Moisture Absorption of Graphite-Epoxy Composites Immersed in Liquids and in Humid Air

ALFRED C. LOOS AND GEORGE S. SPRINGER

Department of Mechanical Engineering
The University of Michigan
Ann Arbor, Michigan 48109

(Received January 15, 1979)

ABSTRACT

Moisture absorption of graphite-epoxy composites immersed in liquids and in himid air were investigated. The moisture content as a function of time and temperature was measured for three materials: Fiberite T300/1034, Hercules AS/3501-5 and Narmco T300/5208. Tests were performed a) with the materials immersed in No. 2 diesel fuel, in jet A fuel, in aviation oil, in saturated salt water, and in distilled water (in the range of 300 to 322 K) and b) with the materials exposed to humid air (in the range 322 to 366 K). The results obtained were compared to available composite and neat resin data.

I. INTRODUCTION

FOR OPTIMUM AND safe design of elements and structures made of composite materials the moisture content of the material must be known. For this reason, considerable attention has been paid in recent years to the problem of moisture absorption by composite materials. However, most of the previous investigations have been concerned with moisture absorption and desorption of graphite-epoxy composites exposed to humid air. Very few data are available on the moisture content of composites submerged in liquids. The first objective of this investigation was, therefore, to determine the moisture content as a function of time and temperature of graphite-epoxy composites submerged in five different liquids: distilled water, a saturated salt water solution, No. 2 diesel fuel, jet A fuel, and aviation oil. The second objective was to study moisture content as a function of time, temperature, and relative humidity of graphite-epoxy composites exposed to humid air. To accomplish these objectives tests were performed and data were generated with three commonly used graphite-epoxy composites: Fiberite T300/1034, Hercules AS/3501-5, and Narmco T300/5208.

J. COMPOSITE MATERIALS, Vol. 13 (April 1979), p. 131

0021-9983/79/01 0131-17 $04.50/0

II. EXPERIMENTAL

All tests were performed with 8 ply unidirectional specimens of nominal dimensions: thickness $h = 1.04$ mm, width $b = 12.7$ mm and length $L = 101$ mm. The specimens were cut from 0.4 X 0.4 m autoclave cured panels which were fabricated from prepreg using standard lay-up and vacuum bagging procedures. The cure cycles used in manufacturing the panels are given in the Appendix. The fiber volume fraction was about 65 percent for the T300/1034 and the AS/3501-5 specimens and about 70 percent for the T300/5208 specimens.

During tests where the specimens were immersed in liquids the specimen temperature was kept constant by placing the liquid container inside a constant temperature chamber. During tests with humid air the specimens were mounted above the surface of a pool of water. The relative humidity of the air surrounding the specimens was regulated by passing preheated air through the vapor (Figure 1). The relative humidity was measured with an Abbeon Hygrometer. The temperature of the air, the water, and the specimens was controlled by heaters and was measured by thermocouples.

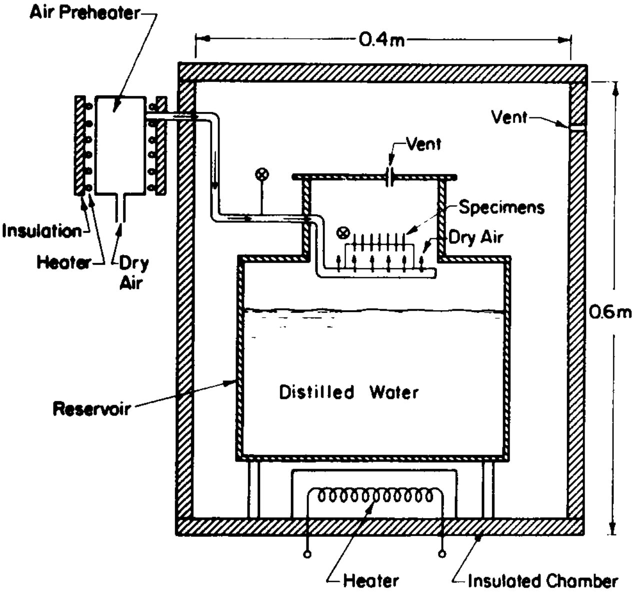

Figure 1. Schematic of apparatus. ⊗ – *thermocouple locations.*

Before placing the specimens into the moist environment (liquid or humid air), the specimens were dried in an oven at 366 K. The dry specimens were then placed in the appropriate environmental chamber and their weight gain was monitored by weighing them periodically on a Mettler Analytical Balance. It has been observed previously [1, 2] that the moisture absorption characteristics of graphite-epoxy composites may change slightly (less than 10 percent) after they have been moisturized once. Since all specimens used in this investigation were moisturized only once, the data reported here are for the first moisturization process. Any changes which might occur in the weight gain characteristics during subsequent drying and remoisturization are expected to be small [1].

The apparent weight gain is due completely to absorbed moisture, provided material (resin or fiber) is not lost during exposure to the moist environment. Previous data indicate that material loss is negligible at the temperatures and moisture levels employed in the present tests. Hence, the measured weight gain was taken to be the same as the moisture content of the material.

All data points referring to results obtained in this investigation are the average of three data. All three data were generally within ±20 percent.

III. MATERIAL IMMERSED IN LIQUIDS

The specimens were immersed in the following liquids: a) Amoco No. 2 diesel fuel, b) Phillips Petroleum Co. jet A fuel, c) Stauffer type 2 synthetic aviation lubricant, d) a saturated NACl-water solution and e) distilled water.

The moisture contents of composites submerged in these liquids are presented in Figures 2–6. For each material the moisture contents are shown as a function of time and temperature. For materials immersed in No. 2 diesel fuel, in jet A fuel, or in aviation oil, the amount of moisture absorbed seems to be insensitive to temperature, at least in the temperature range of the present tests (300 to 322 K). For all three materials tested the maximum moisture content is 0.5 to 0.6 percent. As will be shown subsequently, this is considerably lower than the maximum moisture content achieved during immersion in distilled water, in salt water, or in humid air.

The moisture contents of materials immersed in distilled water or in saturated salt water solution depends upon both time and temperature. However, the maximum moisture content again seems to be insensitive to temperature. As expected, a lower maximum moisture content is reached in salt water than in distilled water.

It has been demonstrated that under most conditions the moisture content of composites may be calculated using Fick's Law (e.g. see the summary given in ref. [3]). These calculations require a knowledge of two parameters, namely the maximum moisture content M_m and the diffusivity D. The values of M_m (taken from Figures 2–6) are listed in Table 1. For distilled water and for salt water the transverse diffusivities D (i.e. the diffusivities normal to the fibers) were also calculated according to the method outlined by Shen and Springer [4]. The resulting D values are given in Figures 7 and 8 and in Table 2. Analytical or numerical solutions of Fick's equation [4, 5], together with the above values of M_m and D provide an estimate of the moisture content of each of the three materials at temperatures other than those employed in the present tests.

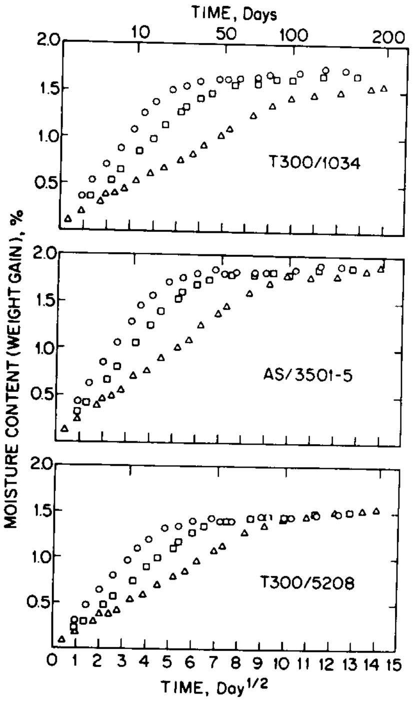

Figure 2. Moisture content as a function of time for three composite materials immersed in distilled water. Immersion temperature, ○ - 322 K; □ - 311 K; △ - 300 K.

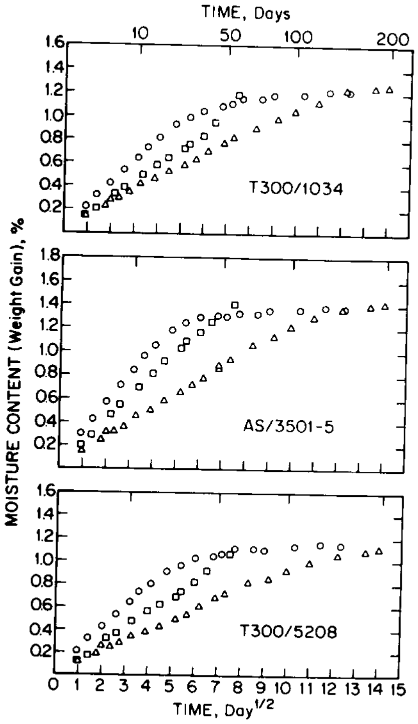

Figure 3. Moisture content as a function of time for three composite materials immersed in saturated salt water. Immersion temperature, ○ - 322 K; □ - 311 K; △ - 300 K.

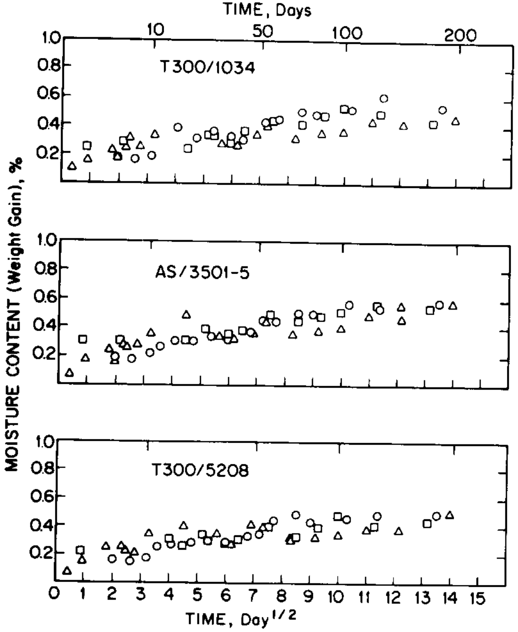

Figure 4. Moisture content as a function of time for ***three composite materials immersed*** *in No. 2 diesel fuel. Immersion temperature, ○ - 322 K; □ - 311 K; △ - 300 K.*

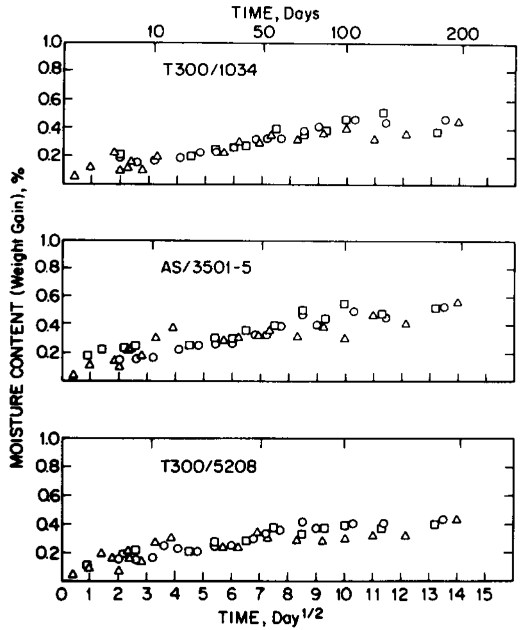

Figure 5. Moisture content as a function of time for three composite materials immersed in jet A fuel. Immersion temperature, ○ - 322 K; □ - 311 K; △ - 300 K.

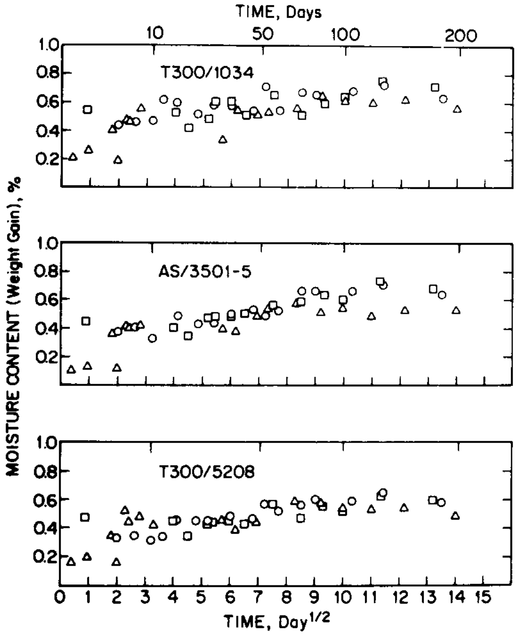

Figure 6. Moisture content as a function of time for three composite materials immersed in aviation oil. Immersion temperature, ○ - 322 K; □ - 311 K; △ - 300 K.

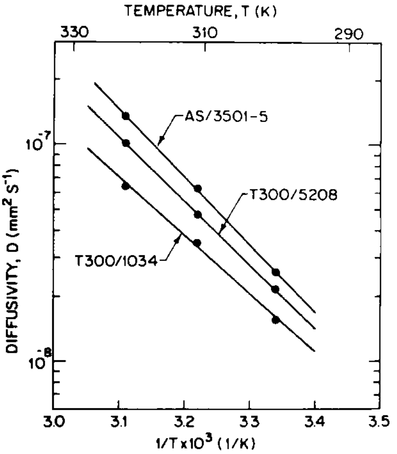

Figure 7. Transverse diffusivity as a function of temperature for composites immersed in distilled water. Circles represent present data. Solid lines are fit to data.

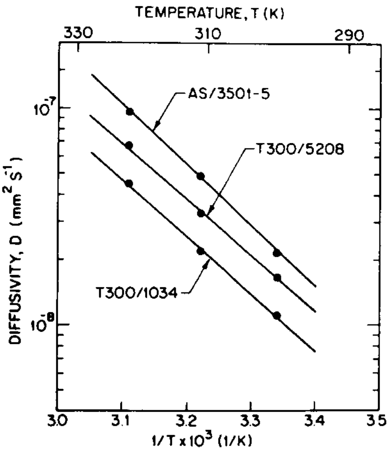

Figure 8. Transverse diffusivity as a function of temperature for composites immersed in saturated salt water. Circles represent present data. Solid lines are fit to data.

Table 1. Summary of Maximum Moisture Content of the Three Material Systems Immersed in Liquids

	Maximum Moisture Content, M_m (%)		
Liquid	*T300/1034*	*AS/3501-5*	*T300/5208*
Distilled Water	1.70	1.90	1.50
Saturated Salt Water	1.25	1.40	1.12
No. 2 Diesel Fuel	0.50	0.55	0.45
Jet A Fuel	0.45	0.52	0.40
Aviation Oil	0.65	0.65	0.60

Table 2. Summary of Constants D_o and C for the Three Material Systems Immersed in Distilled Water and in Saturated Salt Water

	T300/1034		*AS/3501-5*		*T300/5208*	
Liquid	D_o	*C*	D_o	*C*	D_o	*C*
Distilled Water	16.3	6211.	768.	7218.	132.	6750.
Saturated Salt Water	5.85	6020.	53.8	6472.	6.23	5912.

The transverse diffusivity is $D = D_0 \exp(-C/T)$ where D_0 is in $mm^2\ s^{-1}$ and C is in K.

IV. MATERIAL EXPOSED TO HUMID AIR

Moisture absorption of graphite-epoxy composites exposed to humid air has been studied previously. However, there is considerable spread in some of the reported data and there is some question regarding the relationship between the maximum moisture content and the relative humidity. Previously, data for each material were taken in different laboratories making it difficult to assess the reasons for the differences in the results. It was decided, therefore, to determine the moisture absorption characteristics of three materials (T300/1034, AS/3501-5, and T300/5208) simultaneously, under identical conditions.

Moisture content (weight gain) as a function of time was measured under the folloiwng six conditions: Relative humidity = 100 percent and temperature = 322, 344, 366 *K*, relative humidity = 40, 60 percent and temperature = 339 *K*, and relative humidity = 25 percent and temperature = 366 *K*. For the three materials these measurements resulted in 3 X 6 = 18 moisture content versus time plots. The eighteen plots are not presented here individually. Instead, the values of the maximum moisture content M_m and the transverse diffusivity D were evaluated from these plots according to the procedure given in ref. [4]. The data are given below in terms of M_m and D. As was noted before (see Section III) these two parameters are sufficient to characterize the moisture absorption-desorption behavior of the material.

1) Maximum Moisture Content M_m

The maximum moisture content as a function of relative humidity for the three composite systems is given in Figures 9–11. In addition to the data generated in the present tests, data reported by other investigators are also included in these figures. As a reference, the maximum moisture contents of the three neat resins are presented in Figures 12–14. The neat resin data shown in these figures were taken from the literature, the source of the data being indicated in each figure.

It has been found previously that the maximum moisture content can be related to the relative humidity ϕ by the expression [4]

$$M_m = a\phi^b \qquad (1)$$

where a and b are constants which depend on the material. The values of these constants can be obtained by fitting a line through the data points. The a and b values resulting from such curve fitting are tabulated in Table 3. For a given material there is a spread in the reported values of a and b. This spread is probably due to differences in the curing cycles, since the curing process may affect significantly the maximum moisture content [1, 8].

Note that the exponent b is nearly unity for all three materials tested. Previously, Shen and Springer [4] found b to be about 2.0 for T300/1034. The environ-

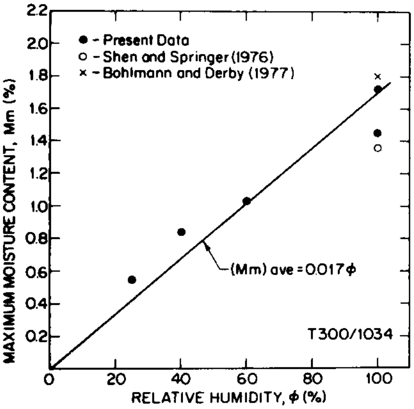

Figure 9. Maximum moisture content as a function of relative humidity for Fiberite T300/1034 composites. Solid line is fit to data.

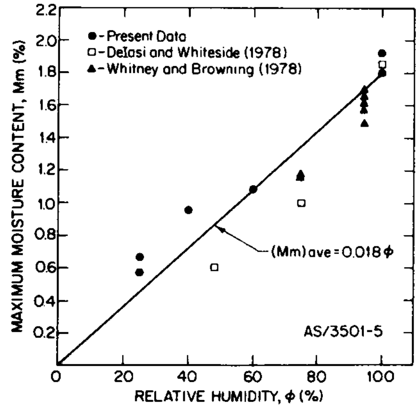

Figure 10. Maximum moisture content as a function of relative humidity for Hercules AS/3501-5 composites. Solid line is fit to data.

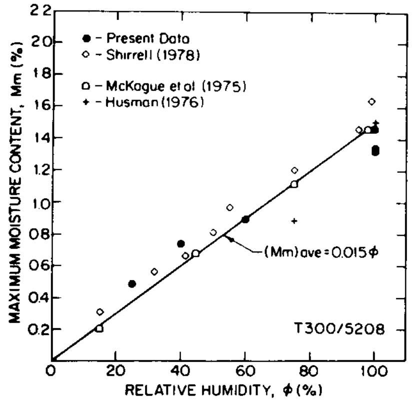

Figure 11. Maximum moisture content as a function of relative humidity for Narmco T300/5208 composites. Solid line if fit to data.

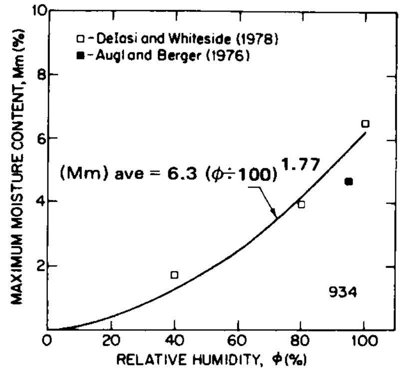

Figure 12. Maximum moisture content as a function of relative humidity for Fiberite 934 neat resin. Solid line is fit to data.

mental chambers used by Shen and Springer were modified to allow better control of the humidity at humidities below 100 percent. With this modified apparatus the value of b was remeasured and was found to be approximately unity. This present result is consistent with those reported by other investigators.

It can be seen from Figures 9–14 and Table 3 that the value of b is not exactly one either for neat resins or for composite systems. In most cases b is slightly higher than unity. The value of b (as well as the value of a) should be measured for each

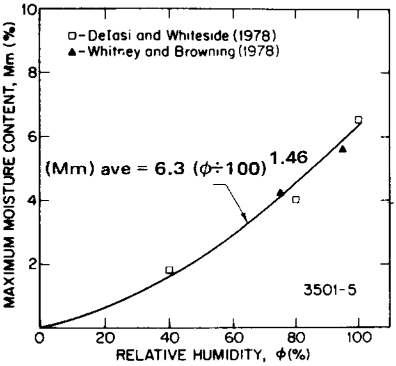

Figure 13. Maximum moisture content as a function of relative humidity for Hercules 3501-5 neat resin. Solid line is fit to data.

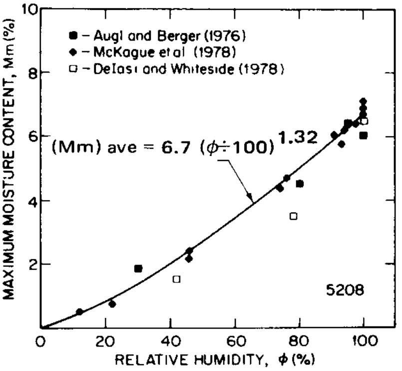

Figure 14. Maximum moisture content as a function of relative humidity for Narmco 5208 neat resin. Solid line is fit fit to data.

Table 3. Summary of the Constants a and b ($M_m = a\phi^b$ when $b = 1$; $M_m = a(\phi \div 100)^b \times 100$ when b is not = 1).

Material	***Investigator***	***a***	***b***
T300/1034	Present Data	0.017	1
	Shen and Springer [4]*	0.014	–
	Bohlmann and Derby [6]*	0.018	–
AS/3501-5	Present Data	0.019	1
	Delasi and Whiteside [7]	0.0186	1.6, $\phi < 60\%$ 1.9, $\phi > 60\%$
	Whitney and Browning [2]	0.016	1.1
T300/5208	Present Data	0.015	1
	Shirrell [8]	0.0155	1
	McKague et al [9]	0.0146	1
	Husman [10]	0.0150	1.81
934 (neat resin)	Delasi and Whiteside [7]	0.063	1.4, $\phi < 60\%$ 1.8, $\phi > 60\%$
	Augl and Berger [11]*	0.049	–
3501-5 (neat resin)	Delasi and Whiteside [7]	0.063	1.4, $\phi < 60\%$ 1.8, $\phi > 60\%$
	Whitney and Browning [2]	0.06	1.22
5208 (neat resin)	Delasi and Whiteside [7]	0.063	1.4, $\phi < 60\%$ 1.8, $\phi > 60\%$
	Augl and Berger [11]	0.059	1
	McKague et al [12]	0.066	1.28

*One data point only.

"batch" of material cured in the same manner since, as was discussed above, the values of these constants may vary from batch to batch. However, it is observed that the value $b = 1$ results in an average M_m which approximates all the data reasonably well (Figures 9–11). Thus, if data are unavailable for a given "batch" of material then $(M_m)_{\text{ave}}$ given in Figures 9–11 may be used to estimate the maximum moisture content.

The maximum moisture content of the composite M_m may also be estimated from the maximum moisture content of the neat resin $(M_m)_r$. By assuming that the fibers do not absorb any moisture, M_m and $(M_m)_r$ are related by the expression

$$M_m = (M_m)_r \, (W_r) \tag{2}$$

where W_r is the weight fraction (percent) of the resin in the composite. The validity of Equation (2) is illustrated in Figure 15. In this figure measured values of M_m are compared with those calculated from the neat resin data. As is seen, there is excellent agreement between the measured and calculated values of M_m. Note that the comparisons could be made only for AS/3501-5, because only for this composite were the maximum moisture contents of both the neat resin and the composite measured by the same investigators. Owing to test to test variations in the material, neat resin data obtained by one investigator cannot be compared with the moisture content of the composite obtained by a different investigator.

Equation (1) does not take into account the variation of M_m with temperature. The value of M_m seems to increase slightly with increasing temperature. However, the changes in M_m due to changes in temperature are usually less than the spread in the data. Hence, the effect of temperature on M_m cannot be determined accurately from the available data. For the purposes of practical engineering calculations variations in the M_m due to temperature may be neglected.

2) Transverse diffusivity D

The transverse diffusivities as a function of temperature of the composites are given in Figures 16–18. Data reported by other investigators are also included in these figures. The transverse diffusivities of the three neat resins, as reported by previous investigators, are summarized in Figures 19–21.

The diffusivity D may be expressed as

$$D = D_o \exp(-C/T) \tag{3}$$

where D_o and C are constants and T is the absolute temperature. Accordingly, all data were presented on a $\log D$ versus $1/T$ graph since on such an Arrhenius plot the data should fall on a straight line. From these lines the constants D_o and C could be evaluated. The resulting D_o and C values are listed in Table 4. As in the case of the maximum moisture content, even for a given material there are variations in the reported diffusivity values. The likely reason for these variations is the differences in the curing processes used in different laboratories. It has been shown that even slight, unintentional differences in the curing process may alter the value of D significantly [1].

In Figures 16–21 data are included only up to 390 K. The diffusivity of T300/1034 was measured by Shen and Springer [4] at a higher temperature (422 K) by immersing the material in saturated steam. These tests resulted in diffusivities which were higher than the values generated by extrapolating the low temperature diffusivity data. In other words, at 422 K the diffusivity of the material was higher than predicted by Equation (3). Recent tests showed that significant cracks develop when the material is submerged in saturated steam [1]. The large increase in D observed by Shen and Springer at 422 K was therefore due to such cracking of the material.

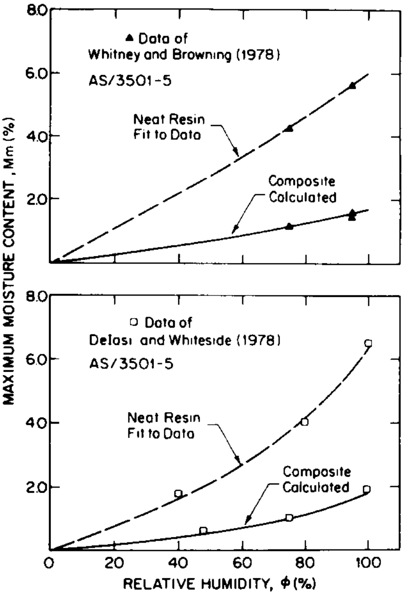

Figure 15. Comparison of the measured maximum moisture content with the maximum moisture content calculated from neat resin data (Equation 2).

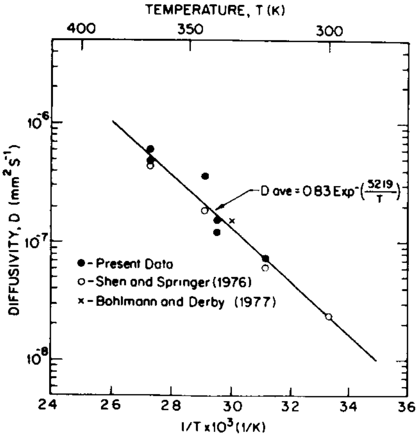

Figure 16. Transverse diffusivity as a function of temperature for Fiberite T300/1034 composites. Solid line is fit to data. (Humid air)

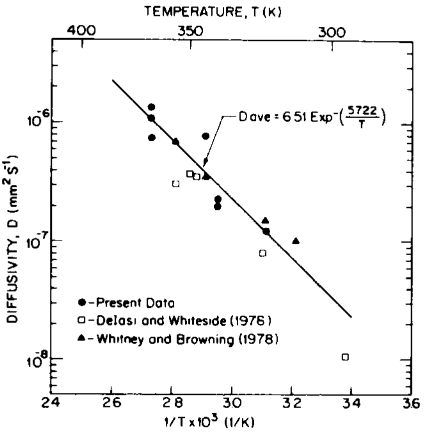

Figure 17. Transverse diffusivity as a function of temperature for Hercules AS/3501-5 composites. Solid line is fit to data. (Humid air)

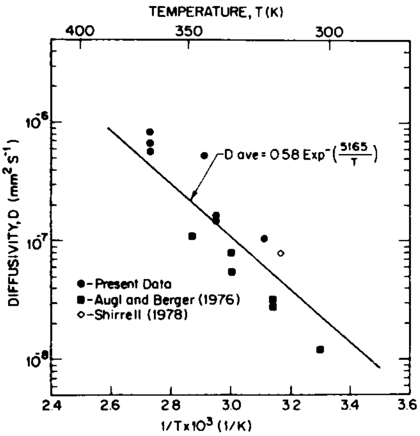

Figure 18. Transverse diffusivity as a function of temperature for Narmco T300/5208 composites. Solid line is fit to data. (Humid air)

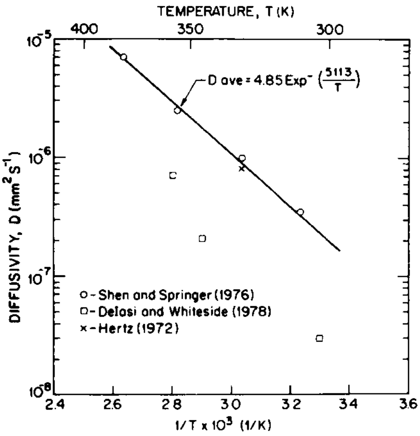

Figure 19. Transverse diffusivity as a function of temperature for Fiberite 934 neat resin. Solid line is fit to data (Humid air)

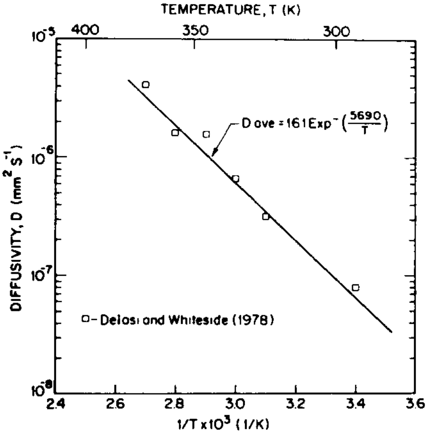

Figure 20. Transverse diffusivity as a function of temperature for Hercules 3501-5 neat resin. Solid line is fit to data. (Humid air)

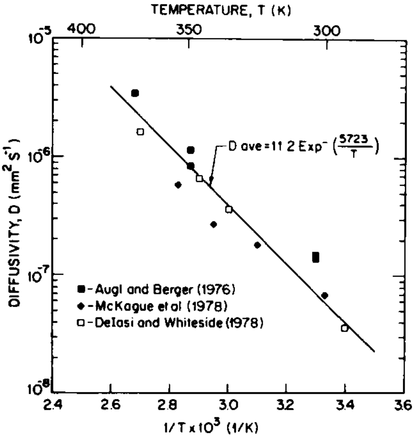

Figure 21. Transverse diffusivity as a function of temperature for Narmco 5208 neat resin. Solid line is fit to data. (Humid air)

The transverse diffusivity of the composite can be estimated from the diffusivity of the resin D_r. If all the fibers are parallel to the surface through which the moisture diffuses, then D may be approximated by the expression [4]

$$D = D_r(1 - 2\sqrt{\pi/V_f}) \tag{4}$$

where V_f is the fiber volume fraction ($V_f < 0.785$). The validity of Equation (4) is demonstrated in Figures 22–24, where measured values of D are compared to those calculated from neat resin data. There is good agreement between the measured and calculated values of D, lending confidence to the validity of Equation (4). Note that comparisons could be made only when the values of D for the neat resin and the composite were measured by the same investigator. Owing to variations in the material, data obtained in different laboratories could not be used in these comparisons.

Table 4. Summary of the Constants D_o and C [$D = D_o \exp(-C/T)$]*

Material	*Investigator*	*D_o($mm^2\ s^{-1}$)*	*C(K)*
T300/1034	Present Data	2.28	5554.
	Shen and Springer [4]	0.44	5058.
AS/3501-5	Present Data	6.51	5722.
	Whitney and Browning [2]	0.44	4768.
	Delasi and Whiteside [7]	28.8	6445.
T300/5208	Present Data	0.57	4993.
	Augl and Berger [11]	0.41	5231.
934 (neat resin)	Shen and Springer [4]	4.85	5113.
	Delasi and Whiteside [7]	16.4	5992.
3501-5 (neat resin)	Delasi and Whiteside [7]	16.1	5690.
5208 (neat resin)	Augl and Berger [11]	2.8	5116.
	McKague, et al [12]	0.051	4060.
	Delasi and Whiteside [7]	4.19	5488.

*Humid air

V. SUMMARY

The following general conclusions can be made regarding the moisture absorption characteristics of T300/1034, AS/3501-5 and T300/5208 graphite-epoxy composites.

1) Material immersed in liquid at temperatures 300 to 322 K
    a) The amount of moisture absorbed by materials immersed in No. 2 diesel fuel, jet A fuel and aviation oil depends on the immersion time but is insensitive to the temperature. The maximum moisture content is 0.5 to 0.6 percent. This value is reached in about 200 days.
    b) The amount of moisture absorbed by materials immersed in distilled water and in saturated salt water depends both on the immersion time and on temperature. The data presented in this paper provide the maximum

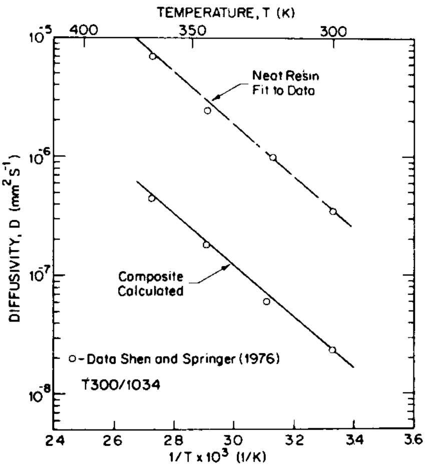

Figure 22. Comparison of the measured transverse diffusivities with the transverse diffusivities calculated from neat resin data (Equation 4).

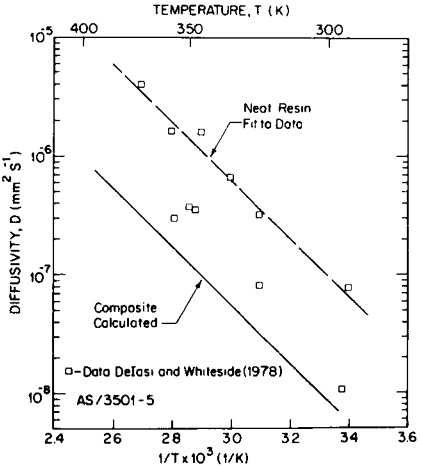

Figure 23. Comparison of the measured transverse diffusivities with the transverse diffusivities calculated from neat resin data (Equation 4).

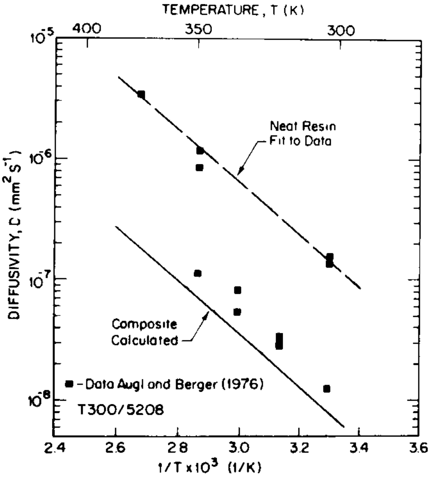

Figure 24. Comparison of the measured transverse diffusivities with the transverse diffusivities calculated from neat resin data (Equation 4).

moisture content and the transverse diffusivity values which (together with Fick's equation) can be used to calculate the moisture content of the material under steady and time varying ambient conditions.

2. Material exposed to humid air in the temperature range 322 to 366 K
   a) The maximum moisture content is related to the relative humidity by the expression $M_m = a\phi^b$, where a and b are constants. There are variations in the reported values of these constants, probably due to differences in the curing processes. The value of b is near unity, but is not exactly equal to one.
   b) The maximum moisture content depends on the relative humidity but is insensitive to temperature.
   c) The maximum moisture content of a composite can be estimated from the maximum moisture content of the resin, provided that the resin and the composite were cured in an identical manner.
   d) The transverse diffusivity follows the Arrhenius plot up to 390 K.
   e) The transverse diffusivity of a composite can be estimated from the diffusivity of the resin, provided that the resin and the composite were cured in an identical manner.
   f) The M_m and D values given in this paper can be used (together with Fick's equation) to calculate the moisture content of the material, as long as the material is not damaged due to exposure to the environment. Significant changes in the material are unlikely to occur below 390 K. At higher temperatures cracks may develop, especially if the environment is simultaneously at a high temperature and at a high moisture level. Cracks which might form under such circumstances may alter significantly the values of both M_m and D.

APPENDIX

Autoclave Cure Cycles

I. Fiberite T300/1034
   1) Vacuum Bag – insert layup into autoclave at room temperature.
   2) Apply full vacuum and contact pressure
   3) Raise temperature to 250°F at 3°F per minute
   4) Hold at 250°F for 15 minutes. Apply 100 psi.
   5) Hold at 250°F and 100 psi for 45 minutes.
   6) Raise temperature to 350°F.
   7) Hold at 350°F for 2 hours.
   8) Cool under pressure to below 175°F.

II. Hercules AS/3501-5
   1) Place vacuum bagged layup into autoclave and close autoclave.
   2) Apply a minimum vacuum of 25 in of mercury
   3) Raise temperature to 350°F at 2.5°F per minute. When laminate temperature reaches 260°F apply 85 psi.
   4) Hold at 25 in Hg, 85 psi and 350°F for 60 minutes.

5) Lower temperature to 150°F at 13°F per minute.
6) Release autoclave vacuum and pressure
7) Remove layup from autoclave.
8) Postcure at 370°F for 3 hrs in an air circulating oven.

III. Narmco T300/5208

1) Place vacuum-bagged layup into autoclave and close autoclave.
2) Apply a minimum vaccum of 22 in of mercury
3) Raise temperature to 275°F at 4–6°F per minute.
4) Hold at 275°F for 60 minutes. Apply 85 psi.
5) Raise temperature to 350°F at 4–6°F per minute.
6) Hold at 350°F and 85 psi for 120 minutes.
7) Cool under pressure to 140°F at 4–6°F per minute.
8) Release autoclave vacuum and pressure.
9) Remove layupt from autoclave.
10) Post cure at 400°F for 4 hrs in an air circulating oven.

ACKNOWLEDGMENTS

This work was supported by the United States Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Dayton, Ohio under contract number F33615-75-C-5165.

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