ambient laboratory atmosphere for 24 hours before testing. It is evident upon comparison with the above data that the one hour exposure to vacuum did not affect the volatile content of these two groups.

However, a significant difference in the volatile content of the sodium doped samples after exposure to ambient laboratory atmosphere can be seen. After one hour, an increase is noted, which could arguably be due to residual moisture from doping. However, there is little doubt that the change observed in the 24 hour value is due to accelerated moisture absorption caused by the presence of sodium.

3.4.2 Identification of Volatiles

It was stated in the previous section that high levels of sodium (3000 series) had no effect on the amount of volatiles released when the samples were vacuumed before testing. But there was concern that the volatile constituents might be altered by the level of sodium contamination. Therefore, the following procedure was developed to investigate this hypothesis.

Prepreg specimens of identical weight were placed in sealed canisters held at 120° F for 16 hours. Samples of gases extracted from the canisters were analyzed using a Perkin-Elmer Sigma 300 Capillary Chromatograph with Sigma 15 data station to obtain quantitative data on the volatiles. Next, samples were extracted for analysis on a Finnigan Model 4000 Automated Gas Chromatograph Mass Spectrometer System, which separates compounds in the GC and then, through computer analysis of mass spectra, determines the compounds present.

An initial series of tests was conducted on AR, WW, and 3000 prepreg material at 150° F to identify the low boiling point effluents. The major constituents were ethanol, isopropanol, and methyl isobutyl ketone, and the minor constituents were ethyl acetate, 2-furancarboxaldehyde, and methyl ethyl ketone. —No dopant effects on either the amounts or the relative amounts of these components were noted. - -

An additional series of tests using a Hewlett-Packard 5710A Gas Chromatograph was conducted at 203°F to determine the amount of phenol present in the volatiles. The quantity of phenol released was strongly influenced by sodium content. The phenol measured in the volatiles of the 3000 ppm specimens was approximately 5 times that observed in the analysis of the water wash samples and 8 times that measured from the as-received samples.

TABLE 4
Volatiles Content - Standard Test

	<u>Group Designation</u>	<u>Volatiles Content (%)</u>	
1 hr. Vacuum	As Received	5.23	
	Water Wash	5.28	
	3000	5.01	
No Vacuum	As Received (24 hours)*	5.22	
	Water Wash (24 hours)*		
	3000 (1 hour)*	5.47	Moisture
	3000 (24 hours)*	7.33	Absorption

*Note: Times listed in No Vacuum set denote length of exposure to ambient conditions before testing.

3.5 Gel Permeation Chromatography

The instrumentation and experimental conditions used to study the prepreg (91LD phenolic resin) were identical to those described in section 2.4. Resin was extracted with THF from a quantity of prepreg which had been calculated to yield a 0.5% solution of resin (by weight) and THF. Three solutions were prepared. The first was taken from a sample of as received material. The second was taken from a water wash sample, and the final solution was from a doped piece of material which had a sodium concentration approximately 3000 ppm greater than the as received prepreg.

Data from the prepreg analyses were compared within the group and also with that obtained from the SC-1008 study. The following are results of those comparisons:

1. The two resin systems appeared to be basically the same; however, a peak was evident in the prepreg (91LD) which was not present in the SC-1008. At this time, the source of the peak has not been identified.
2. The above peak is smaller in water wash and 3000 ppm traces than in those from the as received material.
3. The 3000 ppm samples appear to have lost some high molecular weight constituents and gained some low molecular weight constituents.

The third result is similar in nature to that observed in the sodium doped SC-1008 samples and provides additional experimental evidence of the degrading effect of sodium on these resins.

4. CURED LAMINATE ANALYSIS

Eighteen carbon-phenolic panels were fabricated for test specimens to investigate the effect of sodium concentration on matrix-influenced mechanical properties. The mechanical tests conducted were compression (warp), flexure (warp), and short beam shear. One panel was produced for each property at each of the six targeted sodium levels: as received (AR), waterwash (WW), 500 ppm added, 1000 ppm added, 1500 ppm added, and 3000 ppm added. Sodium was introduced in the prepreg material in the manner described in section 3. The compression and flexure panels were each constructed from four plies of material, and the short beam shear panels were comprised of nine plies.

All panels were cured in a heated press. A hydroclave cure cycle recommended by Thiokol, Wasatch Division, was adapted for use with the press. The steps are listed below.

1. Debulk under full vacuum for 30 minutes prior to cure
2. Increase pressure to 225 psig at room temperature
3. Raise temperature to 180 \pm 10°F; hold for 90-120 minutes

4. When temperature reaches 170°F, increase pressure to 1025 psig at an average rate not to exceed 20 psi per minute
5. Raise temperature to 220 ± 10°F; hold for 60-90 minutes
6. Raise temperature to 310 ± 10°F at a rate not to exceed 1°F/minute
7. Hold at 310°F for a minimum of 5 hours
8. Decrease pressure to 200-250 psig at a rate not to exceed 50 psi/minute while holding at 310°F
9. Cool to 160°F at an average rate of 0.5°F/minute, maximum
10. Continue to cool for an additional 90 minutes, minimum, to room temperature before dropping pressure and vacuum.

Thermocouples were inserted in the edges of the laminates to monitor part temperature and thus to ensure the proper rise rate.

4.1 Laminate Quality Assurance

4.1.1 Nondestructive Evaluation

Several nondestructive evaluation techniques including computer aided tomography (CAT-Scan), radiography, through transmission ultrasound, alcohol wipe, and ultrasonic C-scan were employed to assess the integrity of the panels. The utilization of these methods was not targeted specifically to sodium dopant level analysis. Instead, these series of tests were designed to determine which of the techniques were suitable for evaluation of panels of this material and of these thicknesses. The effectiveness of the methods is summarized briefly in the following paragraphs.

CAT-scan analysis was generally not useful for these thin carbon-phenolic materials. Some visually identifiable surface defects were observed in the scans, and several of these did correlate with assumed low density areas located by alcohol wipe. However, other "suspect" regions identified by one of the methods were not substantiated by the remaining two. Bulk densities were also determined with CAT-scan in five different locations, and the average increased with increasing sodium content. This trend was not present in the actual measured values. However, it must be noted that the CAT-scan values were obtained from a small (.060" wide) slice of the panel.

X-ray analysis provided very little information. Only one defect, a surface bubble, was detected. The samples were too thin for this technique to be successful.

Through transmission ultrasonic measurements were made on each panel at four equally spaced locations along the centerline. Unlike the previously described methods, the effort in this series of tests was directed toward

correlation of signal characteristics with sodium dopant level. Velocity and attenuation data were evaluated; however, no trends were evident. One surface defect was analyzed, and a frequency shift in the wave form was observed. This anticipated result indicated that a 100% scan would be useful in the detection of flaws.

The ultrasonic C-scan inspection proved to be the most useful of the techniques studied. Density variations were readily apparent in the scans, which were run using a Sperry Reflectoscope Model S80. Representative C-scan results for a compression and a flexure panel are shown in Figure 5. Areas which appear white in the figure are regions of high attenuation. High scattering is responsible for much of the apparent density variations around the edges, and the four circles in each panel near the corners are the fixture posts. Overall, the scans indicated a high degree of uniformity in the panels' central portions from which all specimens were taken.

4.1.2 Sodium Content and Resin Content

After the nondestructive evaluations were completed, the panels were machined into the various specimen configurations. Initially, a 1-inch-wide trim area was removed from the perimeter of the laminates. Samples from the trim, adjacent to the specimen area were analyzed to determine sodium content and resin content of each panel. The sodium analysis was performed in the manner described in section 3.1, and the results are shown in Table 5.

The percent resin contents were determined according to the following procedure:

1. Clean material samples and weigh to nearest 0.001 g.
2. Place specimens in Vycor test tube and connect to a flask with cold finger condenser and a vacuum source attached.
3. Evacuate the system to 10 ± 5 mm of mercury absolute.
4. When pressure stabilizes, place one Fisher burner under the samples in the end of the tube. Adjust the flame to cover the sample completely.
5. Pass an additional Fisher burner along the bottom of tube to drive out gases and prevent residue condensation in tube.
6. Continue pyrolysis for approximately 30 minutes or until pressure gauge reading returns to value prior to pyrolysis, whichever is longer.
7. When pyrolysis is complete, cool to room temperature while maintaining vacuum.
8. Turn off vacuum and slowly let air into the test tube until equilibrium is reached. Remove and weigh the specimen to nearest 0.001 g.

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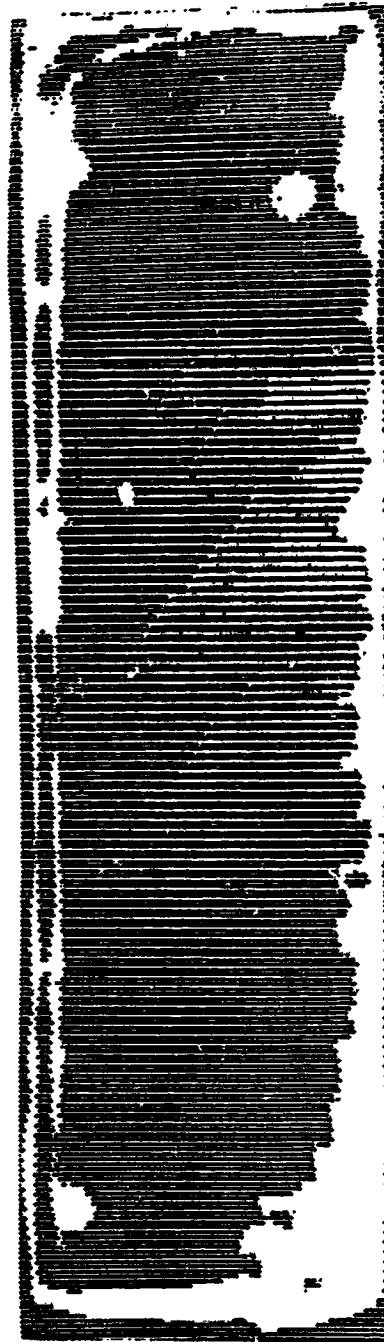
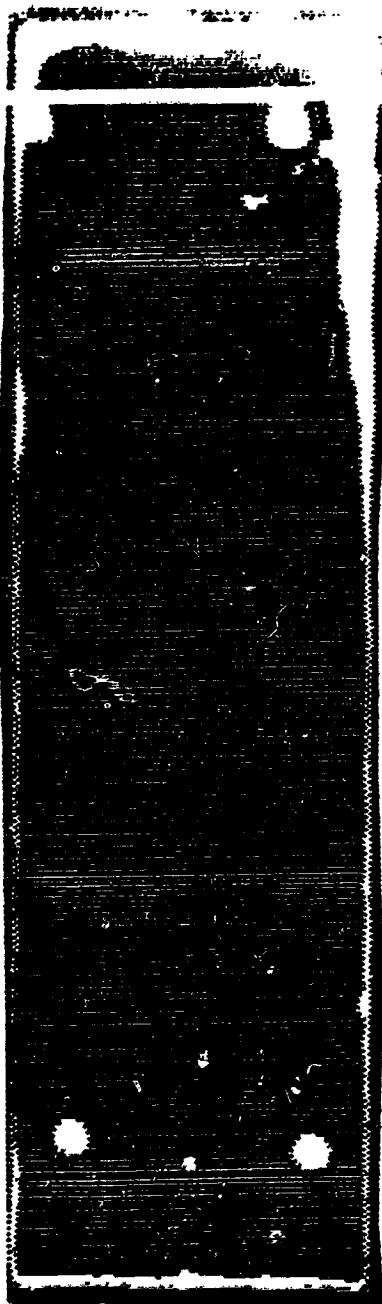


Figure 5. Representative Ultrasonic C-scans of Thin (0.060") Carbon/Phenolic Test Panels.

9. Calculate dry resin content using equations below

$$\text{Resin content (\%)} = (1.00 - \text{final weight}/\text{initial weight})(100)(K)$$

where K is an empirical constant, for this material which equals 2.008.

The resin content for each specimen panel is shown in Table 6.

Table 5. Average Sodium Content (ppm) of Test Panels

Target Sodium Level Panel Designation	AR	WW	500	1000	1500	3000
SBS	610	765	996	1461	2286	3726
COM	642	697	1197	1710	2028	3531
FLX	640	516	1302	1967	2797	4090

Table 6. Average Percent Resin Content of Test Panels

Target Sodium Level Panel Designation	AR	WW	500	1000	1500	3000
SBS	33.1	34.0	33.8	35.4	36.1	33.6
COM	38.3	33.7	39.1	39.5	37.3	37.2
FLX	36.4	34.1	37.7	35.9	37.9	41.0

4.1.3 Microscopy

Two types of microscopy were employed in the investigation: optical and scanning electron. Optical microscopy was used primarily qualitatively. Each specimen was examined to assess void content, to inspect irregularities in surface layers, and to detect abnormalities in ply spacing and orientation. The void content was observed to be low, but no measurements were made to quantify this value. No imperfections in the ply spacing were observed in the sample population. However, in addition to the small "bubble" mentioned previously, two types of surface defects were detected and examined. One type consisted of irregular patterns in the matrix surface layer caused by distortion of the release ply. The second were small indentations extending into the top ply. This flaw was due to either a trapped yarn from the fiberglass overbleed ply or wrinkling of the release ply. All shear and

flexure test specimens were required to be defect-free. Surface-type flaws were permitted in tab regions of compression specimens provided they were an ample distance from the gauge section.

The fracture surfaces of several samples were examined under a scanning electron microscope. Regions were studied to determine whether differences existed in the fiber-matrix adhesion (due to sodium doping) and to compare the chemical analysis of selected areas obtained via the energy dispersive X-ray (EDX) technique.

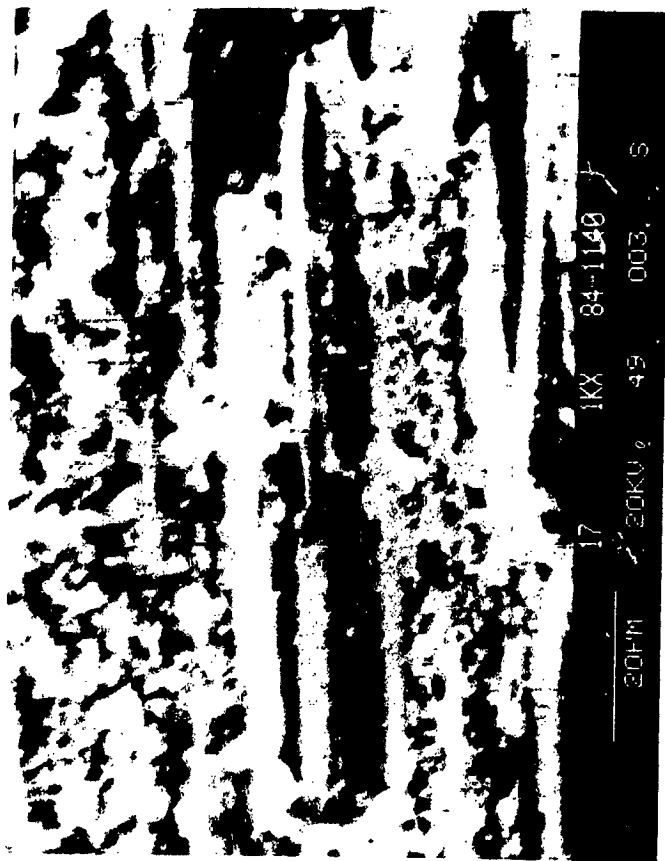
A preliminary indication from this effort is that no apparent differences exist in the interfacial bonding respective to sodium content. Chemical analysis work is also continuing at present, and no definite results are available. However, an example of the information provided by the EDX technique is presented in Figure 6. It is evident that the composition of the particulate on the surface (appears white) shown as the solid trace, does not differ substantially from that of the matrix, represented by the dotted line. The particulate may well be bits of fragmented matrix material. It should be noted that the aluminum and silicon peaks are artifacts of the system. Additional details and results of this analysis will be presented in a subsequent final report.

4.1.4 Thermogravimetric Analysis

Thermogravimetric (TGA) tests were conducted on carbon broadgoods and carbon/phenolic laminates representing various levels of sodium contamination. A Dupont 951 Thermogravimetric Analyzer was used for the study. An isothermal heat treatment at 512 °C for 30 minutes under a nitrogen atmosphere was found to be sufficient to separate sodium contents greater than 500 ppm (sensitivity to approximately 500 ppm).

Samples of carbon fabric were doped to obtain the desired sodium levels using a procedure similar to that described in section 3. The results from tests on these samples are presented in Figure 7. The increase in weight loss with sodium content is apparent, and is attributed to the fact that sodium catalyzes the oxidation of carbon fibers at elevated temperatures.

During evaluation of carbon/phenolic laminates, a dramatic increase in weight loss was noted when samples were tested with normal (50 mL/minute) airflow as compared to results from similar tests conducted with no air flow. This behavior is illustrated by the traces from 1000 ppm added specimens which are shown in Figure 8. The exact cause of this phenomenon is not known at the present time, but the responses are reproducible and investigation is continuing. Since TGA is used as a quality assurance test, the air flow through the test chamber should be monitored and reported with the results to enable meaningful comparison of data.



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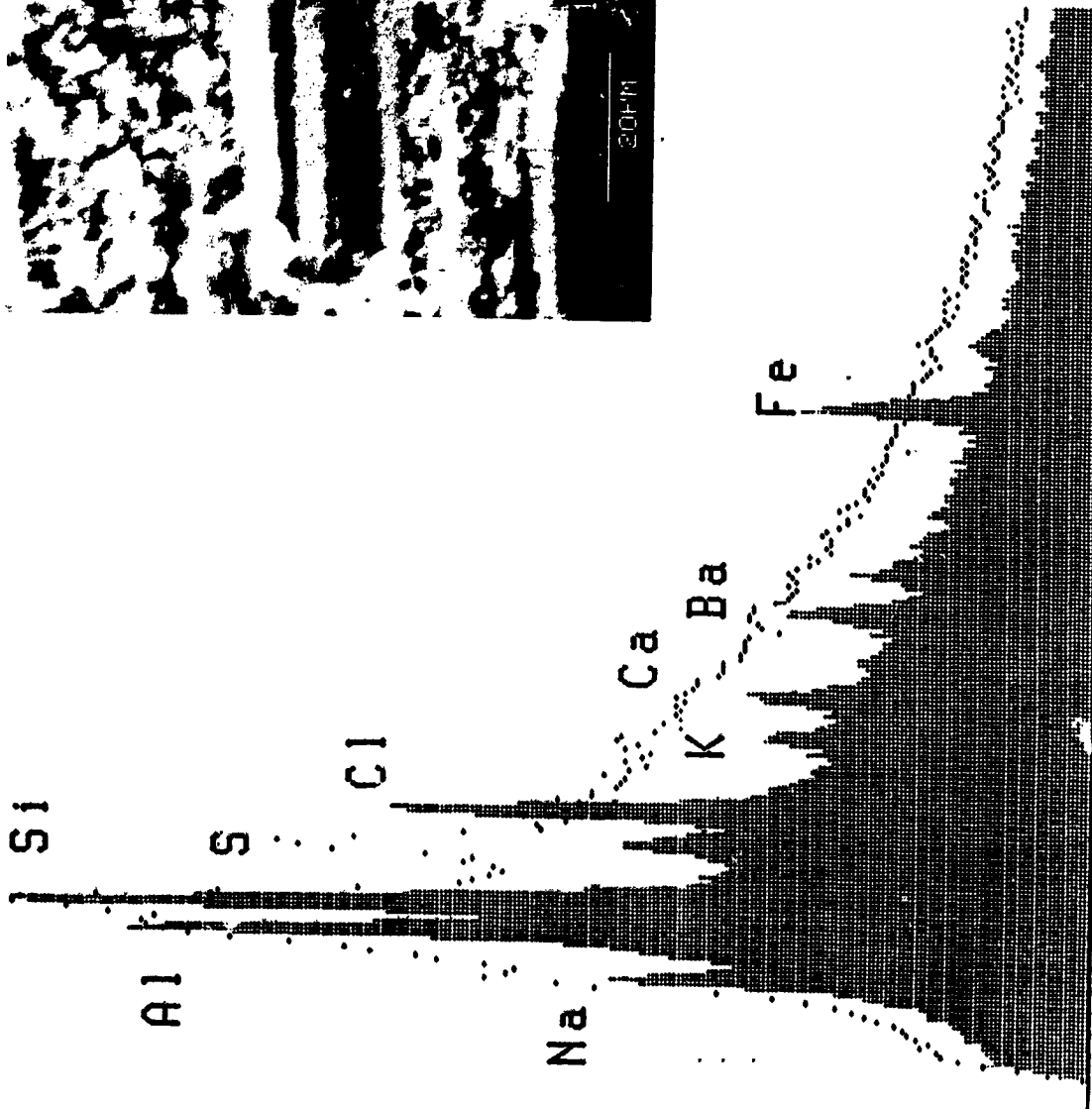


Figure 6. Scanning Electron Micrograph and Chemical (EDAX) Analysis of White Particulate and Matrix of Carbon/Phenolic Material.

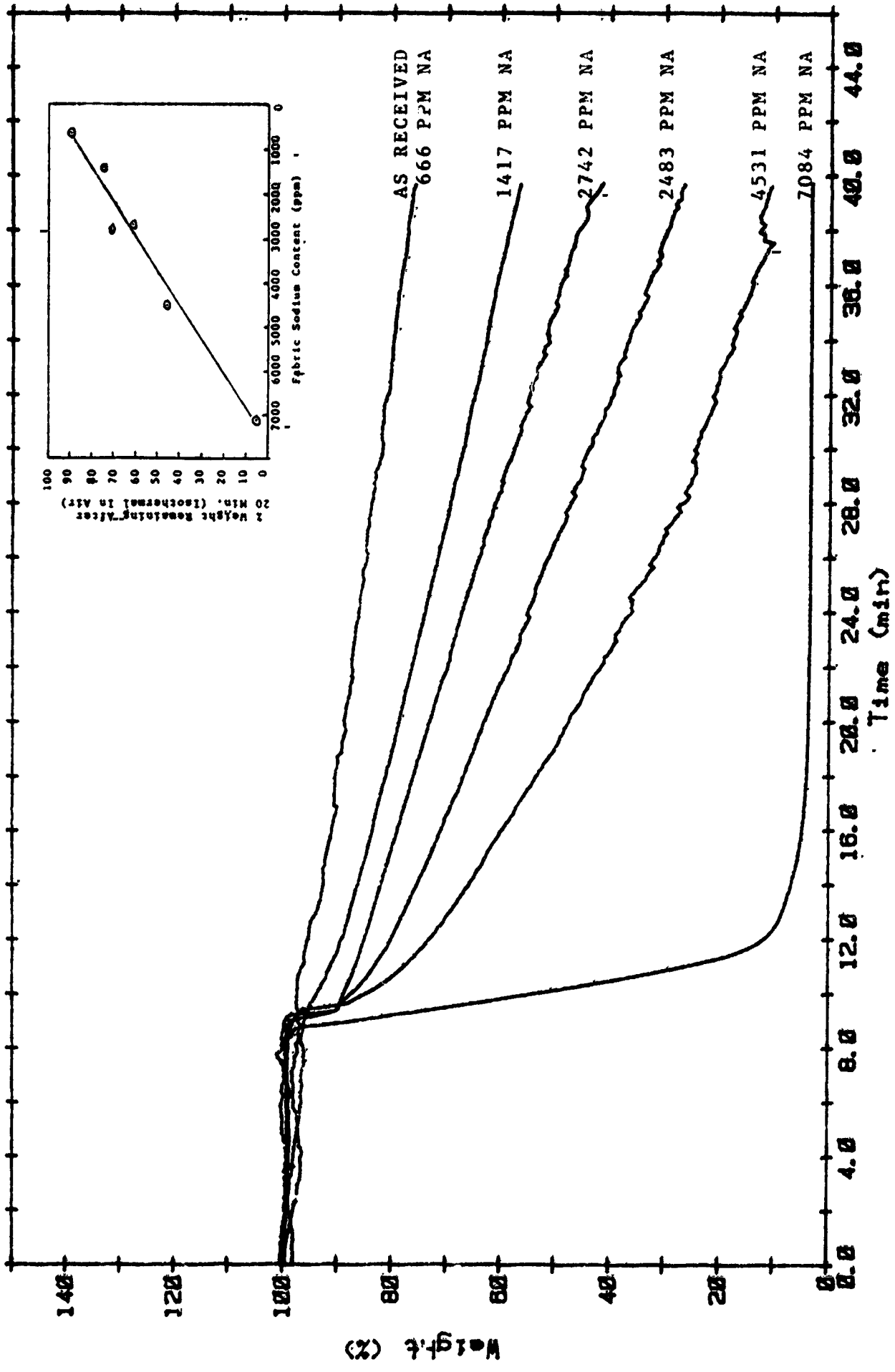


Figure 7. Results of Thermogravimetric Analysis of Sodium Hydroxide Doped Carbon Cloth.

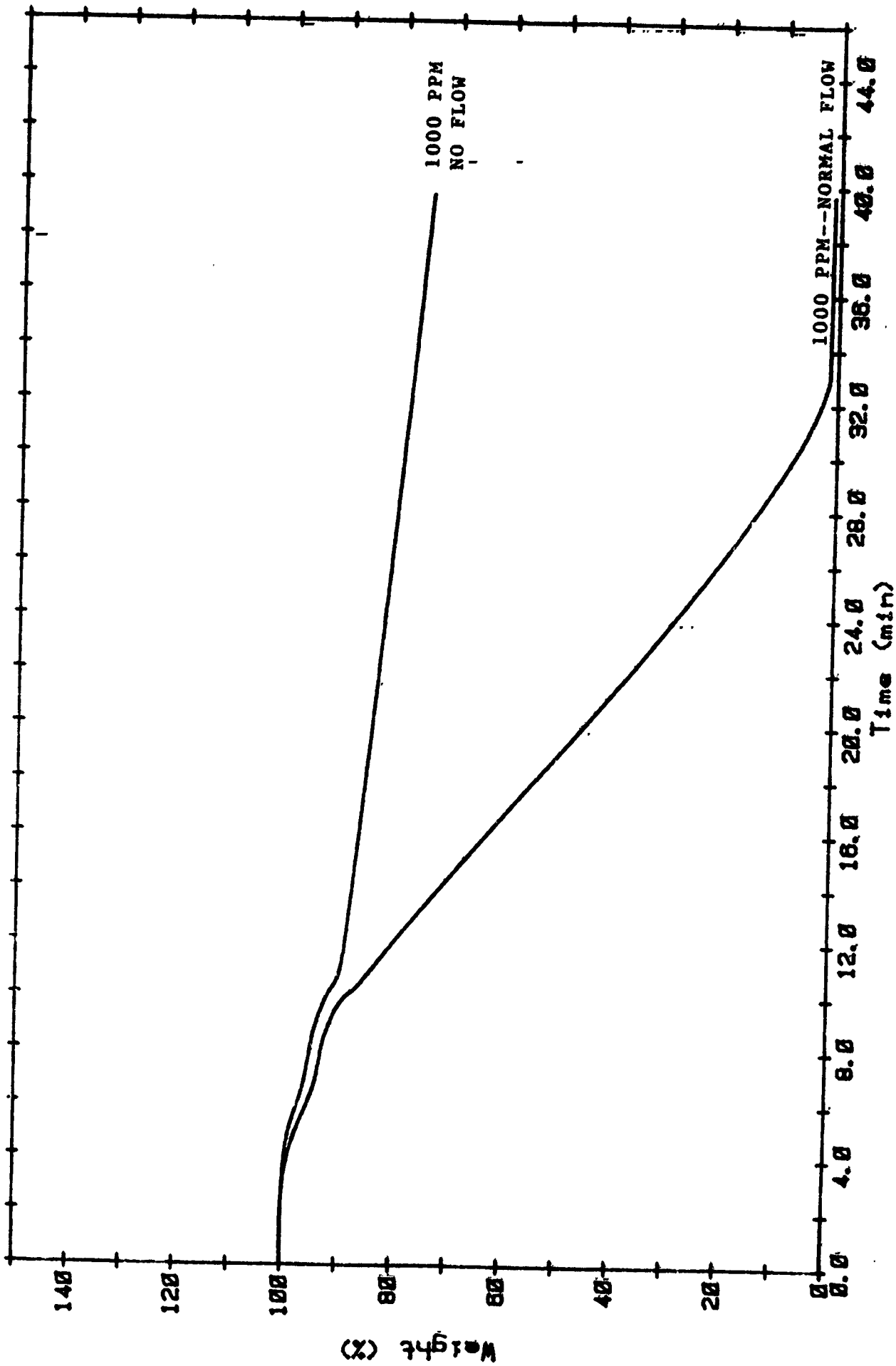


Figure 8. Influence of Air Flowrates on Results of Thermogravimetric Analysis of Sodium Hydroxide Doped Carbon/Phenolic Laminate.

4.2 Mechanical Property Tests

4.2.1 Compression Tests

Compressive strength and modulus values in the warp direction were obtained following ASTM D3410-75, Test for Compressive Properties of Oriented Fiber Composites. The standard requires use of the so-called "Celanese" test fixture, and features a specimen design which has an unsupported gauge length of 0.5 inch. Specimens were constructed from four plies of prepreg which yielded an average gauge section thickness of 0.052 inch.

Tabs were constructed from four plies of the as received carbon-phenolic material and a 0.25-inch, 6° taper was milled into each piece. The tabs were bonded to specimens with AF-191, a supported epoxy bonding film produced by 3M. Bonding was accomplished using a heated press according to the cure cycle recommended by the vendor, with the exception that maximum temperature was 300 °F.

Two-section strain gauges (longitudinal and transverse) were fixed to one side of each specimen and a single gauge was bonded on the opposite side to monitor buckling. Strain and load values were recorded automatically by an Acurex Autodata Ten/50 and a hard copy of the data produced. Tests were conducted in a Baldwin-Emery SR-4 testing machine at a constant cross-head speed of 0.05 inches per minute. Six specimens per sodium dopant level were tested.

Results of the compression tests are presented in Table 7. The strength was not a function of sodium content. However, there was an apparent reduction in modulus values with increasing sodium content. The 500 group was a noted exception to this trend. At present, tests of pure and doped resin are in progress which may provide additional information leading to a better understanding of the observed behavior.

4.2.2 Short Beam Shear Tests

The short beam shear method was used for determination of apparent interlaminar shear strengths. Although not a popular technique for evaluating carbon-phenolic materials, some interesting results were obtained. Problems arise in the use of this method when specimens fail in a complex (9) mode involving both shear and flexural type failures. According to Peters the data from complex failure mode tests should not be used even as a conservative estimate of shear strength. With regard to this argument, it must be emphasized that the significant results of these tests are not limited to comparisons of strengths; failure analysis must be considered.

Specimens were constructed from nine plies of prepreg material, and were machined to provide a square cross-section. Test conditions and specimen geometry as prescribed in ASTM D 2344-76 were followed. The span to thickness and length to thickness ratios were 5:1 and 7:1, respectively, required for carbon yarn reinforcement. The test fixture had an adjustable span to accommodate slight variations in thickness. An Instron model 1125 testing machine was used for these tests, which were conducted at a constant crosshead speed of 0.05 inch per minute. The minimum number of specimens tested for each dopant level was ten.

For a clear understanding of the shear tests results, both strength values and failure analysis observations have been included in Table 8. A comparison of the stress values above suggests that the interlaminar shear strength increased with sodium content. The departure of the 1000 group from the apparent trend cannot be explained at present. Additional research is necessary to further substantiate the response pattern and to determine if this particular group's behavior is simply anomalous. However, in view of the failure analysis, the reporting of the average of the 1500 and 3000 groups as a shear strength is arguable.⁽⁹⁾ Although it is not the purpose of this article to rigorously defend the choice, certain evidence merits consideration. Specimens of these two groups which failed in shear exhibited a higher strength, on average, than those of the lower sodium groups. Further, the high sodium shear failure stresses were interspersed with those produced by flexural and combined failure modes. Therefore, the reported values appear to be reasonable, if somewhat conservative, representations of the shear strength.

It is evident from the results of these tests that the presence of sodium in such levels has toughened or "plasticized" the matrix to enable the material to withstand higher shear loads. The performance has reached a transitional region where failure can occur by either shear, flexure, or a combination of both. The physical phenomena responsible for the observed behavior have not been documented, but the resin test series mentioned in the prior section is expected to provide information necessary to determine the causes.

4.2.3 Flexure Tests

The flexural strength and modulus values in the warp direction were determined according to the procedures stated in ASTM D790-81. Two different load application methods, three-point and four-point bending, are presented in the standard; the three-point procedure was followed. According to Zweben, et al.⁽¹⁰⁾ in their examination of the standard, the specified procedures provide reliable strength data, but the modulus values could be misleading. A suggested correction to this problem was to employ a high span-to-depth ratio. The span on the test fixture was limited to a minimum of two inches. Specimen geometry was designed subject to the restriction to yield a support span-to-depth ratio of 32 to 1. However, the average thickness of the four-ply specimens was 0.057 inch, thus increasing the ratio to 35 to 1. The cross-head rate of 0.104 inch per minute was adjusted to account for slight variations in thickness. Two different rates, averaging 0.140 and 0.096 inch per minute, were used for the AR, WW, and 1000 groups. All groups consisted of six specimens. The higher rate was calculated by interpolation of conditions for 40 to 1 span-to-depth ratio which was realistic for the thinner specimens in these groups.

The differences observed in the strength and modulus values of the AR specimens tested at the two rates were negligible. The effect of the variation was more evident in the WW and 1000 groups. Both strength and modulus values were greater at the higher rate. The amount of the increase was on the order of 10% for all properties except the WW strength which increased by approximately 15%. It is not known at present whether the

Table 7. Results of Compression Tests

<u>Sample</u>	<u>Strength (psi)</u>	<u>Modulus (Msi)</u>	<u>Poisson's Ratio</u>
WW	33836	3.99	.19
AR	36638	3.94	.20
500	34640	4.38	.18
1000	36017	3.67	.22
1500	37069	3.42	.18
3000	33037	2.94	.19

Table 8. Results of Short Beam Shear Tests

<u>Sample</u>	<u>Shear Strength (ksi)</u>	<u>Failure Mode</u>		
		<u>Shear</u>	<u>Flexure</u>	<u>Combination</u>
WW	4.3	11	1	
AR	4.2	8	1	1
500	4.6	10		
1000	4.0	11		
1500	4.8	3	5	2
3000	5.0	2	5	3

Table 9. Results of Flexure Tests

<u>Sample</u>	<u>Flexural Strength (ksi)</u>	<u>Flexural Modulus (Msi)</u>
WW	37.8	2.50
AR	52.3	2.93
500	36.8	2.79
1000	48.7	3.25
1500	46.9	2.87
3000	40.6	2.76

disparities are due to loading rate effects or simply interpanel variability. Additional tests are required for verification.

Results of the flexure tests, failure strength and tangent modulus are presented in Table 9. Average properties for the three groups discussed above were reported. No correlation of modulus values with sodium content is evident. But, there appears to be a relationship between flexural strength and sodium level. As the concentration increases, the failure stress decreases. The WW and 500 groups obviously do not adhere to the pattern. However, from unreported test results of an off-nominal produced WW panel, there is reason to believe that failure stress could be on the order of the AR group. Further testing is required for a clear understanding of the effect of sodium contamination.

4.3 Failure Analysis

4.3.1 Short Beam Shear

The majority of the significant information obtained from the microscopic evaluation of the failed specimens has been discussed in section 4.2.2. Shear failures indicated by cracks parallel to the 0° fibers in the interfacial/interlaminar regions are shown in Figure 9. The cracks appear as white traces on the surface of the specimen.

Another failure mode observed in the specimens but not mentioned previously is a tensile rupture. Evidence of this type of failure can be seen in Figure 10. While many of the visible cracks are along the $0^\circ/90^\circ$ fiber interface, indicative of shear failure, there are several which run at approximately 45° . These cracks through the 90° fiber bundles are due to a resolving of the shear stresses into a tensile mode.⁽¹¹⁾ Fractures of this nature were observed in every group.

A flexural failure of a short beam shear specimen is shown in Figure 11. The failure zone is located at the bottom center of the photograph with the cracks visible as dark lines. Although not clearly reproduced in the picture, the lower two 0° fiber layers fractured due to tensile stress. Some shear and tensile rupture failures are evident, but damage is local to the primary flexural area, suggesting that these cracks may well have occurred subsequent to the initial fracture. As stated previously, the dominant failure mechanism in the majority of the higher sodium content samples was tensile flexure.

An additional type of fracture mode, termed combination, was observed frequently in the higher sodium level specimens. Two mechanisms, shear and tensile flexure, were active in the failure process. Unlike the mode visible in Figure 11, the shear cracks were removed and distinct from the flexural region. In Figure 12, tensile flexure is evident in the white area on the bottom right. Shear cracks are visible as faint white traces left of center of the specimen. From the evidence observed, it appears that these mechanisms acted independently of one another.

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Figure 9. Typical Microstructure of Shear Failure Mode in Short Beam Shear Specimen.



Figure 10. Typical Microstructure of Shear and Tensile Rupture Failure Modes in Short Beam Shear Specimen. Note Cracks at 45° Indicative of Tensile Rupture.

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Figure 11. Typical Microstructure of Flexural Failure in Short Beam Shear Specimen



Figure 12. Typical Microstructure of Combined Flexural and Shear Failure Modes in Short Beam Shear Specimen. Note Flexure at Lower Right and Shear at Left Center.

In section 4.2.2, the conclusion was drawn that there was a transition sodium level below which failures were almost exclusively shear or a shear-produced tensile rupture, and above which flexure and combination failures dominated. Associated with the transition was an apparent increase in shear strength. The cause of this behavior was proposed to be a toughening of the matrix brought about by sodium addition. Miller and Winger⁽¹¹⁾ have observed a similar behavior in short beam shear tests wherein the transition of failure modes is determined by temperature. They have attributed the behavior to a decrease in the modulus of the matrix (softening) when progressing from lower to higher temperatures. The lower modulus material promotes the apparent shear fracture mode. A decrease in strength values with increasing temperature across the transition region was also observed. Data from resin tests now in progress will be necessary to confirm the transition mechanism in this study.

4.3.2 Flexure

The failure analysis of the flexure specimens supports the hypothesis proposed in section 4.2.3 that a relationship exists between flexural performance and sodium content. There appears to be a change in failure mechanisms as evidenced by fracture surface characteristics which is similar to that observed in the shear tests, although the transition is somewhat less distinct.

Three of the AR samples and one of the WW samples broke into two pieces indicative of brittle fracture. The characteristics of the failure surface displayed in Figure 13 were representative of the remaining AR and WW samples. The lower two plies* were completely shattered in a tensile flexure mode. Extensive damage was evident in ply 2 and cracks often were visible in the 0° fibers of the top ply. Note that damage was reasonably local to the flexural failure zone, i.e., there was an absence of trans-laminar and interlaminar cracks extending more than approximately two thicknesses away. The above described features are typical of what was termed brittle failure.

A failed specimen from the 500 group is shown in Figure 14. Several of the surface features evident in the photomicrograph are similar to those described above, but there are noteworthy differences. Again, the lower two plies were shattered in tensile flexure, and damage was local to the flexural failure zone. But, in contrast to the AR and WW groups, damage in ply 2 was not as severe, and cracking in ply 1 was either minor or unobservable at this magnification(20X). These failures are still of the brittle type.

Considering only the extent of failure of the 0° fibers, the performance of the 1000 group was similar to that of the 500 group. However, a change in the failure mechanisms involved was evident. Most significant was the development of large interlaminar cracks between the lower plies. A representative fracture of this type is shown in Figure 15. Concomitant with the interlaminar shear/tensile flexure fracture mode was the extension of cracking beyond the primary failure area. Such behavior represented a departure from the exclusively brittle fracture previously observed to a more "plastic" type, matrix-influenced mode.

* Plies are numbered from the upper surface 1-4.

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Figure 13. Typical Microstructure of Brittle Failure in AR and WW Flexure Specimens.



Figure 14. Typical Microstructure of Brittle Fracture in 500 Flexure Specimen.

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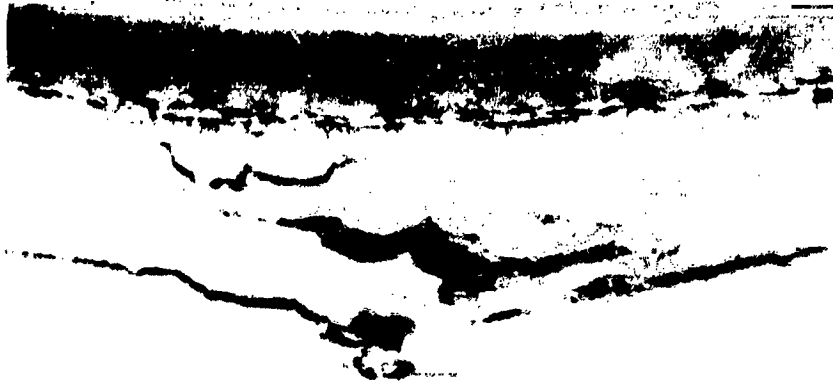


Figure 15. Typical Microstructure of 1000 Group Flexure Specimen. Note Increased Interlaminar Cracking in Lower Plies.

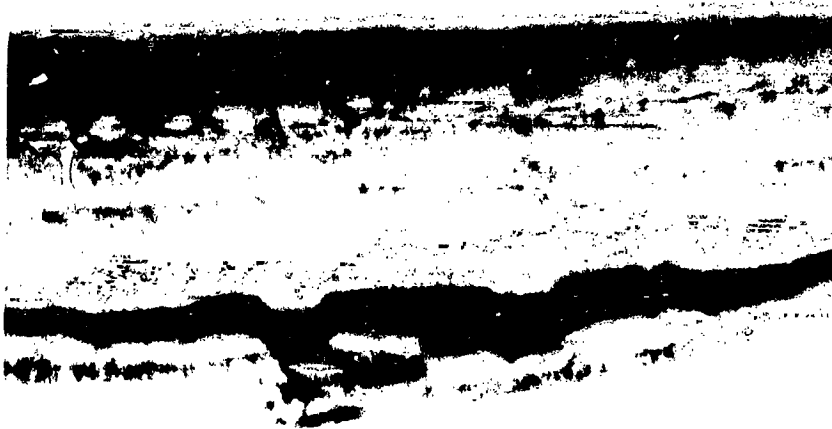


Figure 16. Typical Microstructure of Failed 1500 and 3000 Flexure Specimens. Note Large Interlaminar Crack Between Lower Plies and Absence of Damage in Upper Plies.

At sodium levels of the 1500 and 3000 groups, there were significant changes in the failure characteristics. A representative fracture surface, taken from the 1500 group, is shown in Figure 16. The bottom ply failed in tensile flexure and a large delamination developed between plies 3 and 4. In the majority of the tests, no damage was observed in plies 1 and 2, and in many of these, the third ply survived with little or no damage. The appearance of the specimens suggests that the failure mode has become strongly matrix-influenced at these levels of sodium contamination.

The operative failure mechanisms appear to be functions of sodium content similar to the behavior observed in the shear tests. The transition region is near the 1500 ppm added level. But, at present, the phenomena responsible for this performance are not known. Tests of the matrix material alone may provide additional information necessary for a clearer interpretation of these results.

5. CONCLUSIONS

The investigation described in the previous pages was undertaken to assess the effects of sodium contamination level on the physical properties of phenolic resin and the matrix-influenced mechanical properties of carbon-phenolic composite laminates. Proposed effects of sodium hydroxide addition to the resin, which were consistent with basic resin chemistry, were (1) an increase in the relative percentage of para-substitution, a faster reacting product, and (2) degradation of the resin oligomers.

These hypotheses were supported with experimental evidence from gel permeation chromatography tests. A decrease in high molecular weight constituents and an increase in low molecular weight constituents were noted, indicating resin degradation upon sodium hydroxide addition. Further, an increase in reaction kinetics producing a decrease in gel time and a lowering of polymerization onset temperature were observed at increasing dopant levels. Greater sodium contamination also led to an increase in moisture absorption by the prepreg under ambient conditions and an increase in the phenol efflux measured during volatiles tests.

Properties of cured laminates were also shown to be dependent upon sodium level. An increase in sodium content apparently led to a decrease in compressive modulus and flexural strength and an increase in shear strength. Operative failure mechanisms were related to dopant level, and transitions were observed in the cases of shear and flexural modes. Results from thermogravimetric analysis indicated that higher levels of sodium may also lead to matrix degradation at lower temperatures.

Finally, it was stated at the outset that prior studies had been focused on sodium effects on carbon fibers. Clearly, sodium contamination also has a significant influence on resin and matrix-related properties which should not be overlooked. The results presented have provided an indication of the severity of this problem. Further work is warranted to clarify many points brought out in the investigation and to more firmly establish the relationship between sodium content and material performance.

6. RECOMMENDATIONS

The following recommendations were made based on the findings of the study.

1. Determine relationship between laminate moisture absorption and dopant level
2. Perform elevated temperature mechanical property tests
3. Evaluate the performance of very low sodium content material
4. Assess aging effects
5. Report time at temperature before pressure application in flow tests
6. Monitor volatile efflux and identify constituents
7. Investigate resin modulus as a function of dopant level
8. Include fracture analysis with mechanical property results
9. Initiate interface/bonding studies
10. Institute GPC, FTIR, GC/MS, DSC, and TGA quality control tests.

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