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Equilibrated Moisture Content of Several Carbon Phenolic Composites

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Moisture is known to alter many of the mechanical properties of polymeric based composites significantly. Estimation of the quantity of water in a composite is often necessary to maintain given margins of safety. The amount of moisture in any given material is a function of, among other things, the relative humidity of the environment in which it is stored. This study focuses on the relationship between relative humidity and the equilibrated moisture content of several variants of two distinctly different carbon phenolic composites. One of the materials gave a typical exponential relationship between RH and equilibrated moisture content, whereas the second gave a sigmoidal relationship with the largest increase in moisture between 45–60% relative humidity. The possible relationship between the shape of the curves and the nature of the material constituents is discussed.

Introduction

WATER is known to plasticize many organic polymers. Several authors have documented the same effect in polymeric-based composites.[1–4] This plasticizing effect can result in severe degradation of the mechanical properties of a composite, particularly at temperatures exceeding the glass transition temperature of the polymer. A summary of many of the reported changes in mechanical properties of epoxy-based composites due to moisture found in the literature has been reported previously.[5] Recently, dramatic reductions in the mechanical properties of phenolic-based composites have been documented.[6–8]

Phenolic-based composites are used extensively as ablative surfaces in rocket nozzles, exit cones, and reentry vehicles. Their structural integrity is critical to the operation and survival of the vehicle. Carbon-phenolic-composite-based moisture has been shown to be the cause of at least one major structural failure mode in rocket nozzles.[9,10] Estimation of the amount of moisture in a carbon phenolic part is essential to predicting the mechanical response of that part to elevated temperature and stress.

The amount of moisture in any material is a function of the affinity of the material for water, the diffusion coefficient of water within the material, and the availability of water to the material; that is, the relative humidity of the ambient environment under normal conditions. The diffusivity of several carbon phenolics has been previously published.[5,11–16] These same reports give the maximum moisture holding capacity of each phenolic composite tested, a measure of the affinity of the material for water.[5,11–16] Several authors have indicated that the equilibrated moisture content of epoxy-based composites is a linear function of relative humidity.[1,17–22] Others have found a nonlinear response with other epoxy-based composites.[18,21,23,24] There are few, if any, reported data on the moisture content of phenolic-based composites as a function of relative humidity. This report addresses that topic.

Materials and Methods

One of the major hindrances to determining the equilibrated moisture content of composite materials is the long conditioning time required to reach equilibrium. Analysis of FM 5055 carbon phenolic from preliminary diffusion data indicated that the time required to reach 90% of equilibrated moisture content (starting from any uniform moisture level) for 0.635-cm (0.25 in.)-thick plates, with water diffusing one dimensionally in the in-plane direction (direction of highest moisture diffusivity), from both surfaces, at 21°C (70°F) was 109 days.[25] To attain 99% of equilibrated levels, 228 days of conditioning would be required. To reduce the time required to attain equilibrated moisture concentrations, powdered material was used. However, if absorption to free surfaces is an important mode in the absorption of moisture by the composite, the large increase in external surface area-to-volume ratio introduced in the generation of powder may lead to erroneous results. A study was undertaken to address this possibility.

Surface Area-to-Volume Studies

Carbon-phenolic powder was generated from FM 5055 composite excised from a flat layup billet (#5) produced for characterization in the Baseline Data Generation Program.[26] The powder was sifted through two sets of precision screens to generate three size fractions. Samples of the three size fractions were placed under an optical microscope and 50 random particles were measured with a stage micrometer. The three size fractions were: less than 0.0127 cm (0.005 in.), 0.0127–0.127 cm (0.005–0.05 in.), and 0.127–0.635 cm (0.05–0.25 in.) in diameter. Each fraction was divided into several samples that were conditioned at one of three relative humidities (43, 65, or 75%) at room temperature. The 43 and 65% relative humidities were obtained using constant temperature/relative humidity rooms maintained at the Institute. The 75% relative humidity environment was generated over a saturated solution of sodium chloride.[77] The weight of each sample was monitored as a function of time. Upon reaching equilibrium, 40–140 mg of a sample of powder was transferred to a pre-weighed aluminum capsule. The capsule with sample was allowed to remain open and in the conditioning environment for a minimum of 24 additional hours. The capsule was then sealed, the capsule and sample were weighed, transferred to the Karl Fischer moisture analyzer, and immediately run at 325°F (163°C) with dry nitrogen as the carrier gas. The details of the apparatus and procedure used can be found in a previous report.[28]

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Material Studies

Powdered samples were obtained from two aft inlet rings (404-GB, 404-3) produced for the nozzle of the solid rocket boosters of the Space Shuttle. Both rings were manufactured from FM 5055 carbon phenolic (produced by U.S. Polymeric/Hitco Materials Division, Santa Ana, CA), which is made from CCA-3 carbonized rayon fabric, USP-28 carbon filler, and 91 LD phenolic resin. Ring 404-3 came from the Nozzle Technology Advancement Program and 404-BG from the Data Generation Program. Both rings were cured with Thiokol Corporation's standard 163°C (325°F) cure cycle. The 404-3 ring was machined, glass phenolic laid up on the back surface of the ring, and cured. The 404-BG ring experienced no further heat treatment after the initial carbon-phenolic cure. Powdered samples were also obtained from three lots of MX 4926 (VCK) carbon phenolic (produced by Fiberite Composite Materials Operations, Winoma, MN). (A detailed description of the three materials can be found in another report.[12]) In essence, material 1 experienced a nominal cure cycle, which included a 163°C (325°F) cure, followed by a postcure regime given sequentially in temperature/time as: 88°C (190°F)/2 h; 160°C (320°F)/10 h; 96°C (205°F)/27 h; 154°C (310°F)/30 h; 71°C (160°F)/7 h; and 60°C (140°F)/150 h. Materials 2b and 3b experienced anomalies during the cure process and were postcured only through the 160°C (320°F)/10-h stage.

Each powdered sample was divided into subsamples that were conditioned at various relative humidities (*RH*) at room temperature. The 95% *RH* environment was generated by suspending the samples over distilled water in a closed container. The 65 and 43% relative humidity conditioning were accomplished by using constant temperature/*RH* rooms that were monitored continuously with a Bristol Thermohumidiagraph, Bristol Corporation, Waterbury, Connecticut. The 31 and 75% *RH* chambers were generated with saturated CaCl and NaCl solution respectively. The 0% relative humidity samples were equilibrated in a vacuum at less than 1 Torr.

All samples were brought to equilibrium weight prior to testing. Figures and tables of the weight change of the samples as a function of time can be found in a previous report.[29] Anomalous moisture absorption data for material 1 at 95% *RH* was suspected to be due to the disturbance of the conditioning chamber by repeated weighings of the material. As a result, the powders were left undisturbed for greater than 3500 h prior to making initial runs. Moisture levels in the powders were measured using Karl Fischer titrimetry as stated in the previous section.

Results and Discussion

Size Study

Figure 1 shows the effect on the external surface area to volume ratio of a particle as a function of particle diameter. Two particle geometries are assumed; that is, a particle with spherical or cubic geometry and a particle with a plate-like shape with dimensions $L \times L \times L/10$ where L is the measured diameter of the particle. The points on the graph are demarcations between the three size fractions. As can be seen from the graph, the external surface area-to-volume ratio increases roughly 100-fold from smallest to largest size fraction.

Figures 2 through 4 graphically display the equilibrated moisture contents of the three size fractions by relative humidity. From the graphs, one can see that the measured moisture content of the various size fractions was unaffected by particle size. Apparently, external surface area does not affect the levels of moisture in FM 5055 carbon-phenolic composite. This is not to say that surface area in general has no effect, because of the possibility of large quantities of internal surface area that depends only upon volume. Surface areas in excess of 1000 m²/g have been found in activated carbons.[30] The size variation study dealt only with the FM 5055 material; how-

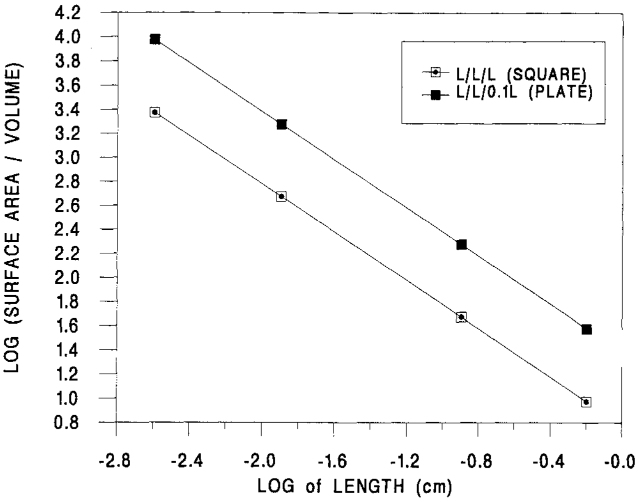

Fig. 1 Change in specific surface area with particle size (assuming two basic particle shapes).

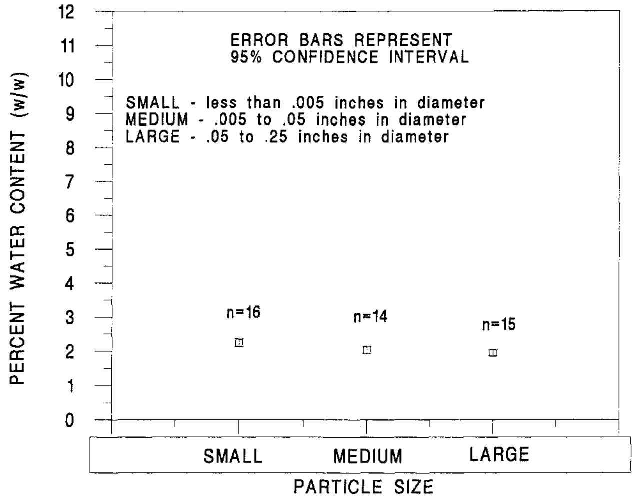

Fig. 2 Effect of particle size on equilibrated moisture content of FM 5055 carbon phenolic (43% *RH*).

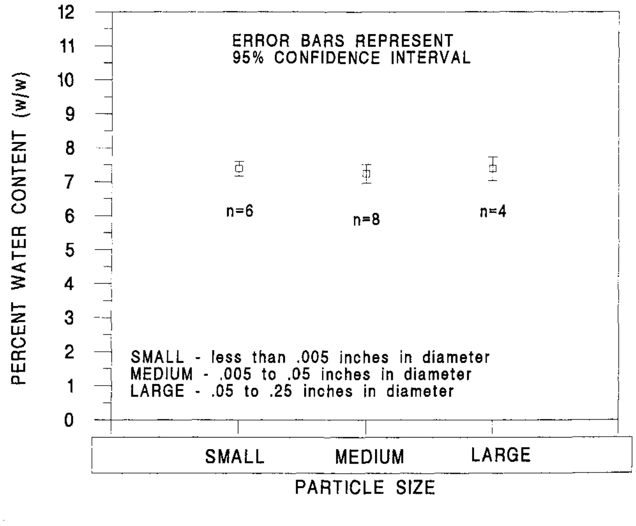

Fig. 3 Effect of particle size on equilibrated moisture content of FM 5055 carbon phenolic (65% *RH*).

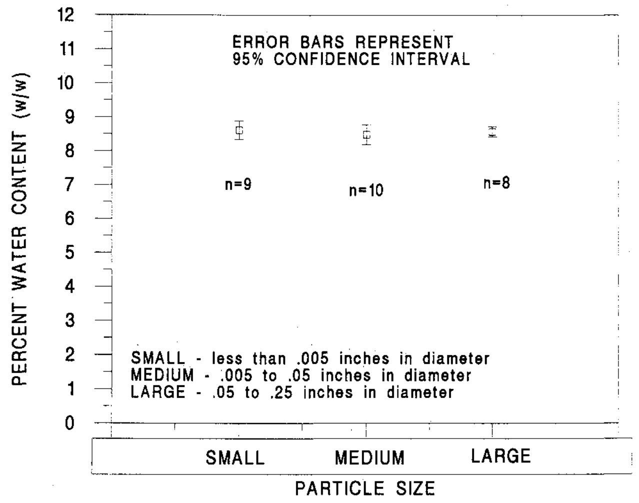

Fig. 4 Effect of particle size on equilibrated moisture content of FM 5055 carbon phenolic (75% *RH*).

ever, there is supporting evidence that this holds true for the VCK data as well; for example, both materials were made with a resole phenolic resin, both materials use rayon-based fibers, and the maximum moisture content *a* of 1.27 × 1.27 × 0.254 cm (0.5 × 0.5 × 0.1 in.) plates of MX 4926 VCK material cured similarly to the 2b and 3b materials was 9.94%, compared with 9.79 and 10.94% for the latter, respectively.

Material Studies

Figure 5 shows the equilibrated moisture content of two aft inlet rings and a plate of FM 5055 carbon phenolic, as determined with Karl Fischer titrimetry, as a function of the relative humidity of the conditioning environment. Figure 6 shows the moisture content of the three MX 4926 (VCK) materials.

The relationship between equilibrated moisture content (M_m) and relative humidity (RH) of the ambient environment has been studied extensively in epoxy and epoxy-based composites. Generally, the relationship obeys an exponential equation of the form: $M_m = a(RH)^b$. A large part of the epoxy literature has been reviewed and summarized by Loos and Springer.[20] In essence, they found that nearly half of the data in the literature supported a value of *b* equal to 1; that is, Henry's law was obeyed. The remainder of the data indicated a value of *b* between 1.0 and 1.9. In no case was the value of *b* found to be greater than 2. Furthermore, when the data for each material system, from all of the reviewed studies, were combined, Loos and Springer found that a value of *b* = 1 resulted in an average M_m that approximated the data *reasonably well.*

Unlike the epoxy data, the VCK phenolic data in the present study were found to require a value of *b* greater than 2 (Fig. 7). A test for lack of fit[31] of the assumed exponential relationship was performed on the three individual data sets. The calculated *F* statistic indicated that the exponential relationship could not be rejected, due to lack of fit, at the 95% level. *P* values for materials 1, 2b, and 3b were greater than 0.75, 0.50, and 0.05. The strong nonlinear nature of the curve indicates that the moisture content of the composite changes little at low relative humidities but very rapidly at high relative humidities. McKague et al.[23] state that *b* diminishes as polymerization advances. Others have concluded that *b*, as well as *a*, are influenced by the void content of the laminate.[22] There is very little evidence to date, in the open literature, that addresses this question.

It is not clear why material 1 gave significantly lower M_m values at the higher relative humidities. One would predict that the presence of microcracks, found in material 1 but not in material 2b, would increase the value of *a*.[32] This was not found to be the case in the present study. The free volume

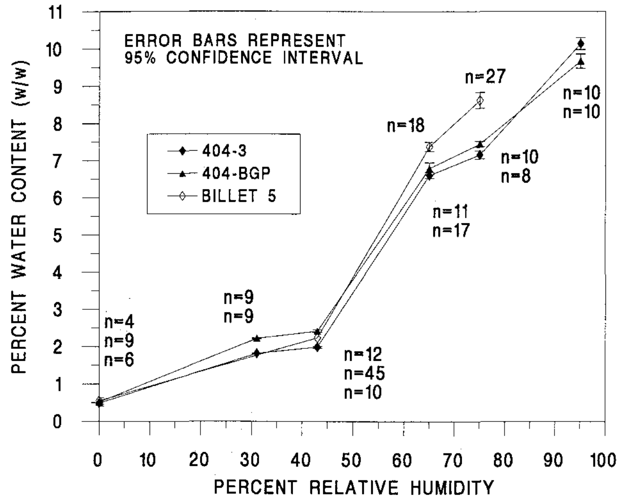

Fig. 5 Equilibrated moisture content of several FM 5055 carbon phenolics.

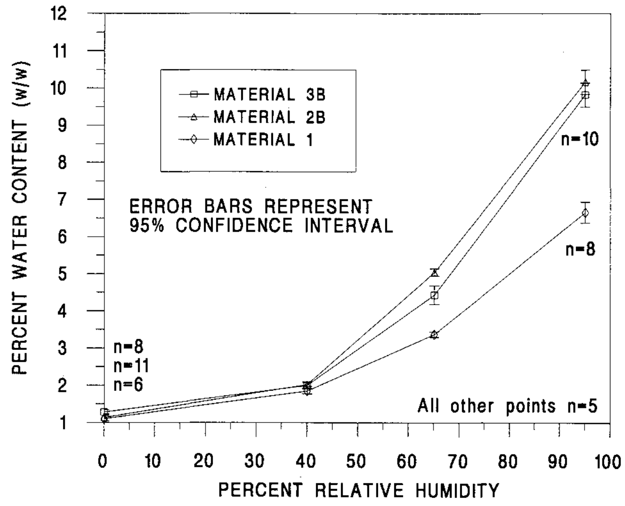

Fig. 6 Equilibrated moisture content of several MX 4926 VCK carbon phenolics.

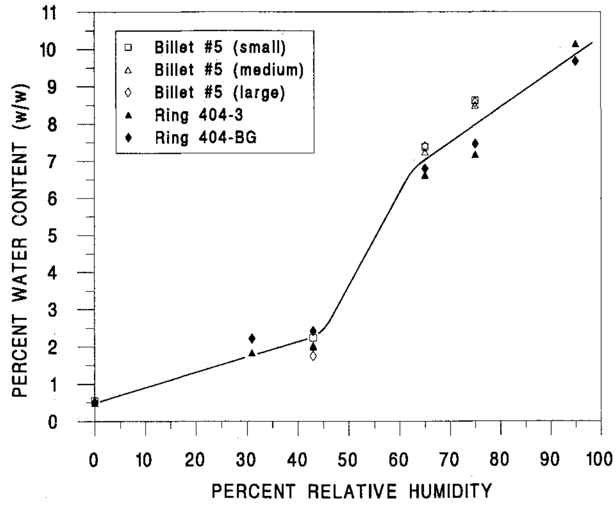

Fig. 7 Mean equilibrated moisture content of three MX 4926 VCK carbon phenolics.

or void content of network polymers is thought to control the maximum moisture content.[19,33] It has been reported that, in general, materials cured to a greater extent had higher values of a[19,23,34,35] and free volume.[19] Others have found that residual stresses in the composite, in general,[36] and at the fiber-matrix interface, in particular,[37] can control the level that a attains. Alternatively, the significantly longer postcuring regime experienced by material 1 (Fig. 8) may have resulted in a higher degree of cross-linking in the network polymer. This may have reduced the number of polar groups on the phenolic macromolecule accessible to water molecules. Hydrogen bonding of water molecules to polar groups is known to be a primary mode of adsorption in organic polymers.[38]

The equilibrated moisture content of FM 5055 as a function of relative humidity displays a significantly different profile than either the epoxy data or the VCK phenolic materials (Fig. 9). A best fit exponential curve for each of the five data sets; that is, the three size fractions of billet #5, the 404-3 and 404-BG rings, was obtained by regression analysis. A test for lack of fit[31] of the assumed relationship was performed. The calculated F statistic indicated that the exponential relationship was rejected, due to lack of fit, at the 95% level. P values for all five data sets were less than 0.001. Unlike the epoxy composites studied in the literature or the VCK phenolic materials reported in this study, the FM 5055 materials contain low-fired rayon-based fibers (CCA-3), which are known to be hydrophilic. All of the epoxy composites reviewed by Loos and Springer were composed of graphitized fibers (T300 or AS). The MX 4926 (VCK) materials studied in this report are composed of carbonized rayon fibers that were fired to temperature levels intermediate between the low-fired CCA-3 and high-fired, PAN-based, T300 fibers. The higher the state of graphitization, the more hydrophobic is the resulting carbon. The presence of hydrophilic fibers in the phenolic system results in two moisture-absorbing phases. It is not surprising, then, that the M_m vs RH curve does not obey a standard exponential relationship.

The sigmoidal relationship for FM 5055 is important for two reasons. First, moisture has been shown to affect the mechanical response of FM 5055 significantly. Second, the steepest part of the curve is around 50% RH, which is in the range of relative humidities most likely experienced by the materials in storage prior to use. This implies that relatively small changes in RH of the storage environment will result in a significant change in the moisture level and a concomitant change in mechanical properties of the composite.

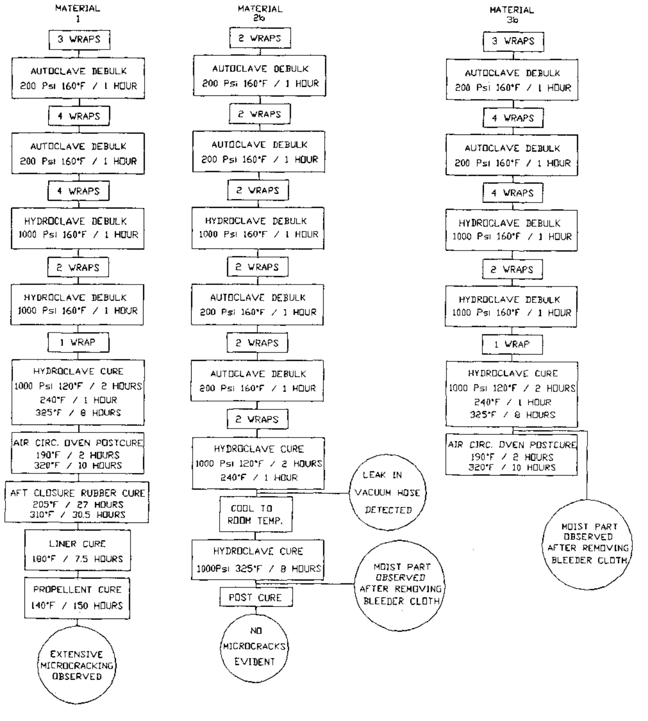

Fig. 8 Schematic of layup and curing process for MX 4926 VCK materials.

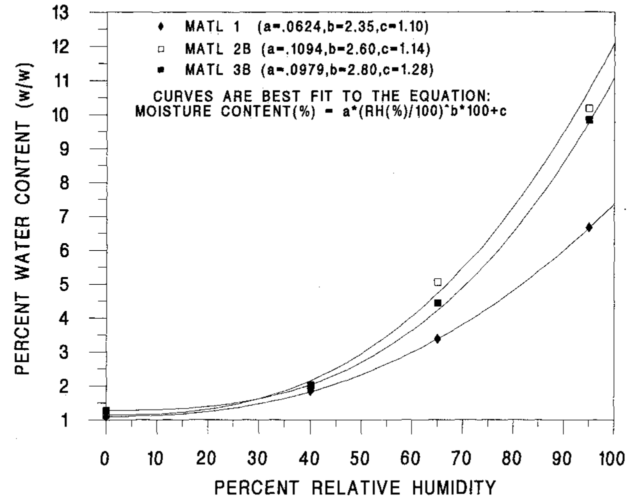

Fig. 9 Mean equilibrated moisture content of several FM 5055 carbon phenolics.

Conclusions

1) MX 4926 (VCK) materials displayed an exponential relationship between RH and M_m.

2) FM 5055 materials gave a sigmoidal relationship between RH and M_m.

3) The exponent b in the relationship between RH and M_m for MX 4926 (VCK) was found to be greater than two.

4) The sigmoidal-shaped curve found with FM 5055 is proposed to be due to the presence of at least two hydrophilic phases in the composite—fiber and matrix.

5) The largest increases in moisture content of the composites studied occurred at the highest RH for the VCK materials, but at 45–60% RH for the CCA-3 materials.

6) Preliminary findings seem to indicate that extensive postcuring, presumably due to increased polymer cross-linking and reduced free volume, may reduce the water-holding capacity of the polymer.

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