WETOMETER FOR MEASUREMENT OF MOISTURE IN COMPOSITES

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ABSTRACT

A combined experimental and analytic approach to moisture diffusion analysis (MDA) has evolved in proof of principle form as a new instrument termed a moisture profilometer. The objective in moisture profilometry is the quantitative analysis of the spatial distribution of moisture within composites and definition of localized internal stress fields. An electrolytic cell is utilized to record cumulative moisture evolution and moisture effusion rate. Variation of cell geometry accommodates either laboratory analysis of small composite damage control specimens or field inspection of limited surface areas of composite structure in an area scanning mode. An important new aspect of moisture profilometry is calculation of the depth profile of moisture concentration from measurement of surface effusion and rate with time. Statistical estimation theory is applied to this problem and preliminary results indicate that concurrent calculations can generate moisture concentration profiles during the course of moisture effusion measurements. Results of initial instrument design and computational analysis will be demonstrated and discussed.

Introduction

Moisture is known to degrade the strength and stiffness of graphite-epoxy composites and the results of recent studies summarized in several workshop proceedings.[1-3] Several detailed studies of uniaxial graphite fiber reinforced epoxy resins[4,5] show that ultrasonic acoustic properties are sensitive to both current moisture content and prior microstructure damage due to moisture absorption-desorption cycling. This discussion briefly outlines the development of a new NDE methodology for direct measurement of moisture concentration and moisture diffusion properties in composite materials. This new nondestructive measurement is termed moisture diffusion analysis (MDA) and provides a quantitative tool for direct evaluation of moisture in composites.

Measurement Methodology

The upper left view of Fig. 1 shows the moisture evolution analyser (DuPont Model 902H) employed in the current studies. This instrument uses an electrolytic measurement and feedback control loop shown in the upper right view of Fig. 1 to measure both the rate of moisture release to a dry carrier gas at controlled temperature. The lower right view of Fig. 1 shows the higher rate of directional moisture release measured on the transfibrous surface of a uniaxial composite where moisture diffusion is along the fiber axis. The lower left view of Fig. 1 shows the conventional full enclosure sample chamber supplied with the instrument. New surface sampling chambers such as the sleeve type for bar specimens and the face plate type for plate specimens are presently under development and testing. These latter sampling chambers permit small area sampling of large composite structure to provide surface mapping for moisture content and moisture diffusion response.

Directional Diffusion Coefficients

Using the fully enclosed sampling chamber, the three principal diffusion coefficients of the uniaxial composite can be evaluated as shown in Fig. 2. The upper left view of Fig. 2 shows the three sample geometries which provide the enhanced diffusion along each of the three composite principal axis. The upper right view of Fig. 2 shows the typical absorption (A) and desorption (D) kinetics of moisture in the pure epoxy matrix at $75^\circ C$. for two successive cycles of exposure and drying. The lower left view of Fig. 2 shows that three successive cycles of moisture absorption and desorption along the fiber axis produces a substantial increase in diffusion coefficients D_2 parallel to the fiber axis. The lower right view of Fig. 2 shows that the temperature dependence of diffusion coefficients parallel to fibers (D_1 in upper curve) and transverse to fibers (D_3 in lower curve) are directionally different. Precise evaluation of the directional diffusional coefficients and their dependence on temperature and moisture cycling is essential for calculations which predict moisture concentration profiles.

Moisture Profilometry

The inversion of the Fickean diffusion equations can be applied to develop a numeric analysis of moisture profiles as shown in the upper left view of Fig. 3. Typical experimental data utilized in this analysis are tabulated in the upper right view of Fig. 3. These data cover an effusion time t_m range which describes the effusion rates J_m for moisture escaping from the surface $t_m \simeq \Delta$ to approximately 20% into the sample thickness at $t_m \simeq 50.5$ min. The lower left view of Fig. 3 shows that the computed concentration profile correctly estimates the fully saturated moisture concentration near the sample surface at 32000 ugm H_2O per cc composite. At greater depths, where $0.2 \leqslant X/L_x \leqslant 0.8$ where experimental data are unavailable, the lower left view of Fig. 3 shows that the analytical estimator produces a cyclic response. The lower right view of Fig. 3 shows that synthetically smoothed moisture effusion data produce the correct moisture profile much farther into the fractional thickness (X/L_x) of

the composite. This analytic approach to moisture diffusion analysis provides for three-dimensional moisture mapping by combining the depth profiling shown in Fig. 3 with the surface area mapping using the face plate sampling chamber described in Fig. 1.

Microstructure Degradation

A summary of MDA analysis of microstructure degradation is illustrated in Fig. 4. The upper left views show a 12-inch bar of graphite epoxy composite aged so as to develop a gradient of moisture concentration with maximum moisture at the lower extremity which is immersed in boiling water for 1132 hours and relatively low moisture in the upper 5.5 inches which is exposed to ambient air. Following the moisture exposure cycle, this bar was thermally cycled between 23°C. and temperatures above the service ceiling temperature of 177°C. (350°F.). The regions of the composite which experience the combined high moisture and high temperature exposure exhibit microfracture. The lower left view of Fig. 4 shows that the length profile of moisture desorption properties is sharply modified at L≈6. The upper right view shows that profiles of moisture absorption response are similarly modified at L≈6 which coincides with the seal region between the zones of low and high hydrothermal damage. The changes in MDA shown in Fig. 4 correlate with microcrack and craze structure where $6 \leqslant L \leqslant 12$ inch due to hydrothermal degradation. Evaluation of interlaminar shear strengths as shown in the lower right view of Fig. 4 shows that samples exposed to high moisture (100°C. H_2O vapor or liquid) display a lower average strength λ_0 and broader strength distribution indicated by lower m in the Weibull cumulative strength distribution. This strength loss correlates with the microcrack formation produced by hydrothermal damage and measured by MDA.

Summary

The results shown above illustrate the development and application of moisture diffusion analysis and as a new multi-purpose NDE tool for moisture and microstructure characterization of composite materials.
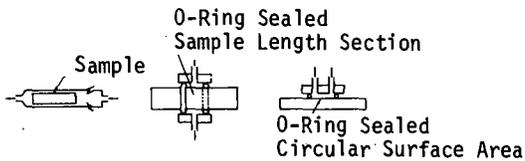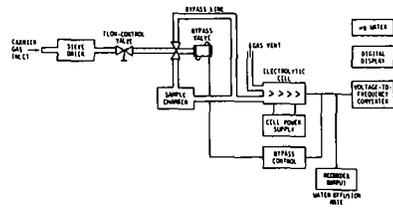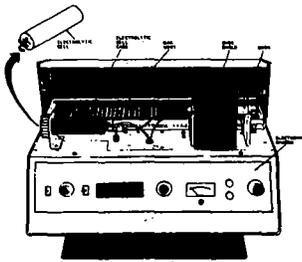
Acknowledgement

References

1. Proceedings of Workshop on Durability Characteristics of Resin Matrix Composites, sponsored by AFFDL and AFML, Battelle Memorial Institute, Columbus, Ohio, Sept. 30 - Oct. 2, 1975.

2. Proceedings of Workshop on the Role of the Polymer Substrate Interphase in Structural Adhesion, sponsored by AFOSR and AFML, University of Dayton, Dayton, Ohio, Sept. 9-10, 1976.
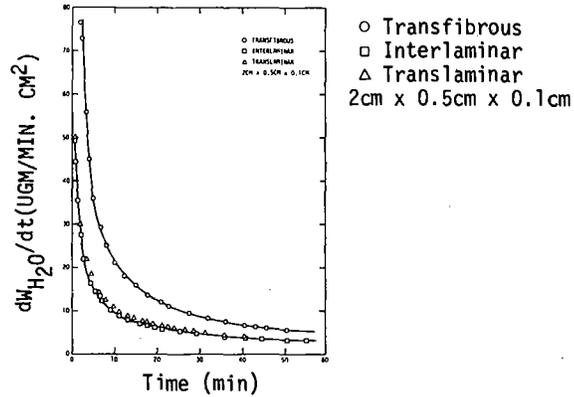
3. Transactions of the Workshop on The Effects of Relative Humidity and Elevated Temperature on Composite Structures, editors: J. R. Vinson, R. B. Pipes, W. J. Walker, and D. R. Ulrich, Air Force Office of Scientific Research Tech., Report AFOSR 77-0030

4. D. H. Kaelble and P. J. Dynes, "Nondestructive Tests for Shear Strength Degradation of a Graphite-Epoxy Composite," ASTM STP 617, American Society of Testing and Materials, Philadelphia (1977), pp. 190-200.

5. D. H. Kaelble and P. J. Dynes, "Methods for Detecting Moisture Degradation in Graphite-Epoxy Composites," Materials Evaluation, 35 (4), (1977), pp. 103-108.

O-Ring Sealed
Sample Length Section

Sample

O-Ring Sealed
Circular Surface Area

Full Enclosure   Face Plate for
Sample Chamber   Single Surface
                        Plate Specimens

Sleeve Type
for Bar Specimens

○ Transfibrous
□ Interlaminar
△ Translaminar
2cm x 0.5cm x 0.1cm
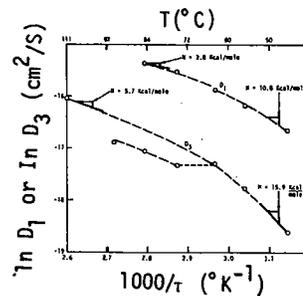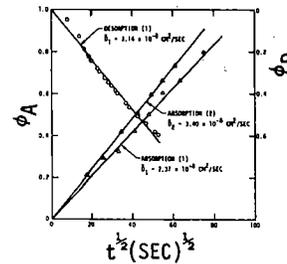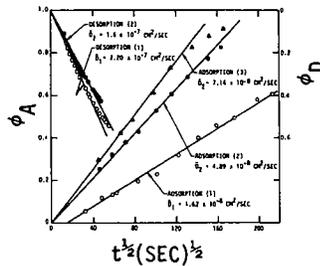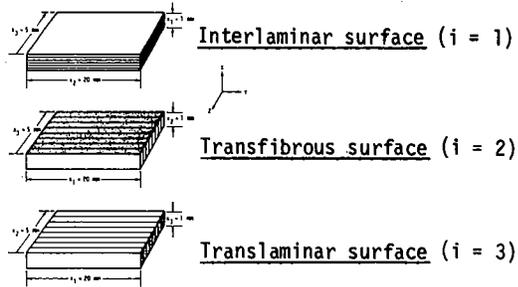
dW_{H_2O}/dt (UGM/MIN. CM^2)

Time (min)

Method:

1. Use moisture evolution analyzer (Du Pont Model 902H)

2. Analyze digital display of total water release for moisture content.

3. Analyze recorder output of moisture effusion rate for depth profile of moisture concentration.

4. Provide special specimen cell designs to isolate small volumes or surfaces on large specimens.

New Results:

1. Can measure and analyze directional diffusion coefficients.

2. Can map local microstructure degradation and predict strength changes in large composite structures.

3. Can measure depth profile of moisture concentration for internal stress analysis.

Figure 1. Measurement methodology

Interlaminar surface (i = 1)

Transfibrous surface (i = 2)

Translaminar surface (i = 3)

$t^{\frac{1}{2}}(SEC)^{\frac{1}{2}}$

ϕ_A

ϕ_D

$T(^\circ C)$

$\ln D_1 \text{ or } \ln D_3 \ (cm^2/S)$

$1000/T \ (^\circ K^{-1})$

Method:

1. Prepare test specimens in three principal axes of composite (i = 1, 2, 3).

2. Analyze cyclic diffusion of pure matrix.

3. Analyze cyclic diffusion along composite principal axes i = 1, 2, 3.

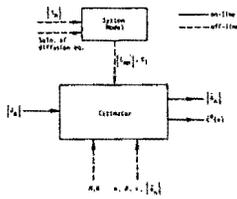4. Temperature dependence of diffusional coefficients D_1, D_2, D_3.

New Results:

1. Can isolate principal axis diffusion coefficients D_1, D_2, D_3 for both absorption (A) and desorption (D).

2. Initial moisture absorption is non-Fickian and relates to microstructure or internal stress relaxation.

3. Initial cycles of moisture absorption and desorption produce 3 to 4 fold increased absorption coefficients $(Di)_A$.

4. Comparison of experimental and theoretical diffusion coefficients shows simple laminate theory does not describe important diffusional properties.
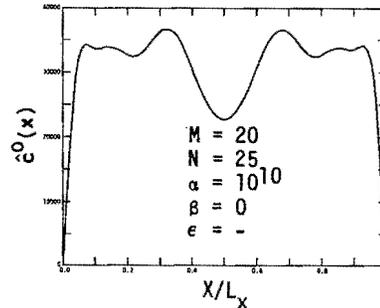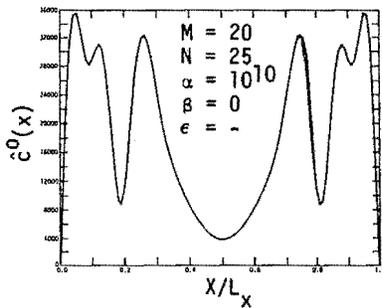
Figure 2. Directional diffusion coefficients

M = number of measurements
N = number of estimations
c_1 = concentration of water in the composite
    corresponding to the chemical potential μ_1
α = a priori bias against large amplitude $c^0(\hat{x})$
β = a priori smoothness which is applied to c^0_x
    in the range $\epsilon\pi$, $(1-\epsilon)\pi$
ϵ = numeric range factor $0 \leqslant \epsilon \leqslant 0.5$
$\{\bar{a}_n\}$ = observationally conditioned average for a_n

m	t_m(min)	$\tilde{J}_m$(μgm min^{-1})
1	1.5	80.6
2	2.2	62.6
3	3.0	49.7
4	4.5	37.4
5	5.5	32.7
6	6.4	30.3
7	7.0	27.6
8	9.2	23.1
9	11.2	20.3
10	13.2	18.2
11	16.0	16.0
12	17.7	15.0
13	19.5	14.0
14	21.2	13.1
15	25.5	11.8
16	29.3	10.6
17	35.7	9.40
18	40.7	8.52
19	44.3	8.18
20	50.5	7.20

M = 20
N = 25
$\alpha = 10^{10}$
$\beta = 0$
$\epsilon = -$

M = 20
N = 25
$\alpha = 10^{10}$
$\beta = 0$
$\epsilon = -$

Method:

1. Measure moisture effusion rate versus time.

2. Develop numeric estimation theory for calculation of moisture concentration versus depth.

3. Graph estimated concentration profile based on experimental data.

4. Graph estimated concentration profile based on synthetic smoothed data.

New Results:

1. Calculated moisture concentration agrees with independent experiments.

2. Concentration profile based on experimental data indicates internal structure.

3. Proof of concept for moisture profilometry is demonstrated.

Figure 3. Moisture profilometry
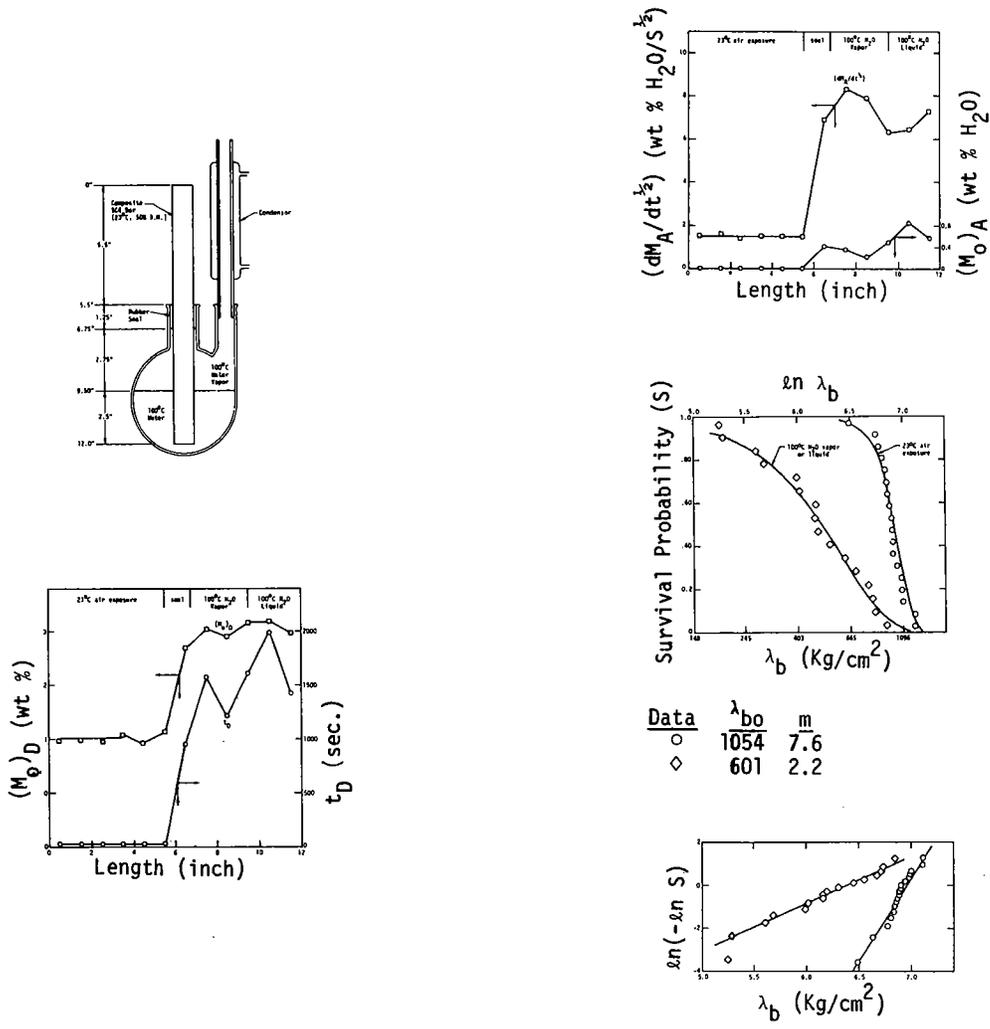
Method:

1. Apply variable moisture exposure along the length L of composite bar then subject to uniform thermal cycling.

2. Map the initial absorbed moisture $(M_o)_D$ and characteristic absorption time t_D versus length.

3. Map the initial moisture of desorption $(M_o)_D$ and characteristic absorption time t_D versus length.

4. Define variable moisture aging effects upon microstructure and shear bond strength.

New Results:

1. Moisture **absorption** kinetics highly sensitive to microstructure degradation.

2. Moisture **desorption** kinetics highly sensitive to microstructure degradation.

3. Mapping of microstructure and strength degradation demonstrated using moisture diffusion analysis.

4. MDA is a new tool for service inspection of composite structures.

Figure 4. Microstructure degradation