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Anomalous Swelling Behavior of FM 5055 Carbon Phenolic Composite

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Carbonized rayon-based phenolic composites are used extensively as ablative surfaces in the design of aerospace hardware. Historically, their performance has been inconsistent. Many of the anomalous events documented to occur in these materials can be traced to the material's volatile constituents. The largest volatile component (> 80%) is known to be water. Water not only acts as a pore pressure producing gas but has been shown to plasticize cured phenolic resins. The location of water within the material and the relative hydroscopic tendencies of the various components of the composite are of interest in understanding the mechanism of these various anomalous events. This study measured the swelling response of a typical carbon phenolic composite in the three primary material directions. The data obtained suggest that at low and high relative humidities the incremental increase in moisture absorption can be attributed primarily to the resin whereas at intermediate relative humidities the water is moving largely into the carbonized fibers.

Introduction

PHENOLIC-BASED composites are used extensively as ablative surfaces in rocket nozzles, exit cones, and for the leading edges of re-entry vehicles. They are known to absorb significant amounts of water from the ambient environment.[1] Water has been shown to be the primary driver of at least one of the major failure events seen in these materials.[2–4] Furthermore, water is known to be a plasticizer of phenolic-based composites and to significantly alter their mechanical properties particularly above the cured resins glass transition temperature.[5,6]

The absorption of water by many polymers and polymer-based composites has been shown to result in swelling of the materials.[7–12] A change in the dimensions of a part, due to swelling, may adversely affect the performance of the entire system. In addition, a nonuniform moisture distribution leads to the presence of residual stresses within the composite which have been shown to be sufficiently large to cause localized fracture of the polymer in an epoxy/graphite composite.[13] Even under a uniform moisture distribution, residual stresses in a composite can result from dissimilar swelling behavior of the matrix and fibers.[14–16] The swelling stresses thus created may lead to the creation of microcracks if the strength of the matrix or matrix/fiber interface is exceeded. Theses microcracks can lead to further degradation of the mechanical properties of the composite. Residual tensile swelling stresses in excess of 25 MPa (3625 psi) and compressive stresses in excess of 70 MPa (10,150 psi) have been calculated for a epoxy/graphite (AS/3501-5) composite.[9] Other authors using Fourier-transform infrared spectroscopy have documented evidence that swelling stresses are sufficient to cleave bonds in a cross-linked, TGDDM-DDS epoxy system.[17]

Recently, anomalous moisture absorption behavior has been reported for low-fired rayon-based phenolic composites.[18] In addition, rayon fiber morphology has been shown to significantly affect the moisture diffusion and gas-permeability characteristics of these materials.[19–21] This study was undertaken to determine the magnitude of swelling in FM 5055 carbon phenolic as a function of equilibrated moisture content and material direction and to determine if the location and relative affinity of these various sites for water within the composite could be determined.

Materials and Methods

Cylindrical specimens 5 cm (2 in.) long by 0.635 cm (0.25 in.) in diameter were machined from an FM 5055 aft inlet 404 ring produced for the data base generation program.[22] Specimens were excised so that the 5-cm dimension was oriented in one of the three primary orthogonal directions of the composite [warp fiber aligned, fill fiber aligned, or normal to the plane of the plies (across ply)].

Conditioning Environments

Eight different saturated salt solutions were created and placed in thick-walled polyethylene containers to a depth of approximately 2.54 cm (1 in.). Suspension racks were produced from solid glass rods. One suspension rack was placed in each container. A polyethylene mesh screen was attached to each glass suspension rack approximately 5 cm above the surface of each saturated solution. The as-machined specimens were weighed in grams to four decimal places and the length measured in inches to four decimal places. Two specimens of each orientation were placed in each of the eight containers on the polyethylene screen above the saturated salt solutions. A thick polyethylene cover was securely placed on top of each container and all of the containers were placed in a 49°C (120°F) incubation oven. In addition, a set of specimens was placed at 40 and 65% relative humidity at room temperature in constant temperature/humidity rooms. A final set of specimens was immersed in distilled water at 49°C (120°F).

The relative humidity of the ambient air over each of the eight solutions was measured with a General Eastern Relative Humidity Meter (Model 400C) at room temperature. The results of these measurements can be found elsewhere.[23] In addition, these measurements were compared to values found in the literature.[24–27] In general there was excellent agreement between empirical and literature values.

Equilibration of Specimens at Various Relative Humidities

Periodically, the specimens were removed and weighed to monitor the moisture content of each specimen. At less-frequent intervals, specimen lengths were measured after cooling to room temperature in a polyethylene bag. All specimens were conditioned over 13,000 h (approximately 1.5 years). The change in weight of each specimen as a function of square root of time in the conditioning environment was monitored to determine when the specimens were equilibrated. Incremental changes in moisture content require longer periods of time as a specimen approaches equilib-

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rium. Furthermore, the rate of diffusion of moisture into a material is strongly related to the conditioning temperature, with lower temperatures reducing the moisture diffusion rate.[28] Because of these facts, some of the specimens conditioned at room temperature were not completely equilibrated upon completion of this phase of the study.

Vacuum Drying of Conditioned Specimens

Following the conditioning period, the specimens were removed from their conditioning chamber, weighed, and their length measured. They were then placed in a vacuum oven at 115°C (240°F) and 1 Torr. Periodically, they were removed and weighed. The specimens were dried for a total of 2112 h. All specimens reached equilibrated weights prior to final removal from the vacuum oven. The data for each specimen can be found in another report.[23]

Results

Figure 1 shows the mean equilibrated moisture content of each set of specimens from each conditioning chamber as a function of the relative humidity of the conditioning environment. Relative humidities were taken from literature temperature/relative humidity data.[24–27] A sigmoidal relationship was found between the two variables. This data confirms earlier findings on FM 5055 carbon phenolic.[18] Subsequent studies on two glass and two silica phenolic composites gave linear relationships between relative humidity and moisture content.

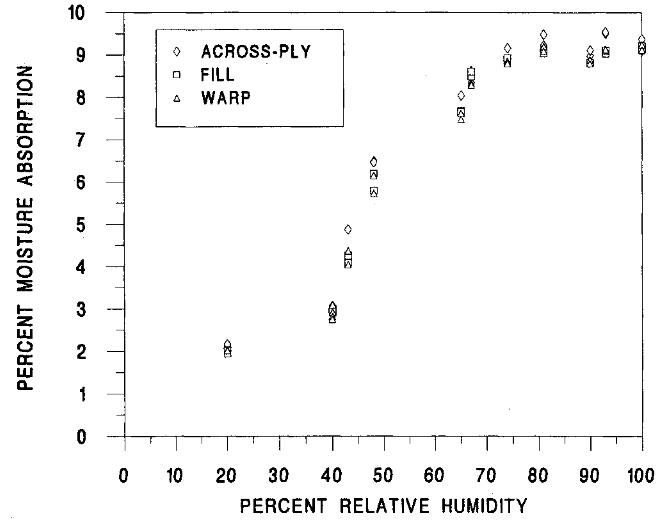

Fig. 1 Equilibrated moisture content of FM 5055 swelling specimens as a function of the relative humidity of the conditioning environment.

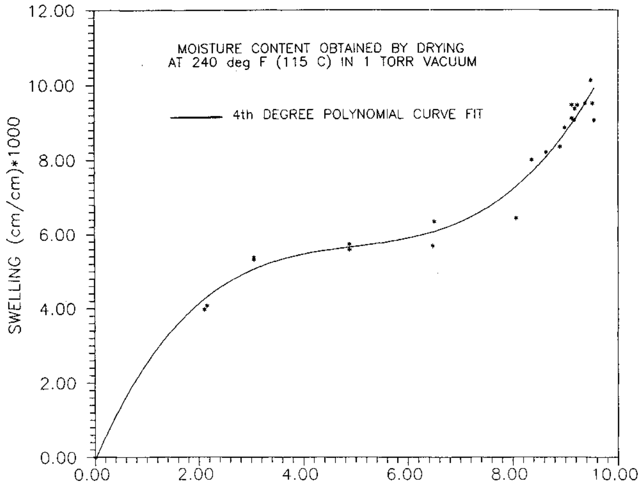

Fig. 2 Swelling response of FM 5055 carbon phenolic in the across-ply direction.

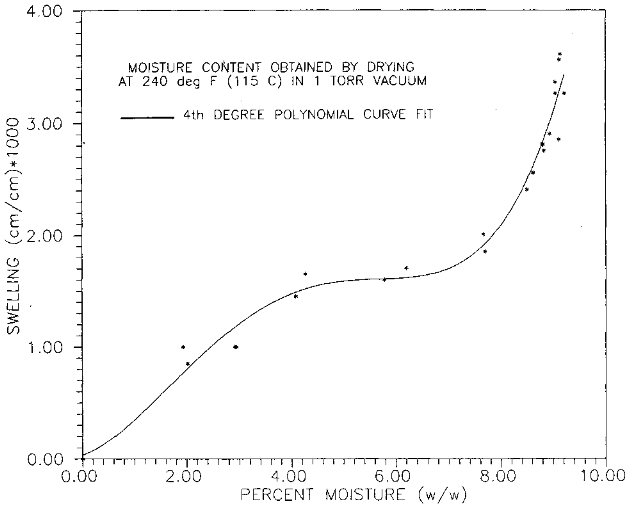

Fig. 3 Swelling response of FM 5055 carbon phenolic in the fill direction.

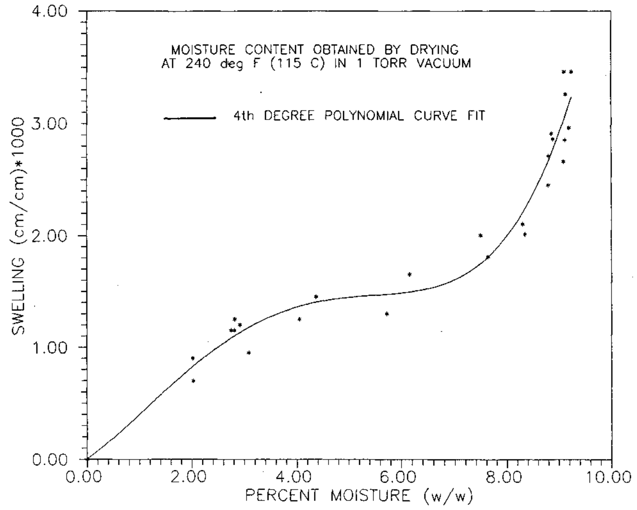

Fig. 4 Swelling response of FM 5055 carbon phenolic in the warp direction.

Swelling

Figures 2–4 show the equilibrated linear swelling of each specimen of FM 5055 in the three primary orthogonal directions (warp, fill, and across ply) as a function of equilibrated moisture content of the material. Using regression analysis, a fourth-degree polynomial was fit to each of the equilibrated data sets and can be seen in the figures. The curves were assumed to go through the origin. This assumption is technically incorrect, but can be used with a minimum of risk for two reasons. First, a previous report showed that room temperature vacuum-dried FM 5055 contained only one-half of 1% moisture when dried further at 163°C (325°F).[1] At 115°C (240°F) that value would be reduced further. Second, the trend of the low moisture content data appears to indicate the swelling curve passes close to the origin. The fourth-degree polynomial accounted for between 96 and 98% of the least-squares residuals indicating a fairly good fit of the curve to the data. Figure 5 shows the three fourth-degree polynomial curve fits on one plot. The larger swelling in the across-ply direction, as opposed to the two fiber directions, is clearly evident.

Figure 6 shows the equilibrated volume swelling of FM 5055 as a function of moisture content of the material. A fourth-degree polynomial was fit to the mean data and is shown in the figure. The fourth-degree polynomial for this data accounted for 100% of the least-squares residuals.

Most swelling data in the literature are for transitional (nonequilibrated) moisture contents.[7,9,11–13,29,30] The equilibrated data that are available were obtained on graphite/epoxy systems.[31] Some researchers have found a linear relationship between transi-

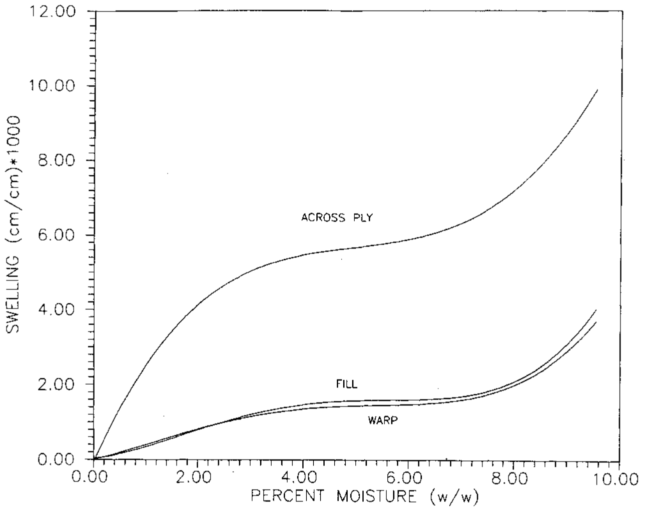

Fig. 5 Fourth-degree polynomial curve fits to swelling data in the three primary material orientations of FM 5055.

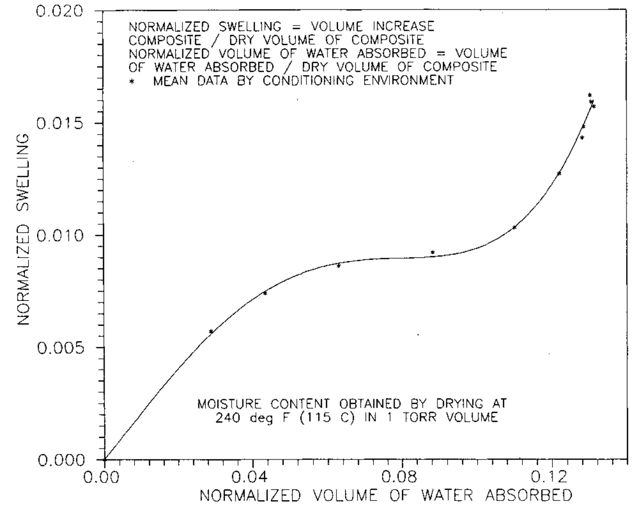

Fig. 6 Normalized volume swelling of FM 5055 carbon phenolic as a function of the normalized volume of water absorbed.

tional moisture content and the degree of swelling.[11,13] Others have found an exponential relationship.[25,26] Still others have found a true sigmoidal relationship.[7] Crossman et al.[31] found both a logarithmic and an exponential relationship between the equilibrated moisture content and swelling in the two transverse directions of two unidirectional graphite/epoxy composites. No explanation was given for the unexpected behavior. Material differences appear to account for most of the variation in shape of reported curves.

The specimens in some of the conditioning environments in this study had not reached equilibrium before being removed. The question then arises, what is the effect of a nonequilibrated condition, i.e., a moisture gradient, on the swelling response of FM 5055? Figures 7–9 are comparison plots of the equilibrated data (13,104 h total conditioning time) with transitional data (1512 h total conditioning time) by material orientation. As can be seen from the figures, the transitional data falls to the left and above the equilibrated curve or at higher swelling levels for the same moisture contents. The differences are small, however. The differences are probably due to the nonlinear nature of the equilibrated curve and the fact that at high moisture levels the slope of the curve is very steep. This means for specimens equilibrated under conditions that eventually result in high moisture levels, that during transition to equilibrium, the outer portions of the specimen, which becomes saturated first, tend toward the high swelling values observed for high moisture content material. When the swelling response is integrated over the volume of the specimen the higher moisture content material adds a disproportionate amount to the average level of swelling.

Swelling Efficiency

Swelling efficiency is the change in volume of the composite divided by the volume of water absorbed by the composite. It is a good indication of the "free volume" within the composite. Free volume is defined as that volume not occupied by the actual mass of a molecule plus the volume it occupies because of thermally dependent harmonic vibration that excludes all other molecules from its domain. Free volume in polymers is the result of packing irregularities of the molecular chains and in carbon fibers because of microvoids generated during the heat treatment process of the polymer precursor.

Water molecules can exist in polymeric media in at least two states, unbound as well as bound to the polymer molecules. Bound water molecules are thought to be responsible for the swelling response. It is assumed that bound water molecules are immobilized and that unbound molecules are contained in the polymer's free volume and are relatively free to travel. Many researchers have found that polymers swell by an amount less than the volume of absorbed water.[7,32,33] A number of authors have found that swelling is negligible until the moisture concentration reaches a threshold volume. They proposed that this threshold volume of water is equivalent to the free volume of the graphite/epoxy composites studied.[9,11,30] The hysteretic nature of the absorption/desorption swelling curves was used as support for this conclusion.

Figure 10 shows the swelling of FM 5055 as a function of the amount of water absorbed. The dependent and independent variables in Fig. 10 are columns I and D, respectively, in Table 1. A swelling efficiency of 1.0 indicates that the volume of water

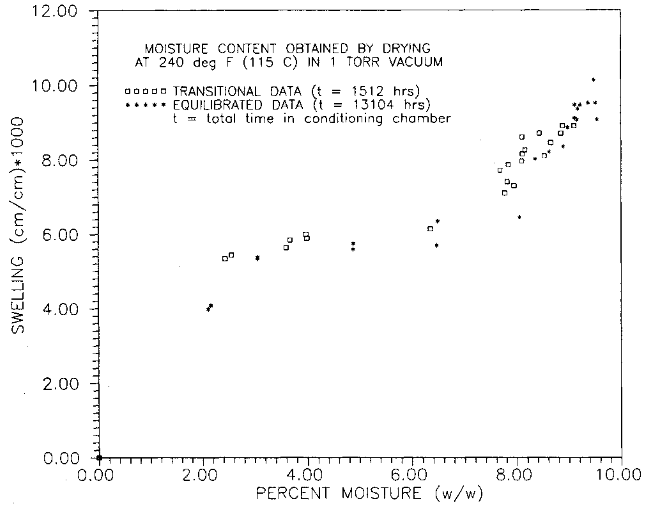

Fig. 7 Transitional and equilibrated across-ply swelling of FM 5055 carbon phenolic as a function of the total moisture content of the composite.

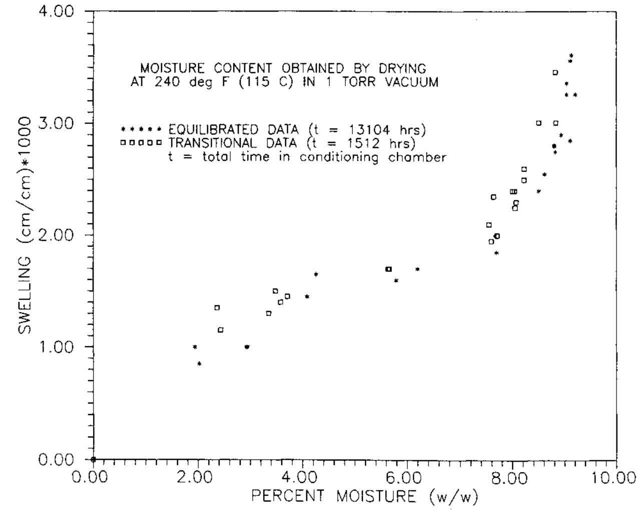

Fig. 8 Transitional and equilibrated fill swelling of FM 5055 carbon phenolic as a function of the total moisture content of the composite.

absorbed was equal to the volume increase in the material. As can be seen from the graph, a large volume of the absorbed water must be occupying free volume within the composite.

A plot of cumulative swelling efficiency as a function of moisture content can be seen in Fig. 11. Swelling efficiency was highest at low moisture contents (approximately 20%) then decreased to a minimum at roughly 7% moisture content by weight where only 9% of the water was accounted for by changes in volume of the composite. Finally, the curve moves back up to 12% efficiency for a fully saturated material.

The dependent variables in Fig. 12 are the free, swelled, and total volume occupied by the absorbed water. The graph shows that the vast majority of the water absorbed by FM 5055 occupies free volume within the material and that the swelled volume accounts for only a small fraction of the total absorbed water.

Figure 13 shows the incremental volume swelling efficiency of FM 5055. This curve is the first derivative of the fourth-degree polynomial given in Fig. 6. It shows that the majority of the swelling in FM 5055 can be accounted for by the first and last few percent of absorbed water. The CCA-3 low-fired rayon fibers are known to absorb in excess of 15% water by weight. Assuming the phenolic resin accounts for most of the swelling in the composite, the phenolic matrix may have the highest affinity for water, the highly porous fibers absorb most of the intermediate moisture and again the polymer absorbs another aliquot of water at the highest moisture contents. In subsequent studies on glass and silica phenolic composites, swelling was found to be a linear function of moisture content. This further supports the proposition that the

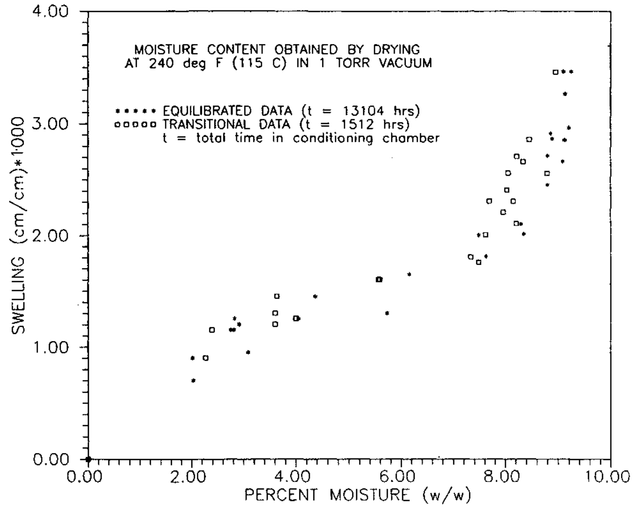

Fig. 9 Transitional and equilibrated warp swelling of FM 5055 carbon phenolic as a function of the total moisture content of the composite.

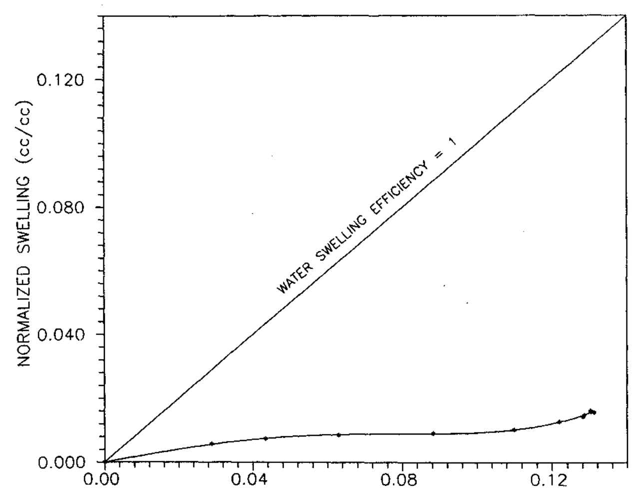

Fig. 10 Normalized volume swelling of FM 5055 carbon phenolic as a function of the normalized volume of water absorbed.

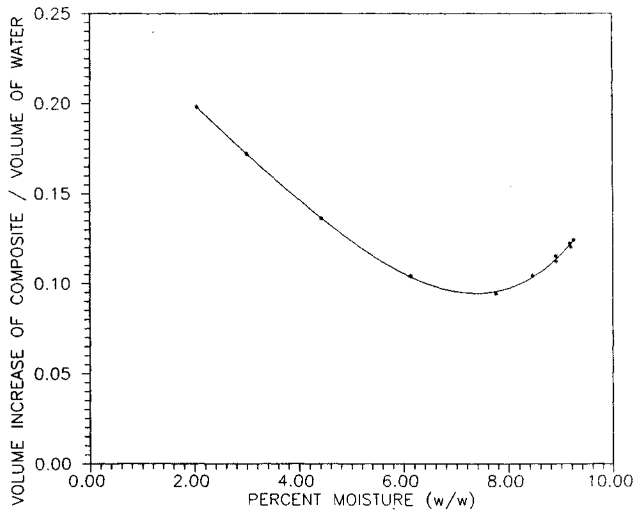

Fig. 11 Swelling efficiency of water in FM 5055 carbon phenolic composite as a function of total moisture content.

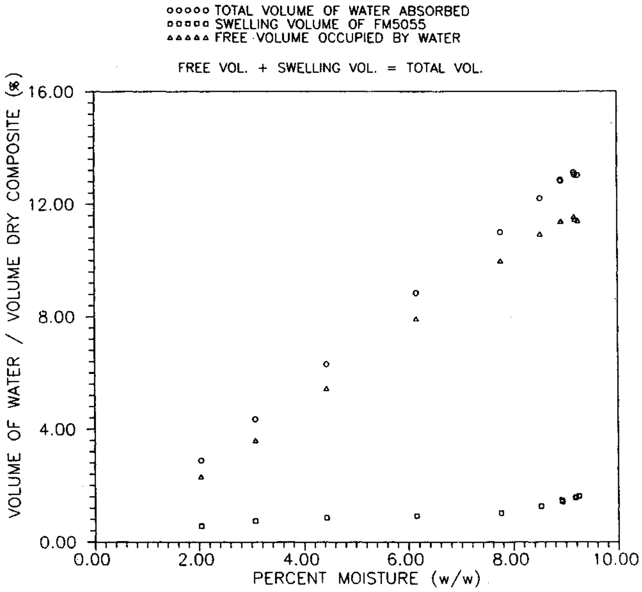

Fig. 12 Free and swelled volume of FM 5055 occupied by absorbed water.

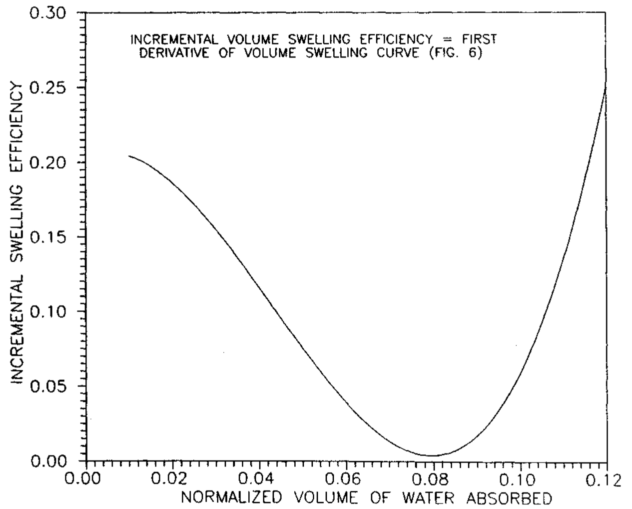

Fig. 13 Incremental volume swelling efficiency of FM 5055 carbon phenolic.

Table 1 Mean swelling data by conditioning environment[a]

	Mean cond. specimen weight, g	Mean dry specimen weight, g	Dry FM 5055 density, g/cc	Vol. water per vol.^{3} dry FM 5055, cc/cc	Mean moisture content W/W, %	Mean A/P swell, cm/cm	Mean fill swell, cm/cm	Mean warp swell, cm/cm	Change in FM 5055 Vol. per vol. dry FM 5055, cc/cc	Change in FM 5055 vol. to vol. water, cc/cc	Free vol. of dry FM 5055 occupied by water, %
Solution	A	B	C	D	E	F	G	H	I	J	K
Calcium chloride	2.3239	2.2776	1.4205	0.0289	2.0383	0.0040	0.0009	0.0008	0.0057	0.198	2.32
Potassium carbonate	2.3807	2.2798	1.4219	0.0630	4.4200	0.0057	0.0016	0.0014	0.0086	0.136	5.44
Magnesium nitrate	2.4432	2.3016	1.4356	0.0883	6.1400	0.0060	0.0017	0.0015	0.0092	0.104	7.91
Sodium nitrate	2.4898	2.2944	1.4319	0.1220	8.4550	0.0081	0.0025	0.0021	0.0127	0.104	10.93
Sodium chloride	2.5073	2.3019	1.4355	0.1281	8.9067	0.0087	0.0029	0.0027	0.0143	0.112	11.38
Potassium chloride	2.5042	2.2938	1.4311	0.1312	9.1900	0.0098	0.0031	0.0028	0.0157	0.120	11.55
Potassium bisulfate	2.5161	2.3102	1.4410	0.1285	8.9000	0.0092	0.0028	0.0028	0.0148	0.115	11.37
Potassium phosphate	2.4689	2.2601	1.4096	0.1302	9.2383	0.0093	0.0035	0.0034	0.0162	0.124	11.41
Distilled water (120°F)	2.4849	2.2759	1.4195	0.1304	9.1633	0.0092	0.0034	0.0032	0.0159	0.122	11.45
65% relative humidity	2.4510	2.2746	1.4183	0.1100	7.7617	0.0064	0.0019	0.0019	0.0103	0.094	9.97
40% relative humidity	2.3384	2.2688	1.4146	0.0434	3.0000	0.0054	0.0010	0.0011	0.0074	0.172	3.59

[a] C = Mean volume of dry specimens/B, D = [(A − B)C]/B, E = [(A − B)/B]100, I = [(F+1)(G+1)(H+1)] − 1, J = I/D, K = (D − I)100.

inverse sigmoidal shaped curve in carbon phenolics is due to multiple absorption sites with varying degrees of affinity for water.

Summary and Conclusions

1) The sigmoidal shape of the moisture content/relative humidity curve for bulk FM 5055 material has been verified.

2) An inverse sigmoidal-shaped curve was found for the swelling of FM 5055 as a function of the moisture content of the material.

3) Large increases in moisture content at intermediate moisture levels resulted in negligible increases in volume of the composite.

4) Transitional swelling data gave higher values of swelling than equilibrated swelling for the same moisture content but only to a small extent.

5) Less than 20% of the water absorbed by the composite can be accounted by the swelling of the material indicating a large free volume within the composite.

6) The unaccounted for volume of water absorbed by the fully saturated composite indicates that dry FM 5055 has a free volume of approximately 11.5% and an apparent density of approximately 1.61 g/cm^3.

7) It is proposed that the phenolic network polymer is responsible for the majority of the absorption of water at low and high moisture levels whereas the fibers absorb most of the intermediate moisture content water.

8) These findings appear to indicate that there are multiple sites for the absorption of water in the cured resin and that these sites vary in their affinity for water.

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