NASA Contractor Report 3387

Experimental Determination of the Effects of Moisture on Composite-to-Composite Adhesive Joints

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Experimental Determination of the Effects of Moisture on Composite-to-Composite Adhesive Joints

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1. INTRODUCTION

The use of adhesive bonding in components of aircraft structures offers the possibility of 15 % weight saving while maintaining mechanical strength as well as a 20 % cost reduction in fabrication and maintenance than their riveted counterparts. However, the long term performance of these adhesive bonded structures (adhesive and fiber-reinforced-polymer-matrix composite) depends on the stability of these materials in the service environment. Experimental studies have shown that these materials absorb moisture during exposure to humid environments and that the absorbed moisture causes degradation of their mechanical properties. In fact, the effect of temperature and humidity are considered to be the primary environmental variables which influence the structural behavior of epoxy adhesives and composites. Therefore a thorough knowledge of the rate and mechanisms of transport of water in the adhesives and reinforced composites is needed as a basis for understanding the mechanism of degradation of properties and as a basis for developing improved materials and joint design.

Previous studies of water transport in polymers and composites have been based on data obtained from measurements of the rate of absorption of water to saturation under isothermal conditions and the application of analytical diffusion models to attempt to explain these data. Basically, these are bulk measurements. The diffusion process can be complicated, especially in the case of composites and joints, and the analysis of the limited experimental data available can be further obscured by requiring many assumptions (Refs. 1 and 2). To obtain the necessary experimental data for a more detailed and direct understanding of water transport mechanisms, a sensitive and reliable method is required to determine the local concentration of water as a function of depth of penetration, adhesive and joint design, relative humidity, and time and temperature of exposure.

Several experimental approaches have been under development to determine localized moisture content in graphite-reinforced composites. These approaches include chemical analysis of degradation products generated during laser irradiation (Ref. 3), correlation between bulk moisture content and dielectric constant (Ref. 4), and moisture desorption from thin microtomed slices of composite (Ref. 5). To date, the application of these methods to the investigation of steep moisture gradients or complex structures such as adhesive bonded composites has not been demonstrated.

Within the past two years we have developed a nondestructive experimental technique for quantitative analysis of localized moisture concentration in polymeric materials (Refs. 7 and 8). The approach is based on conditioning specimens in D_2O instead of H_2O and using nuclear reaction analysis to measure the resultant deuterium concentrations in the specimens.

In the program described in this report, the nuclear probe for deuterium (NPD) has been applied to the study of moisture sorption in adhesive bonded composite joints. The effect of the bulk and localized moisture content on the room temperature and elevated temperature mechanical properties is evaluated. For this evaluation, two epoxy adhesives, EA-9601 film (121°C curing) and FM-300 film (177°C curing), and AS/3501-5A graphite epoxy composite were chosen. Single lap joint specimens were fabricated and baseline mechanical properties of these joints, in a dry condition, were measured. Specimens were conditioned in D_2O at 49°C (120°F) and 77°C (170°F), and 70% and 90% relative humidity (RH) to three moisture levels.

Moisture profiles were evaluated through the composite and joint thickness of all specimens, along the length of the joint of each specimen, and in the vicinity of the composite/adhesive interface in the high stress region of the joint. Mechanical properties were measured at room temperature for all the D_2O conditioned specimens and at elevated temperatures for some of the specimens.

The authors wish to acknowledge Dr. James Whiteside for technical discussions throughout this program, Arnold Landon for specimen preparation, Fred Kuehne for maintaining the Van de Graaff accelerator, and Herb Baker, Joe Drauch and Joe Martines for technical support.

2. EXPERIMENTAL PROCEDURES

2.1 MATERIALS

Base laminates were six ply graphite/epoxy made from Hercules AS/3501-5A 30 cm wide tape. The two adhesives were Bloomingdale FM-300 and Dexter-Hysol EA-9601 supported films (Table 1).

TABLE 1 - MATERIALS USED TO FABRICATE SPECIMENS

Material Name	Composition	Vendor	Form
Magnamite	GR/EP (AS-1/ 3501-5A), Lot No. 1120, Roll No. 2	Hercules, Inc.	30 cm wide tape prepreg
FM-300	Modified epoxy, Batch No. B-87, Roll No. B-580	Blooming-dale	Adhesive film on carrier
EA-9601	Modified epoxy, Lot No. 203, Roll No. 96	Dexter/ Hysol	Adhesive film on carrier

2.2 SPECIMEN DESIGN

2.2.1 Overlap Shear Specimens - To ensure that the base graphite/epoxy laminate was strong enough to carry shear loads, a six ply $(0,45,135,135,45,0)_T$ layup was selected. Doublers were used to introduce the shear load in the plane of the bonded joint. The base graphite/epoxy laminate was used for doublers since it was of the correct thickness. The 0-degree axes of the base laminates and doubler laminates were parallel to the long dimension of the specimen. The lap joint adhesive was selected because it also was of the correct thickness and required only one bonding cycle. A sketch of the specimens is given in Fig. 1a.

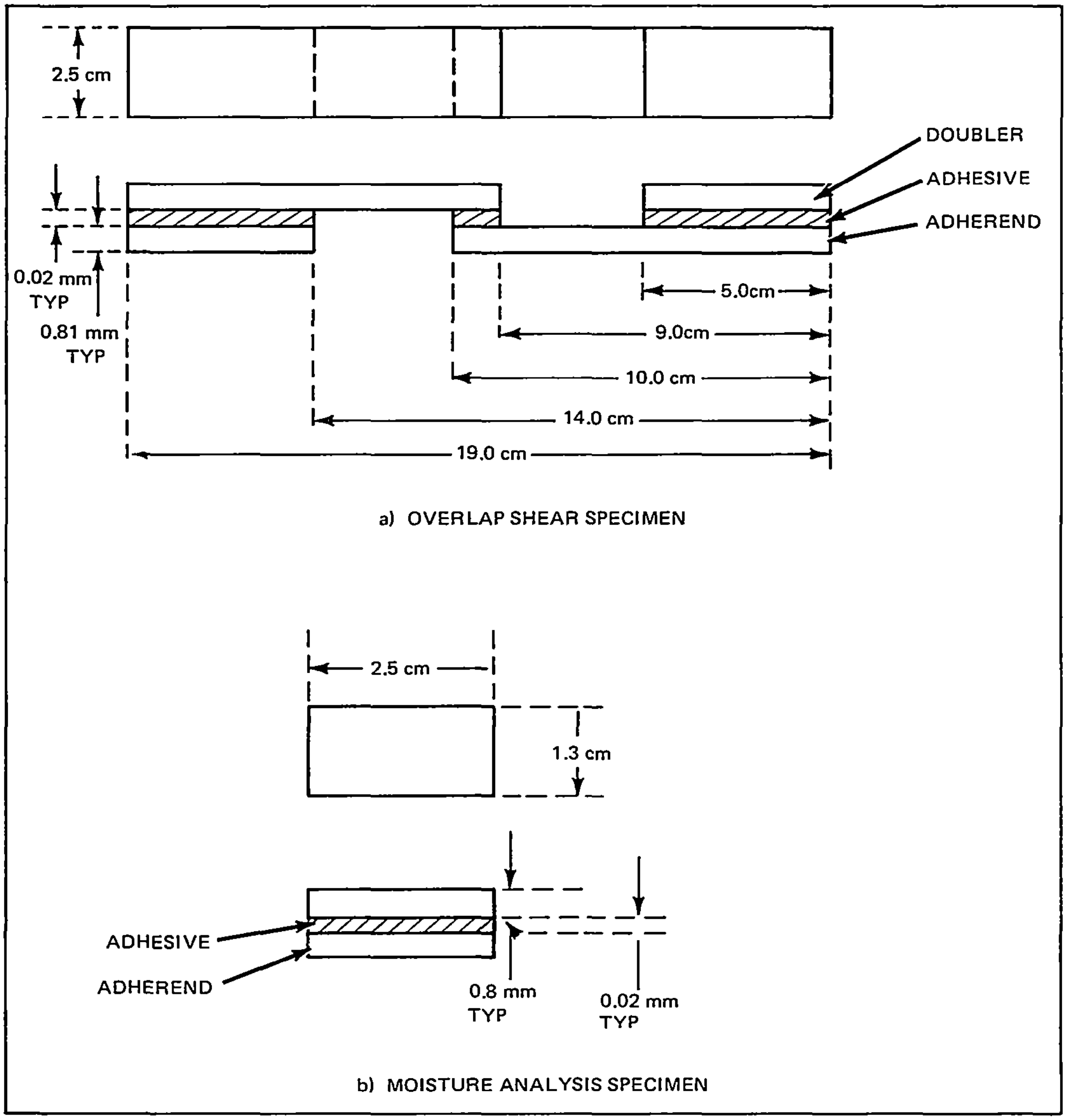


Fig. 1 Typical Specimen Geometry

2.2.2 Moisture Analysis Specimens - These specimens were 1.3 x 2.5 cm bonded sandwich, as shown in Fig. 1b. The composite adherends were 6 ply as described in section 2.2.1.

2.2.3 Diffusion Measurement Specimens - These were 2.5 x 5.0 cm x 0.81 mm specimens of six-ply AS/3501-5A laminate cut from larger panels as required.

2.2.4 Pure Adhesive Specimens - These were 25 x 25 x 0.25 mm specimens of FM-300 and EA-9601.

2.3 SPECIMEN FABRICATION

2.3.1 Layup of Base Panels - Base panels, 6 ply x 46 x 79 cm were laid-up per GM3013 specification. This procedure is described in the appendix.

2.3.2 Autoclave Cure and Post-Cure Cycles - All panels were placed in a convection autoclave and cured as per the Grumman recommended cure cycle (GR-100B). This procedure is described in the appendix. The fully cured panels had a fiber volume fraction, V_f, of 0.62 and were 0.81 mm thick.

2.3.3 Bonding Operations - The 2.5 x 19 cm overlap shear specimens were gang-bonded with their doublers in place; this configuration is shown in Fig. 1, except that the panels were 69 cm wide. Specimens were bonded per GSS20350 under a vacuum bag in an autoclave. This procedure is described in the appendix.

2.3.4 Preparation of Moisture Analysis Specimens - At least one face and two adjacent edges of each specimen were finely polished. The outer face was polished to facilitate location of the ^{3}He beam on the edge of the specimen during profiling, whereas the polished edges enabled us to obtain a precise measurement of the thickness of the composite and adhesive layers within the individual specimens. Representative photomicrographs of the cross-section of FM-300 and EA-9601 bonded specimens are illustrated in Fig. 2.

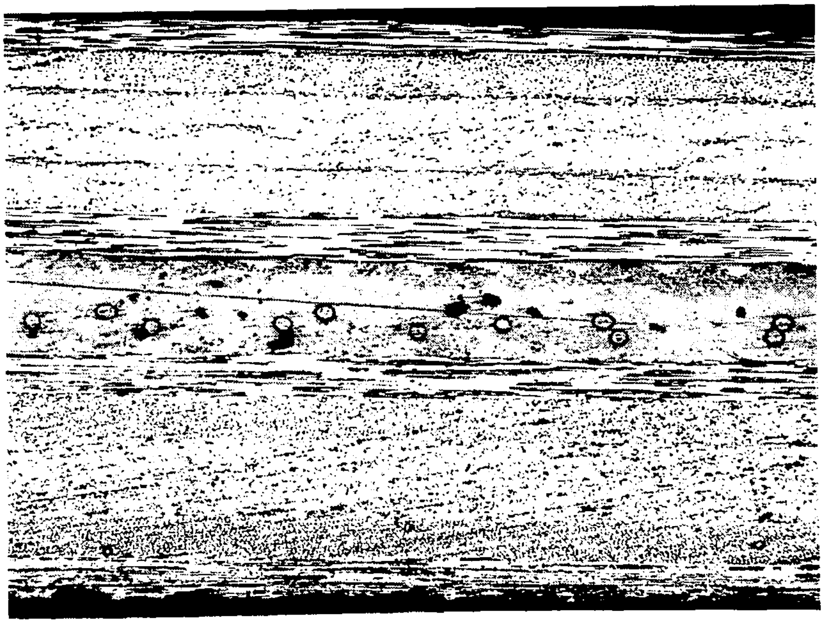
2.4 MOISTURE CONDITIONING

Saturated salt solutions were used to create and maintain constant relative humidity for specimen conditioning. Sodium chloride and potassium sulfate were selected because their saturated aqueous solutions produce the desired relative humidity (approximately 75% and 95%) and, more importantly, the relative humidity is essentially insensitive to temperature. Over the 10 -100°C range, the H_2O relative humidity change for NaCl and K_2SO_4 solutions is 76.6 - 73.7% and 98.5 - 93.0%, respectively (Ref. 8).

The vapor pressure of D_2O has been reported to be slightly lower than that of H_2O over the 49 - 77°C temperature range (Ref. 9). Measurements of the vapor pressure of saturated solution of NaCl and K_2SO_4 in D_2O indicate a relative humidity of 70% and 90%, respectively. These were the humidity levels used throughout this investigation.

All specimen types (6-ply graphite/epoxy coupons, pure adhesive, bonded moisture analysis specimens and single overlap shear specimens) were dried to constant weight at 77°C. Subsequently they were exposed to combinations of controlled temperature and relative humidity. This was accomplished by placing the saturated solutions in the bottom of large sealable glass chambers and by mounting specimens in exposure racks which held them above the solution such that they were only in contact with the vapor. The chambers were placed in large ovens maintained at either 49°C or 77°C. The temperature of the chambers were monitored continually and the observed temperature variation was within ±2°C. Specimens were removed after specific time intervals, depending on their intended use and the desired bulk moisture content.

a) FM-300



b) EA-9601

Fig. 2 Cross-Section of Bonded Graphite Epoxy Laminates

2.5 MOISTURE PROFILING

Each specimen was sectioned on a diamond wheel at liquid nitrogen temperature and the exposed edge was then polished at room temperature to remove any adhesive that may have been smeared over the composite during the cutting. The specimens were then mounted into the sample holder of the reaction chamber which is maintained at a vacuum of 10^{-6} torr. The sample is advanced through the beam by a micrometer drive that has a positioning accuracy of 10 µm. The measurement of deuterium concentration in the near surface region of materials is accomplished by using the $D(^3He,p)^4He$ nuclear reaction. A finely collimated beam of ^3He ions from a Van de Graaff accelerator is incident on the specimen. In the interaction of the ^3He beam with the deuterium in the sample matrix, high-energy protons are emitted, and these are detected by a silicon surface barrier detector located at an angle of 165° to the incoming beam. The emerging protons form a distinct, isolated group in the charged particle energy spectrum. The proton yield is directly proportional to the deuterium concentration within the reaction volume. Absolute deuterium concentrations can be determined by comparing the proton yield from the sample under study to the yield from a reference sample (deuterated phthalic acid and/or TiD_2) after correcting for the different stopping powers of the samples.

For an incident ^3He energy of 1.2 MeV, the probing depth is about 2.5 µm. A beam current of 0.5 na is used to reduce local heating of the specimen to a level at which there is no depletion of moisture during the measurement. Each measurement was segmented by the on-line computer system to demonstrate the stability of the D_2O content as a function of time during ^3He ion bombardment. For this experimental configuration the lower level of detectability for D_2O is 0.01 wt% in an epoxy resin.

After the profiling is complete, each specimen is photomicrographed to determine the presence of any irregularities in the vicinity of the scan region and to precisely locate the profiling positions.

2.6 MOISTURE DIFFUSION

Specimens of 6-ply graphite epoxy laminate and pure adhesives dried to constant weight at 77°C were exposed in groups of four specimens to each temperature/relative humidity condition. Specimens were periodically removed, cooled to room temperature and weighed to the nearest 0.1 mg. The rate of change of the bulk moisture content, which was obtained from the weight gain, was used to compute the moisture diffusivity.

2.7 MECHANICAL PROPERTIES

An Instron Testing Machine equipped with a Temperature Cabinet was used to measure the shear stress at room temperature and at 82°C. A minimum of three specimens was tested for each combination of temperature and relative humidity. Elevated temperature measurements were conducted after a soak period at temperature for 4 minutes. Calculations indicate that this soak period does not alter the specimen moisture content.

3. DISCUSSION OF RESULTS

3.1 MOISTURE DIFFUSIVITY

Moisture diffusivity and equilibrium moisture content in AS/3501-5A laminate and both adhesives were measured at all temperature/humidity combinations using conventional gravimetric methods. The results shown in Figs. 3 - 8 represent the average of four specimens. Composite specimens (25 x 50 x 0.8 mm) approach saturation after approximately 6 and 20 days at 77°C and 49°C, respectively (Figs. 3 and 4). No evidence of secondary absorption was observed up to 82 days, at which time the exposure was terminated (Ref. 10). Adhesive specimens (25 x 25 x 0.25 mm) also appear to exhibit typical diffusion behavior at 49°C (Figs. 5 and 6) but at 77°C there is evidence of an absorption maximum after short exposure times followed by a weight loss (Figs. 7 and 8). This effect is most pronounced for EA-9601 conditioned at 77°C/90% RH where the weight loss is rapid after 1 day. The weight loss is probably caused by the leaching out of low molecular weight species from the adhesive by the absorbed D_2O. We have observed similar weight loss from graphite epoxy immersed in boiling water. It has been proposed that these low molecular weight species may result from inhomogeneous mixing during cure and resultant entrapment in low crosslink density regions of the epoxy (Ref. 11).

The equilibrium moisture content, M_∞, was computed from the difference between the saturation level, M_s, and the intercept, M_i, obtained from the least square fit to the initial linear portion of the curves. The positive value for M_i is ascribed to the instantaneous adsorption of water on the specimen surface. For the composites, M_i was approximately 0.12-0.15% D_2O. The resultant values of M_∞ for AS/3501-5A are listed in Table 2. These are in agreement with the equilibrium H_2O contents which had been previously reported for AS/3501-5A and AS/3501-5 at similar temperatures and relative humidities (Refs. 1 and 2). The estimation of M_∞ for pure adhesives was more difficult. Since the specimens were thin and had textured surfaces they had a very large surface to volume ratio. This resulted in an appreciable amount of adsorbed water which was difficult to quantify precisely because of the rapid

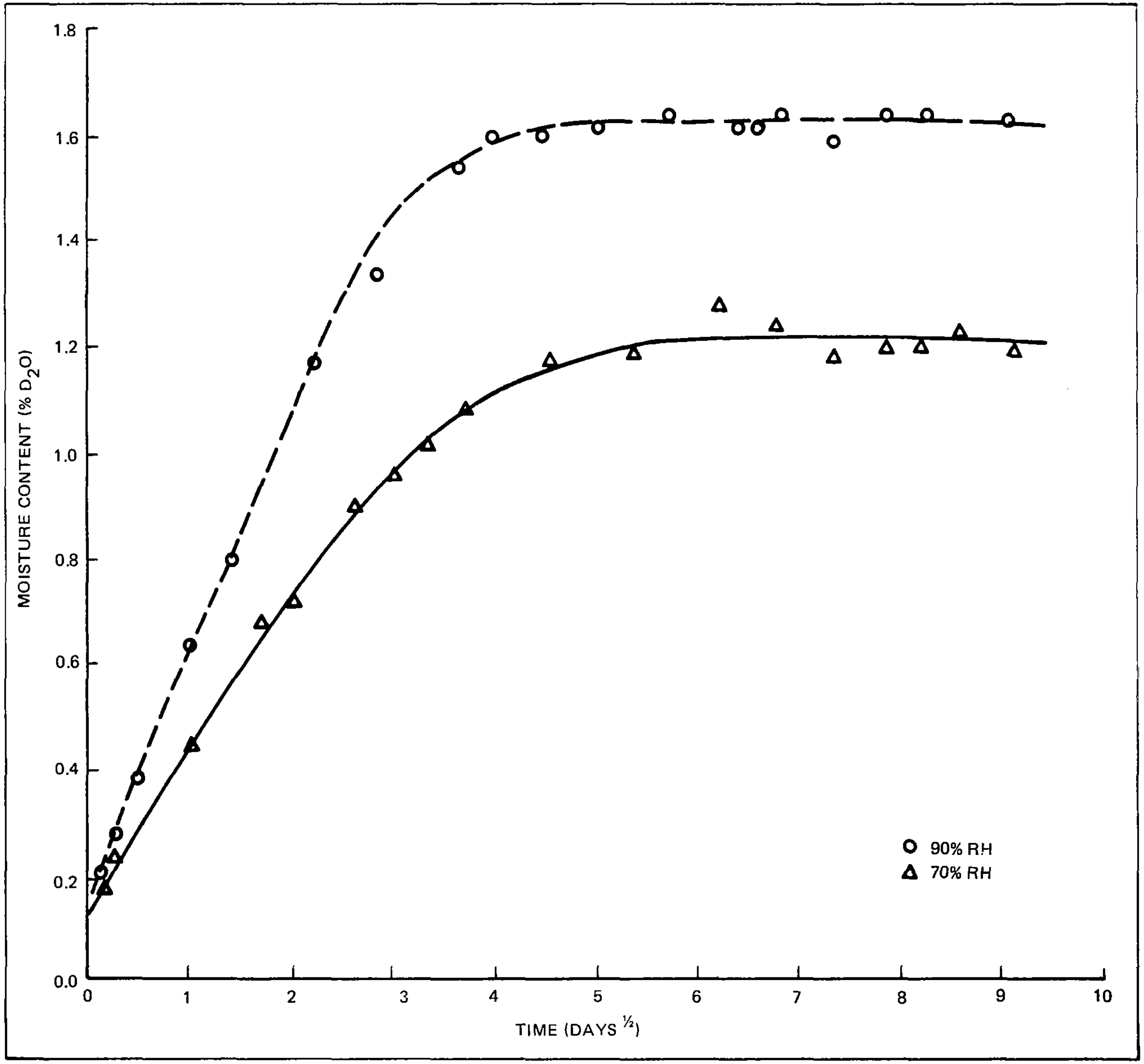


Fig. 3 Moisture Absorption by AS/3501-5A at 49°C

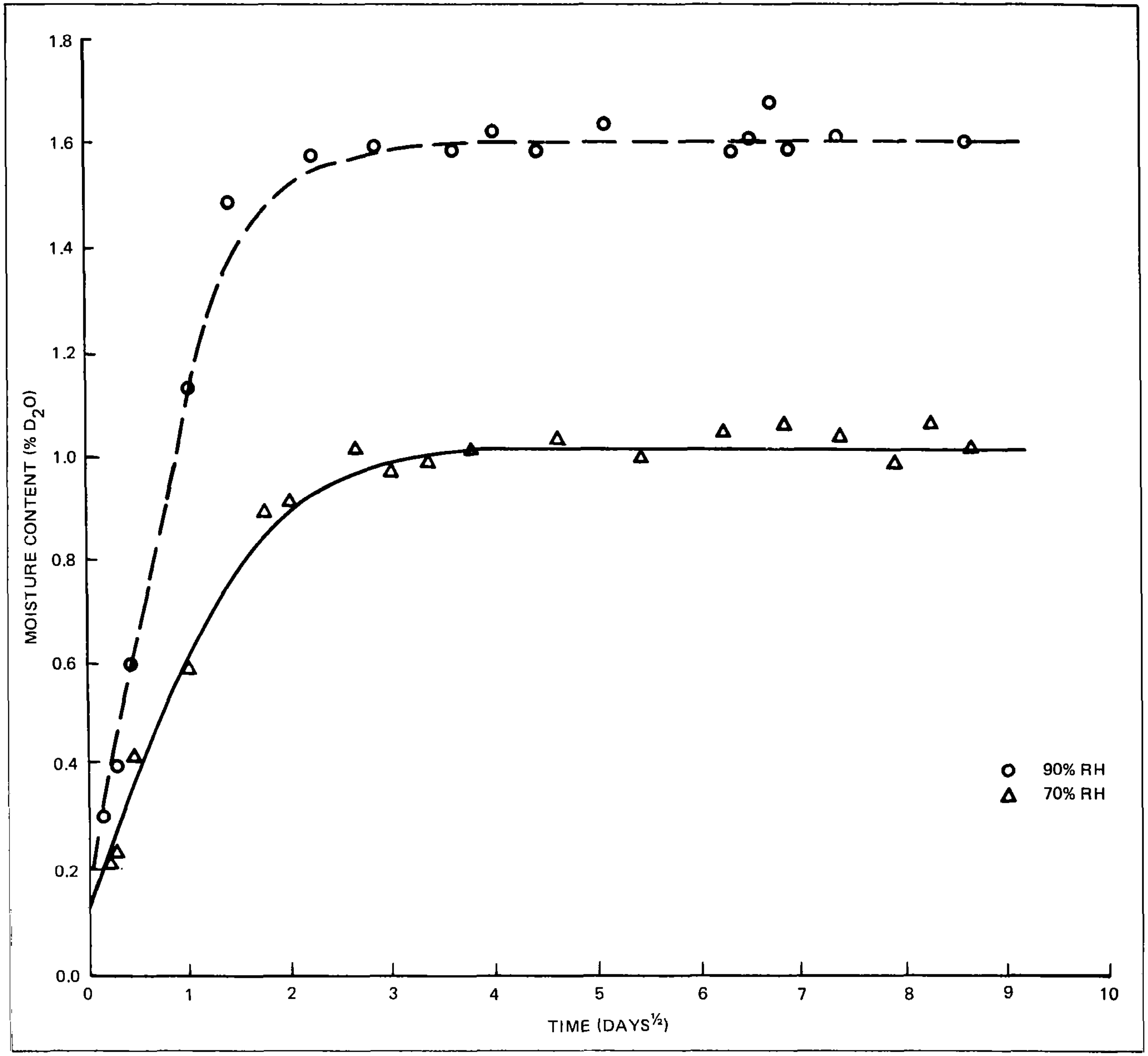


Fig. 4 Moisture Absorption by AS/3501-5A at 77°C

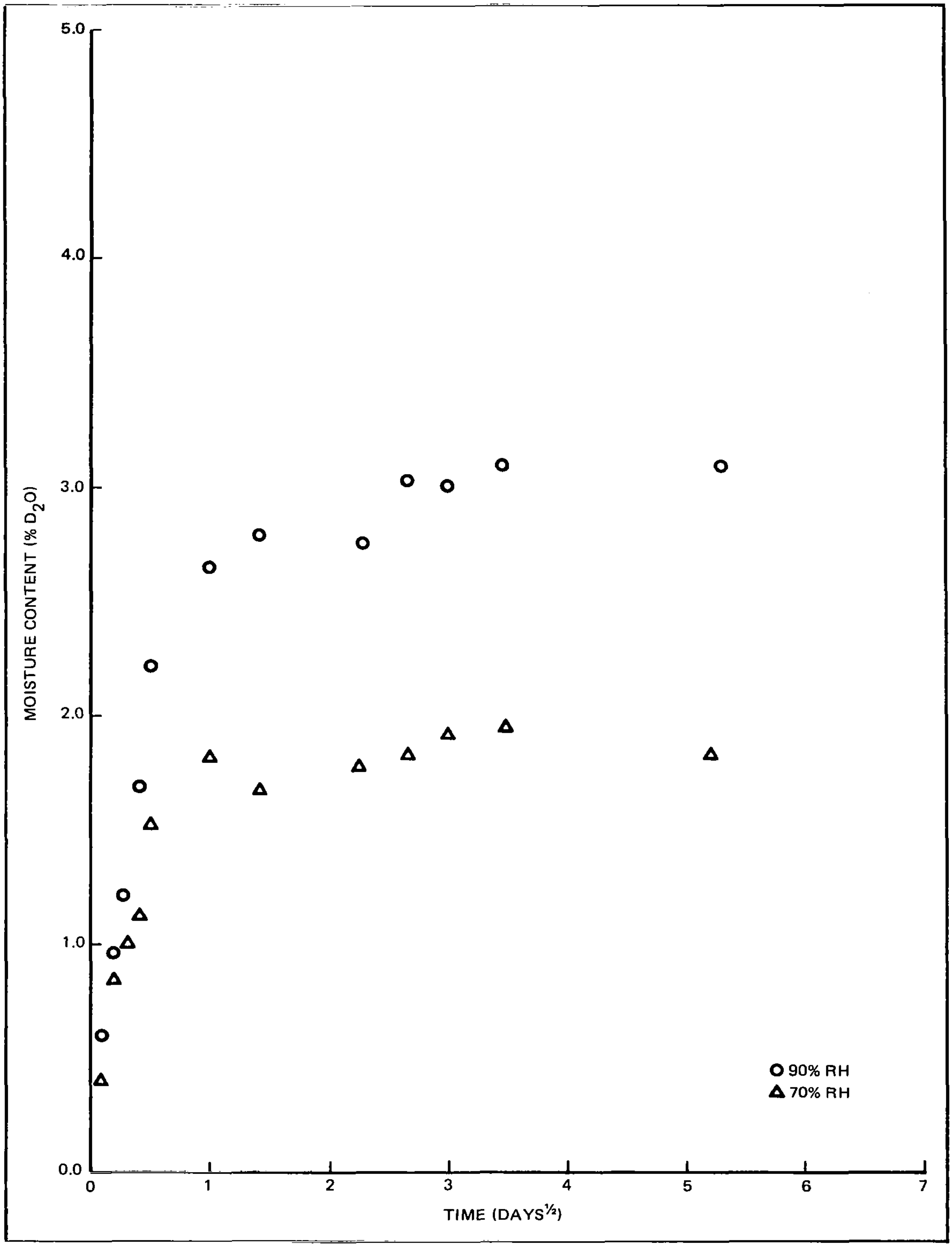


Fig. 5 Moisture Absorption by FM-300 Adhesive at 49°C

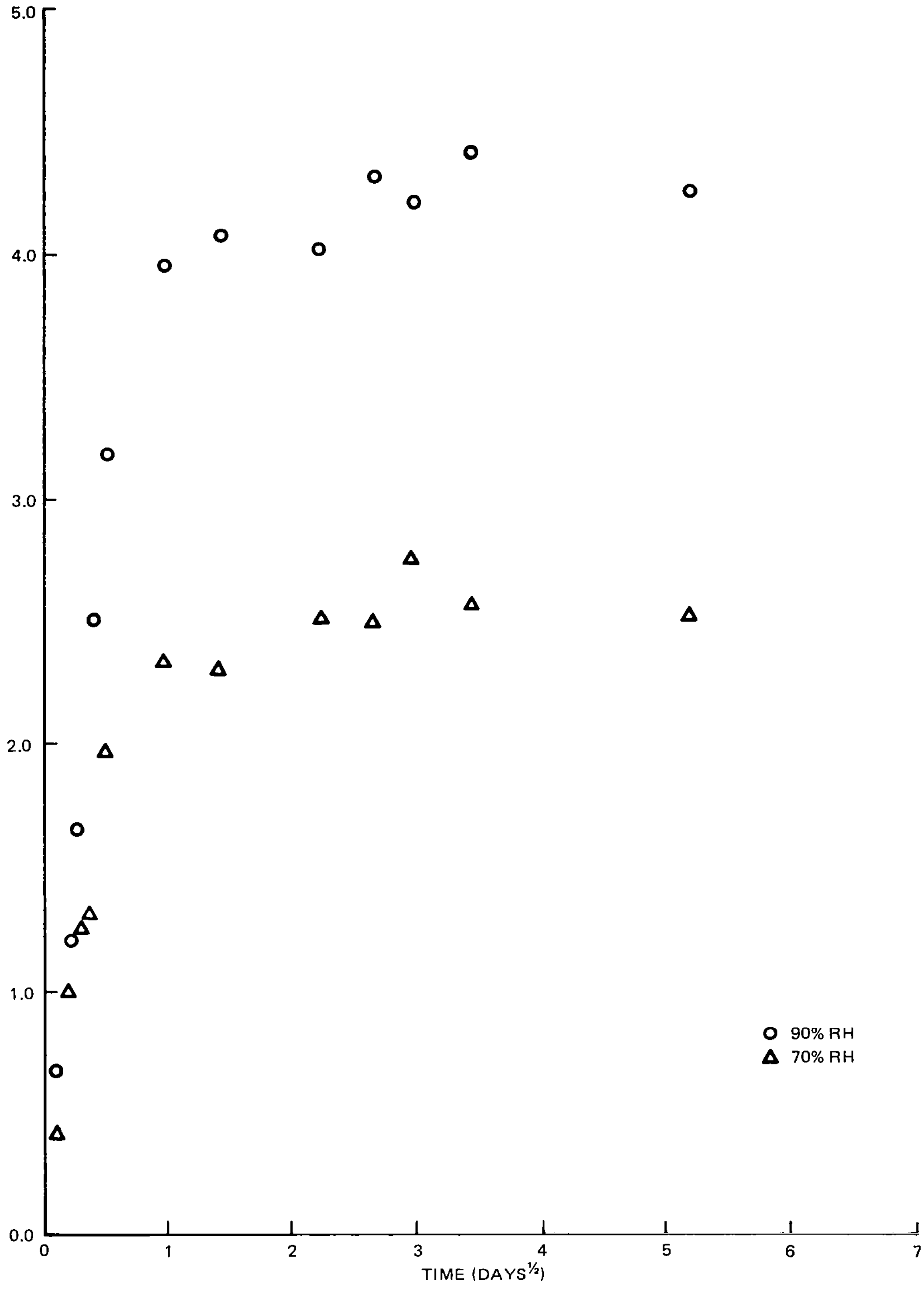


Fig. 6 Moisture Absorption by EA-9601 Adhesive at 49°C

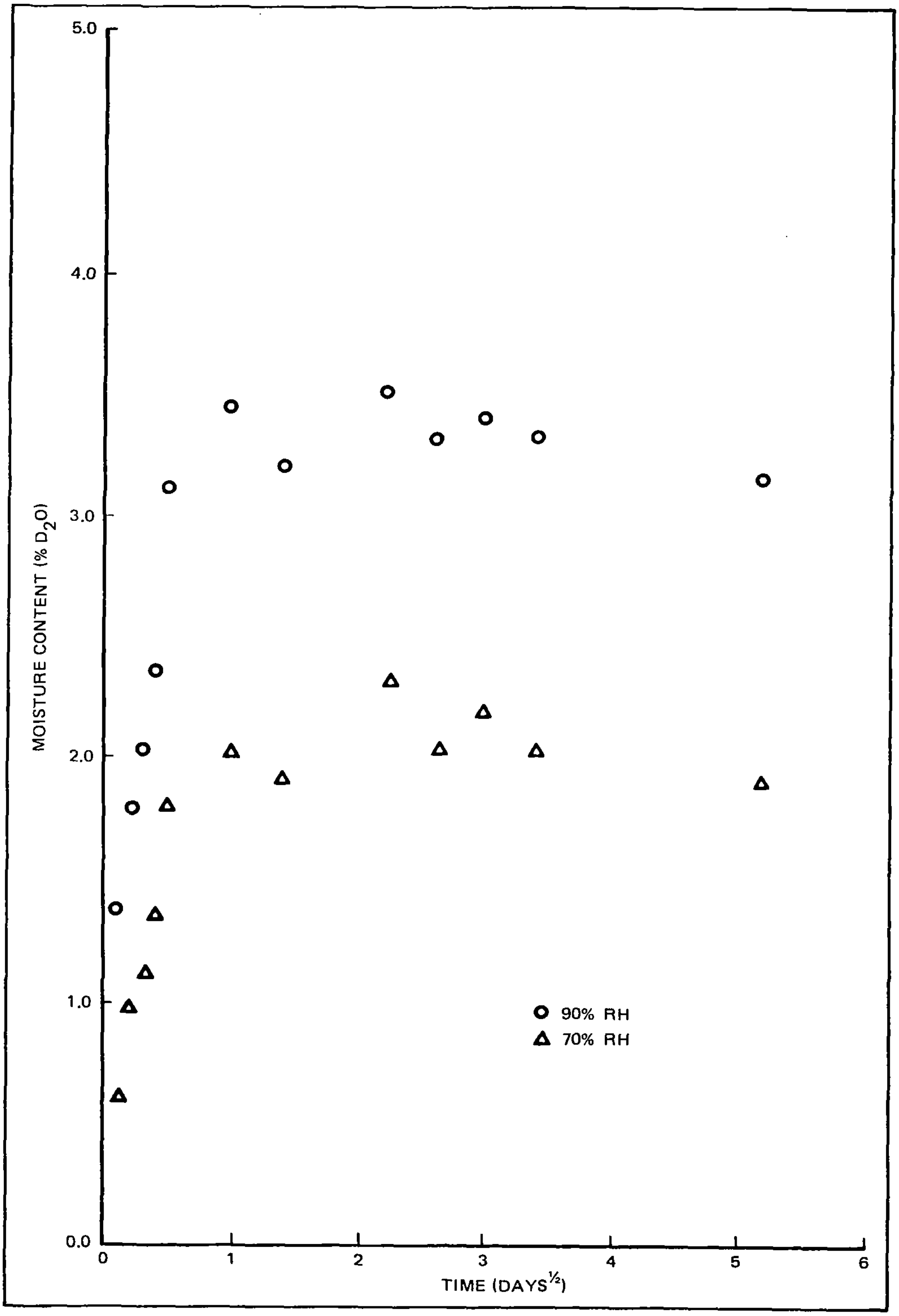


Fig. 7 Moisture Absorption by FM-300 Adhesive at 77°C

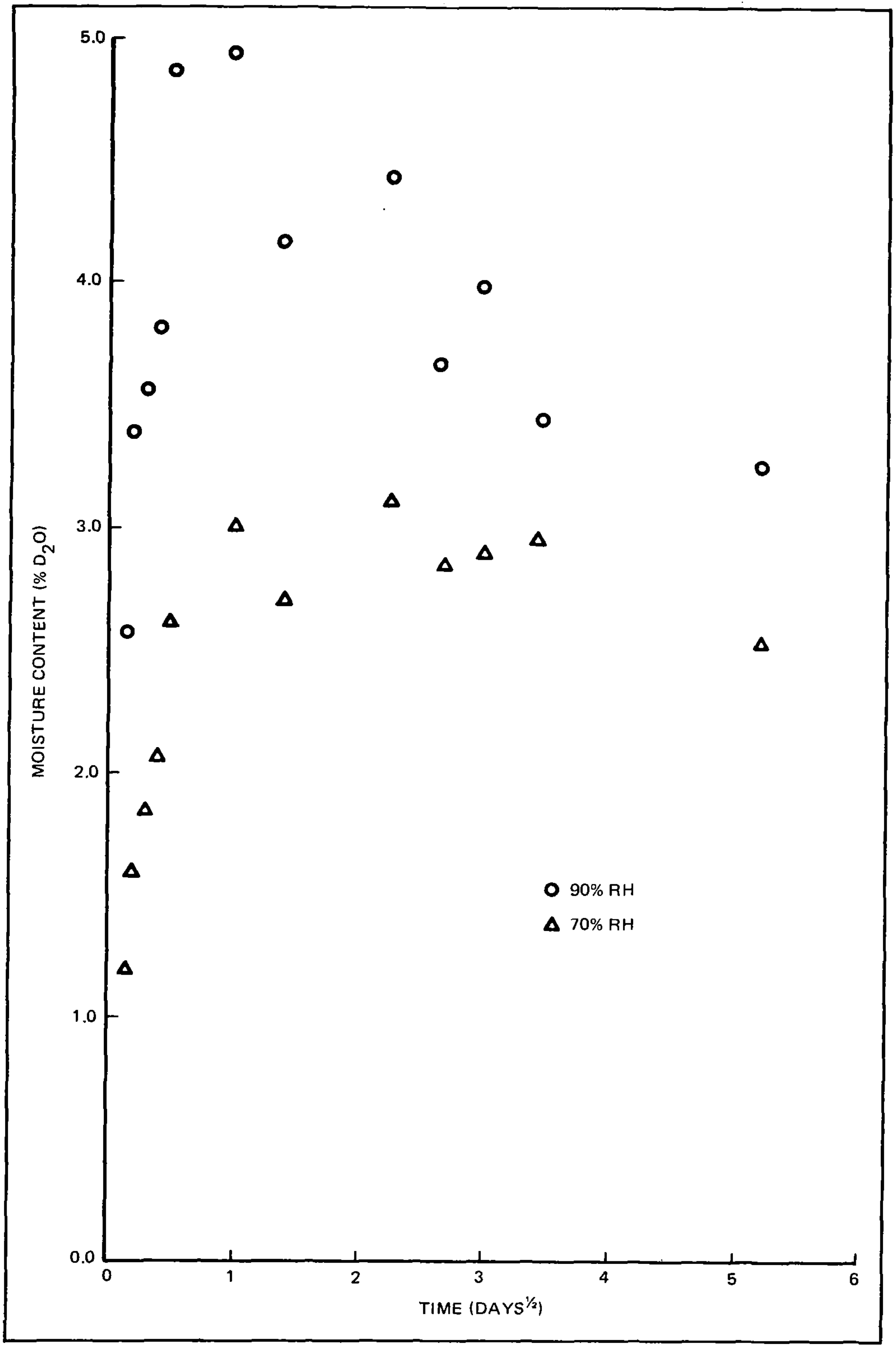


Fig. 8 Moisture Absorption by EA-9601 Adhesive at 77°C

weight gain due to moisture diffusion into the specimens. Furthermore the apparent saturation level M_s was difficult to evaluate accurately by this technique because of the small initial specimen weight (causing considerable scatter in the day-to-day measurements) and the competitive leaching process. However, within these limitations we have estimated M_∞ for both adhesives and the results are summarized in Table 2.

TABLE 2 - DIFFUSIVITY AND EQUILIBRIUM MOISTURE CONTENT OF COMPOSITE AND ADHESIVE

Material	T(°C)	RH(%)	D(mm²/s)	M (%)
AS/3501-5A	77	70	3.7×10^{-7}	0.87
		90	4.3×10^{-7}	1.45
	49	70	1.2×10^{-7}	1.07
		90	1.1×10^{-7}	1.48
FM-300	77	70	1.3×10^{-6}	2.06
		90	1.2×10^{-6}	2.78
	49	70	3.3×10^{-7}	1.67
		90	2.9×10^{-7}	2.99
EA-9601	77	70	8.9×10^{-7}	2.78
		90	8.9×10^{-7}	4.71
	49	70	2.2×10^{-7}	2.49
		90	2.2×10^{-7}	4.44

Moisture diffusivity can be deduced from the initial portion of the moisture absorption curves according to the following equation

$$D = \frac{\pi}{16} \left(\frac{F\ell}{t^{1/2}}\right)^2 \frac{1}{E}$$

where F = $(M_t - M_i)/(M_s - M_i)$
M_t = moisture content at time, t
M_i = moisture content instantaneously absorbed on surface
t = exposure time
ℓ = specimen thickness
E = edge correction factor

The method of Springer and Shen (Ref. 12) was used to compute the edge correction factor which was equal to 1.14 for the 6-ply laminate. No correction factor was applied to the adhesive data because this effect is considered to be negligible compared to the uncertainty associated with accurate measurement of M_∞ and M_i. The diffusivities listed in Table 2 were computed by this method with the exception of EA-9601 at 77°C. The latter was estimated from the Arrhenius equation using the measured diffusivity at 49°C assuming an activation energy of approximately 11 kcal/mole. The values of D_2O diffusivity are in agreement with those reported for H_2O in AS/3501-5A, i.e., 5.0×10^{-7} mm^2/s and 1.0×10^{-7} mm^2/s at 77°C and 44°C, respectively (Ref. 2).

3.2 COMPARISON BETWEEN BULK H_2O and D_2O ABSORPTION

The equivalence between the H_2O and D_2O diffusivity and equilibrium moisture content in graphite epoxy has been demonstrated previously (Ref 7). This equivalence was confirmed for bonded specimens during this investigation from the bulk moisture absorption at 77°C, 70% RH. Table 3 contains the bulk H_2O and D_2O contents for FM-300 and EA-9601 bonded specimens as determined from gravimetric analysis. The equivalent D_2O content for specimens conditioned in an H_2O atmosphere is computed from the D_2O/H_2O molecular weight ratio of 1.11 and is shown in parentheses in the table. Specimens were conditioned for a total of 165 days in H_2O atmosphere with no additional moisture absorption beyond that measured after 70 days. (Calculations indicate that these specimens should approach their equilibrium moisture level within 30 days at 77°C.) This equilibrium level is confirmed by the moisture profile data in Section 3.3.

The data in Table 3 indicate a greater spread in the moisture content for D_2O conditioned specimens than those conditioned in H_2O. These differences may be ascribed to variations in adhesive thickness (see Section 3.3). However, in spite of the spread in the data, which is typical for gravimetric measurements on small specimens, excellent agreement exists between the average D_2O and the corrected H_2O moisture content in both specimen types at all moisture levels.

TABLE 3 - COMPARISON BETWEEN BULK H_2O AND D_2O ABSORPTION IN BONDED SPECIMENS AT 77°C, 70% RH

Adhesive	Time (days)	H_2O (D_2O), %	D_2O, %
FM-300	6	0.80 ± 0.04 (0.89)	0.91 ± 0.14
	12	1.04 ± 0.03 (1.15)	1.17 ± 0.13
	70	1.31 ± 0.03 (1.46)	1.46 ± 0.10
EA-9601	6	0.91 ± 0.06 (1.01)	1.04 ± 0.16
	12	1.13 ± 0.06 (1.26)	1.35 ± 0.22
	70	1.34 ± 0.02 (1.49)	1.61 ± 0.05

3.3 MOISTURE PROFILING

The moisture profiling of specimens took place over a three month period in which more than 40 samples were analyzed. Each moisture conditioned specimen was sectioned at two points nearly equidistant from the ends. After polishing the exposed surfaces, one section was probed along the adhesive from edge-to-edge, and the second section was probed in the transverse direction from face-to-face. Figure 9 illustrates the sections indicating the direction and approximate positioning of the two scans. The adhesive scans were made using a beam spot size of 125 x 125 μm which is approximately half the bond thickness. In order to maintain high resolution in the direction of the moisture gradient for the transverse scans, the beam size used was 25 x 200 μm.

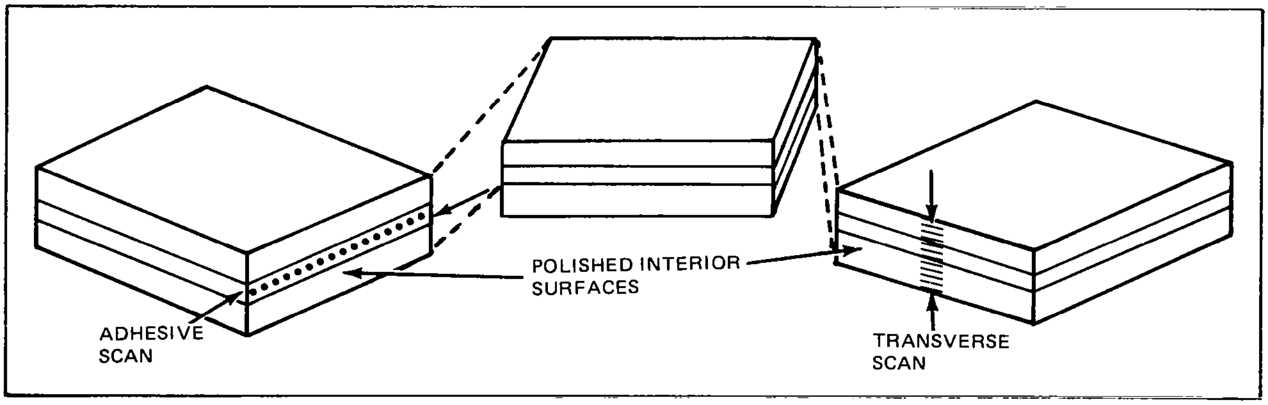


Fig. 9 View of Specimens After Sectioning the Moisture Conditioned Sample and Location of the Probing Beam for the Moisture Profiling (not drawn to scale)

This 25 μm beam width is approximately 20% of the ply thickness. The number of measurement points varied for each scan since the scanning increments were selected so that the general shape of the profile could be determined.

In Fig. 10 through 21, we show the typical moisture profile data obtained using the nuclear probe for four different conditions of sample exposure which are representative of the entire set of conditions compiled in Table 4. For each condition and duration of exposure there is an adhesive scan and a corresponding transverse scan. Each data point represents a single measurement and the error associated with the data reflects only the counting statistics of the measurement. However, the data point shown by the open circle, corresponding to the surface of each specimen, is the mean value of the moisture content measured at several points along the saturated outer surface of a few specimens. This point indicates the level of saturation for the adhesive in the case of an adhesive scan and for the composite in the case of a transverse scan. A curve (solid line) is drawn through the data not as a fit but as an indication of the trend of the moisture profile and the dashed line portion of the curve is an extrapolation tending toward the saturated moisture level (open circles). In each of the transverse scans the spatial extent of the composite and the adhesive as determined from the photomicrograph, is indicated in the figure.

Precise correlation of the measured moisture content relative to the distance from the composite surface or edge of the adhesive was accomplished using photomicrographs of the "as-probed" specimens. Typical photomicrographs shown in Fig. 22 and 23 contain clear beam spots along the length of the adhesive (adhesive scan) and a dark band across the specimen (transverse scan). The transverse scan beam spots are not as clear as those of the adhesive scan because of the narrow width of the collimated beam and the closeness of the measured points. The beam spot darkening can be attributed to a combination of radiation damage of the epoxy and to the formation of color centers resulting from entrapment of ^{3}He within the near surface region of the specimen.

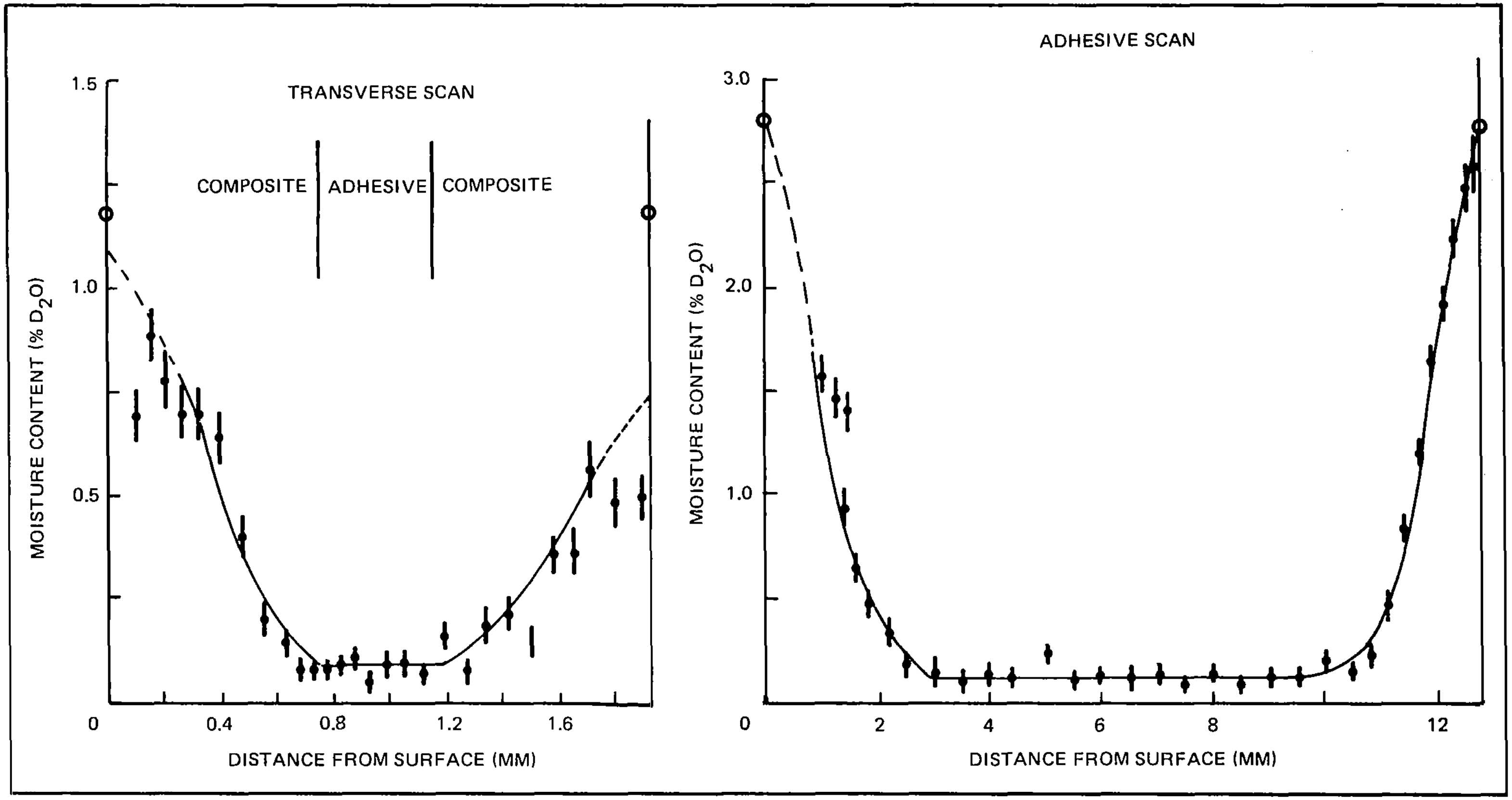


Fig. 10 Moisture Profiles for FM-300 Bonded Specimen Conditioned at 77°C, 70% RH for 6 Days

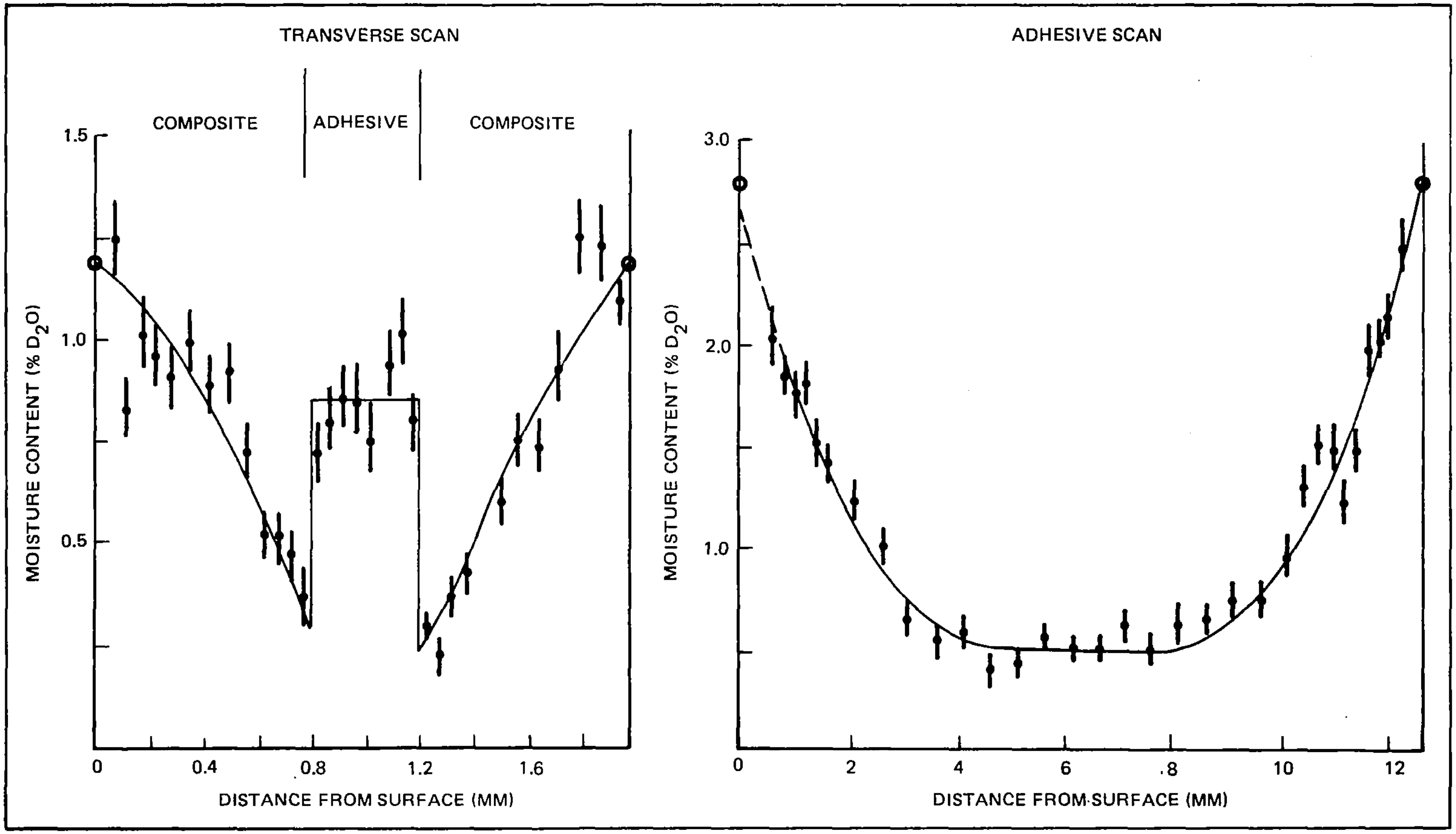


Fig. 11 Moisture Profiles for FM-300 Bonded Specimen Conditioned at 77°C, 70% RH for 12 Days

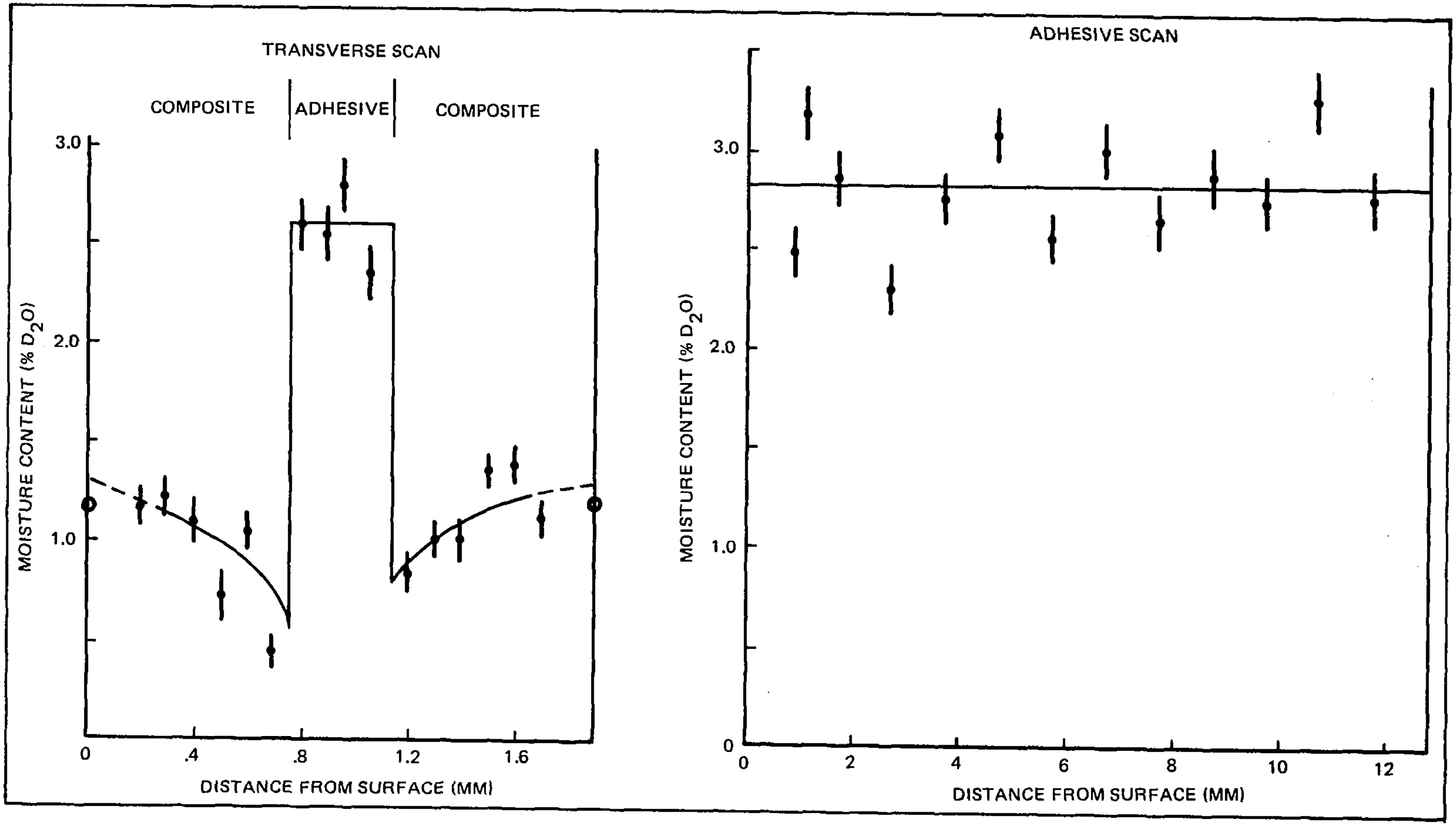


Fig. 12 Moisture Profiles for FM-300 Bonded Specimen Conditioned at 77°C, 70% RH for 70 Days

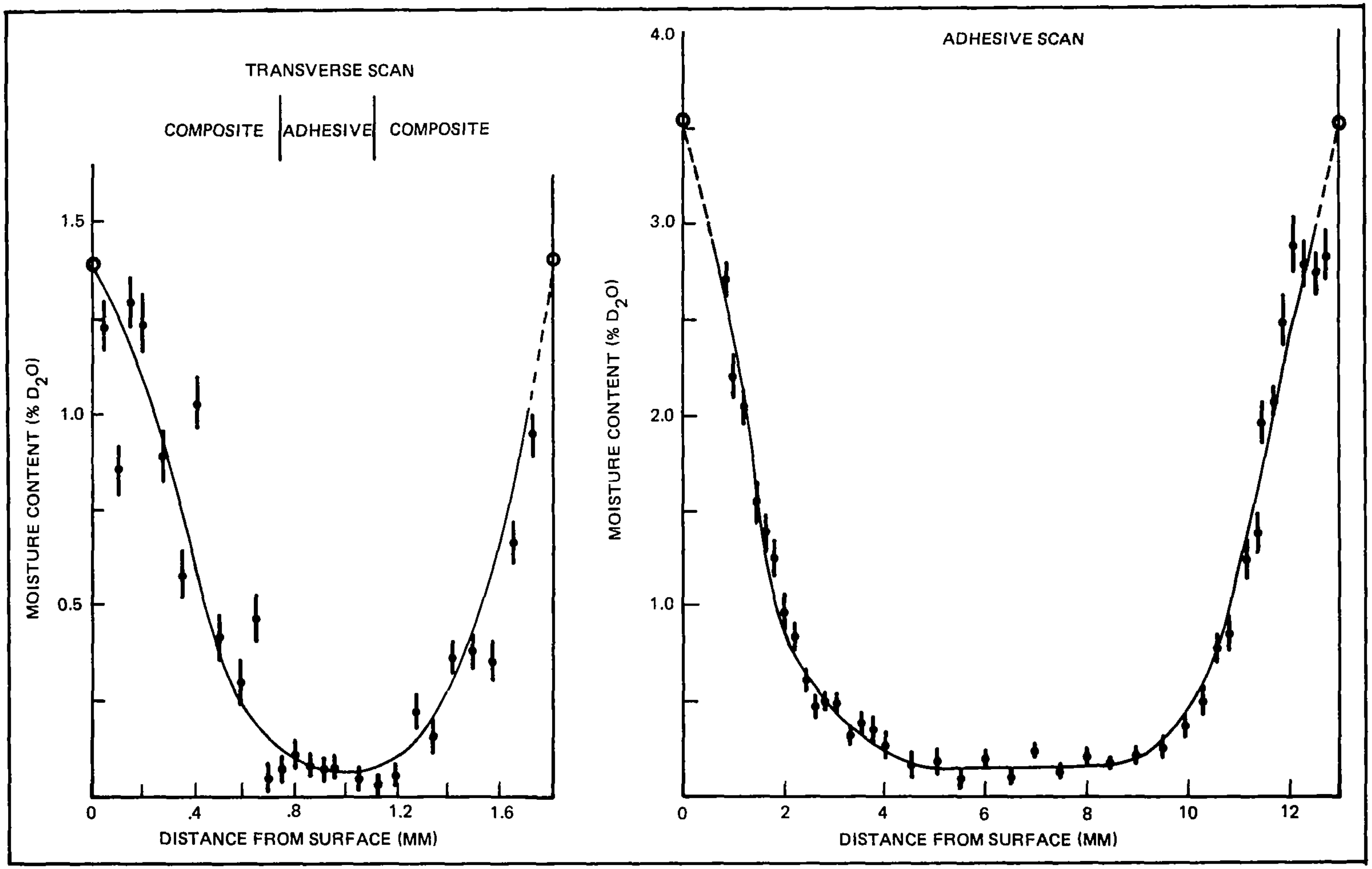


Fig. 13 Moisture Profiles for FM-300 Bonded Specimen Conditioned at 77° C, 90% RH for 6 Days

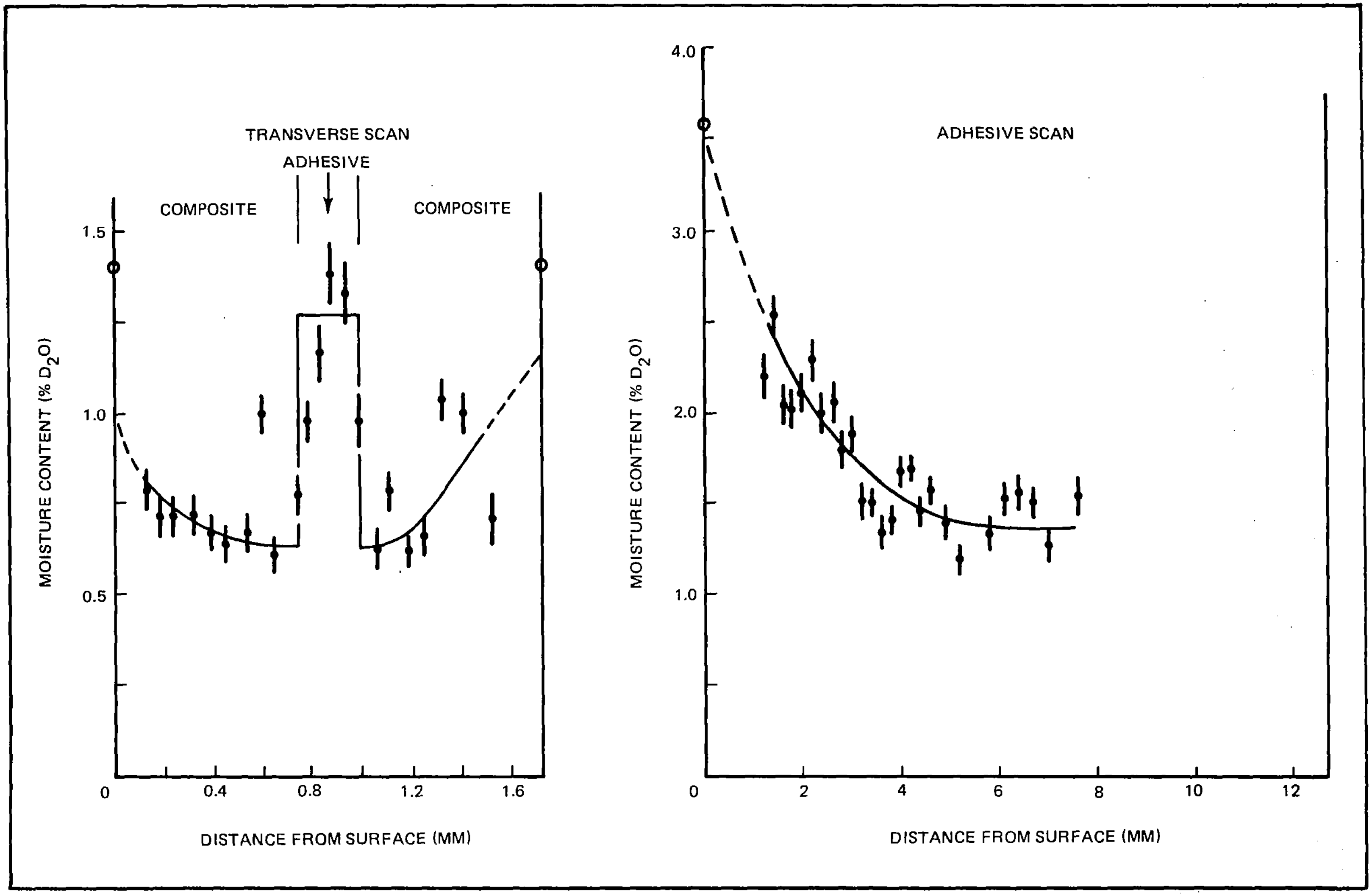


Fig. 14 Moisture Profiles for FM-300 Bonded Specimen Conditioned at 77° C, 90% RH for 12 Days

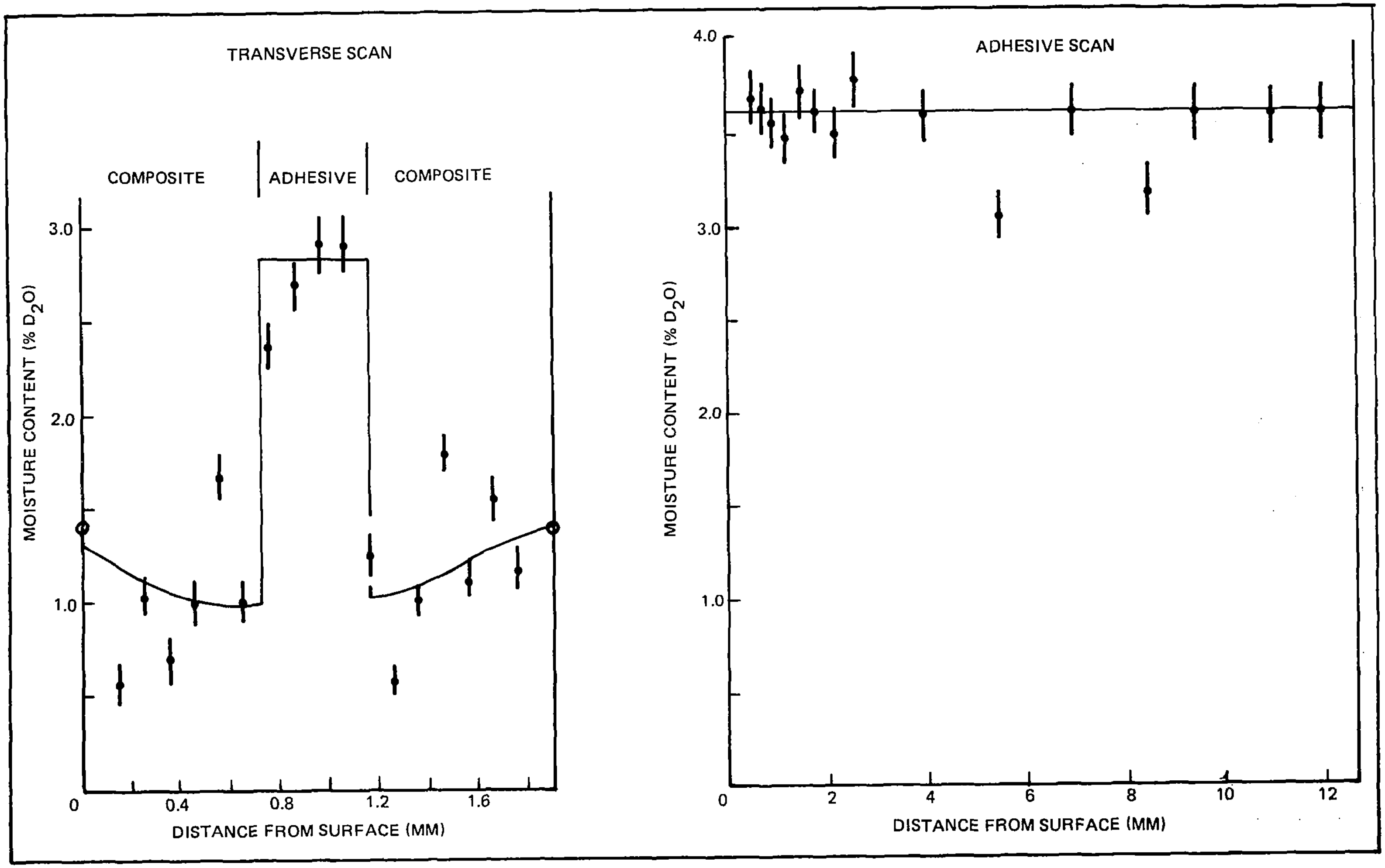


Fig. 15 Moisture Profiles for FM-300 Bonded Specimen Conditioned at 77° C, 90% RH for 70 Days

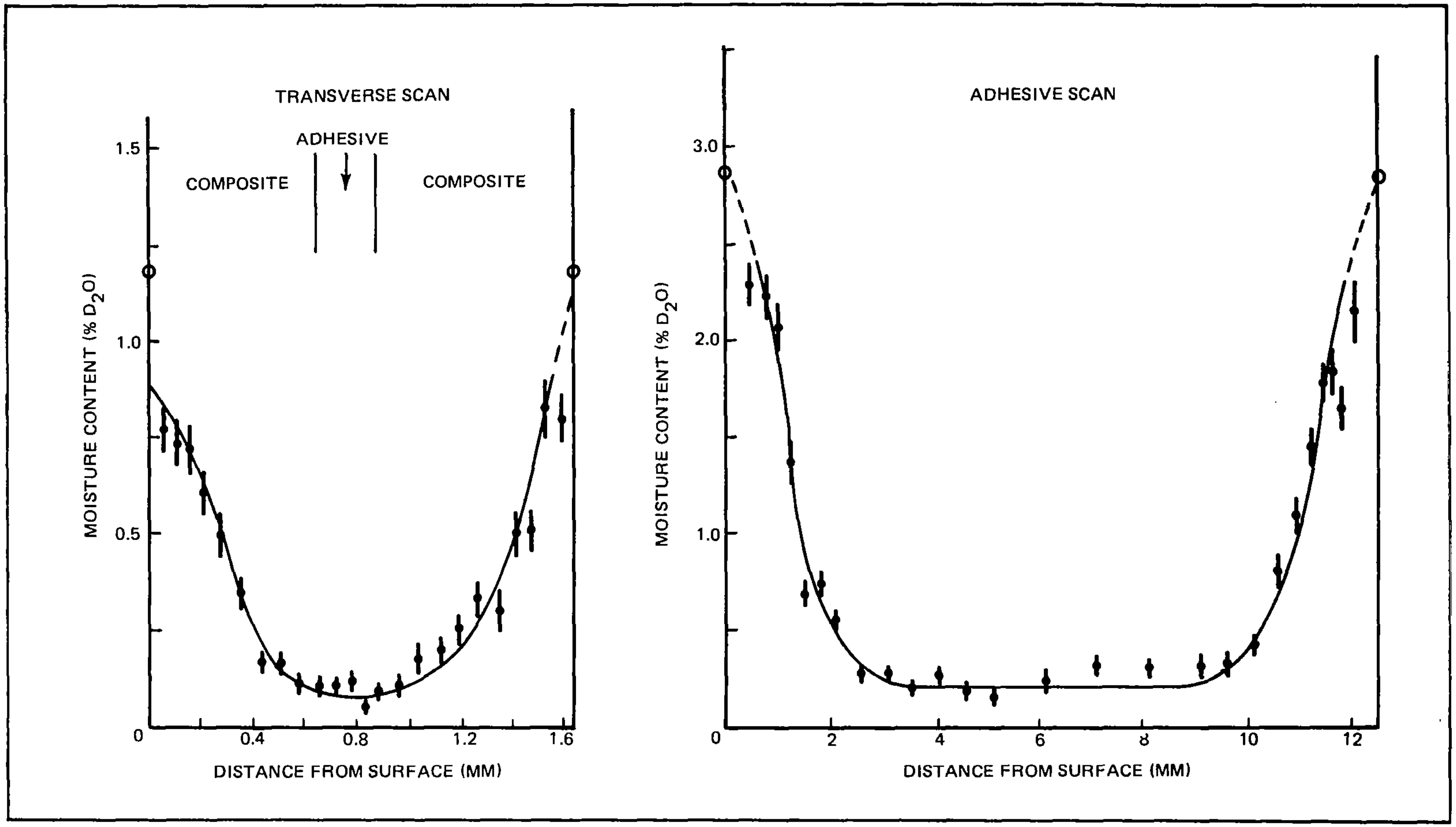


Fig. 16 Moisture Profiles for EA-9601 Bonded Specimen Conditioned at 49°C, 70% RH for 23 Days

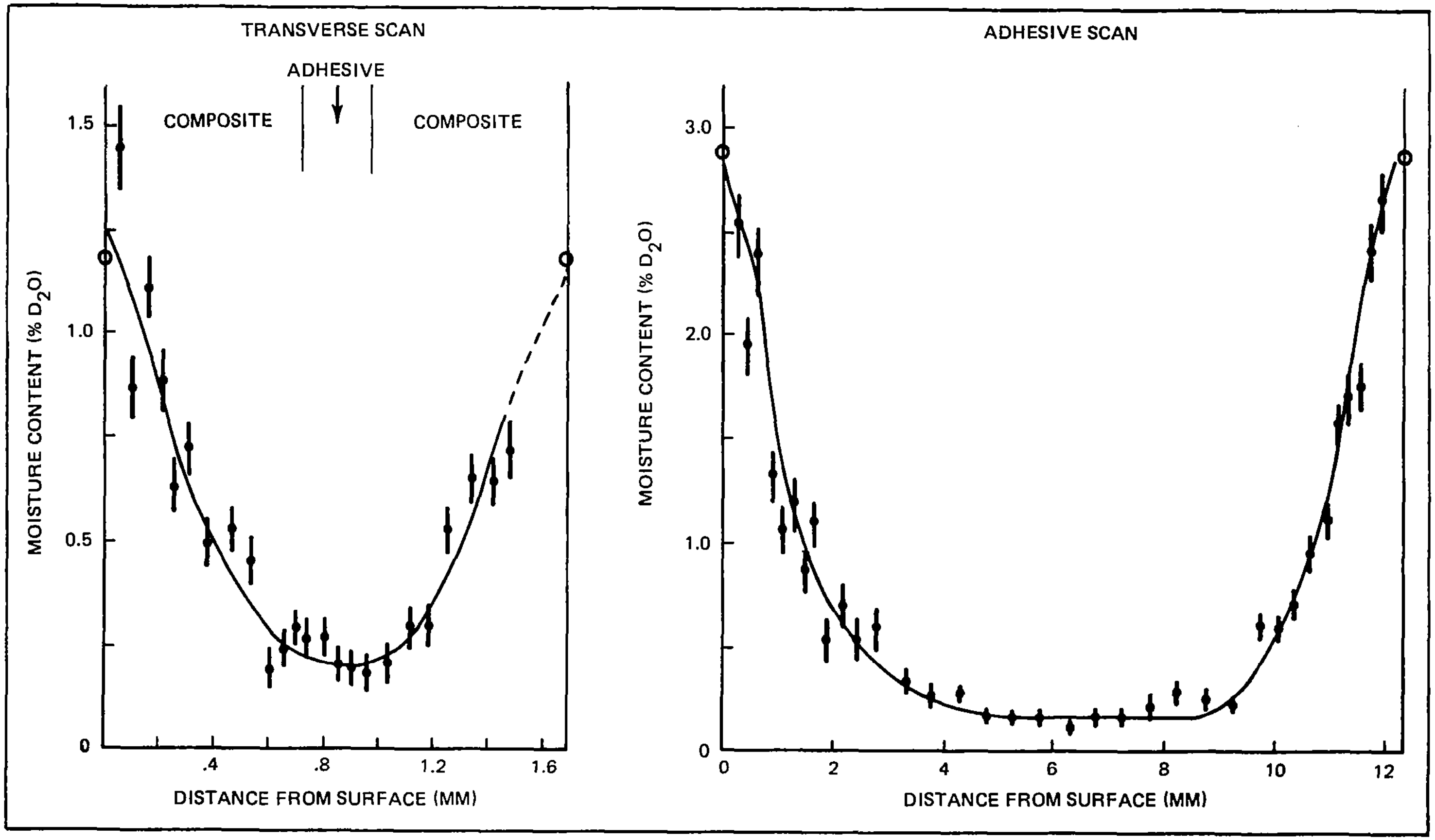


Fig. 17 Moisture Profiles for EA-9601 Bonded Specimen Conditioned at 49°C, 70% RH for 40 Days

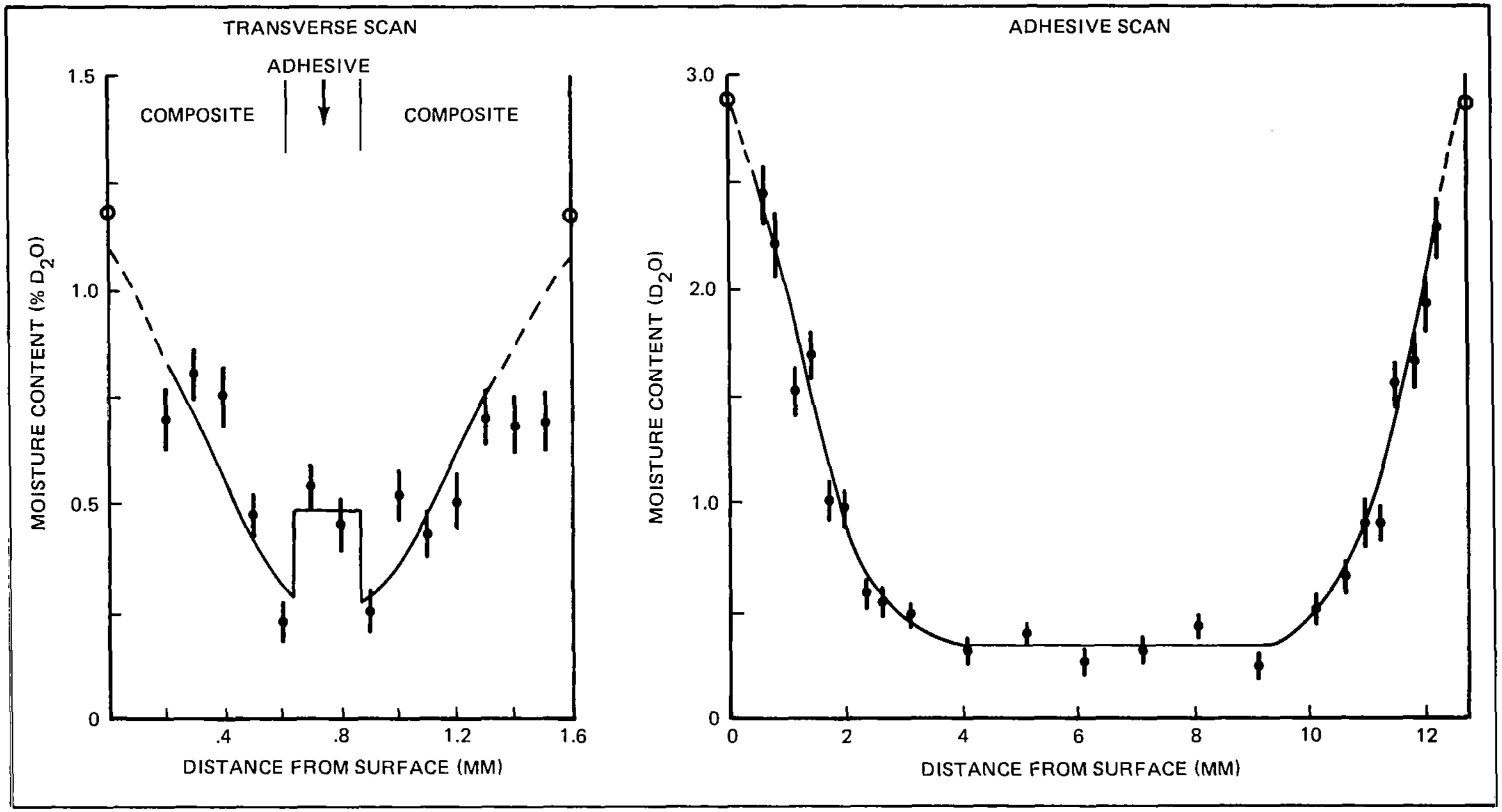


Fig. 18 Moisture Profiles for EA-9601 Bonded Specimen Conditioned at 49° C, 70% RH for 70 Days

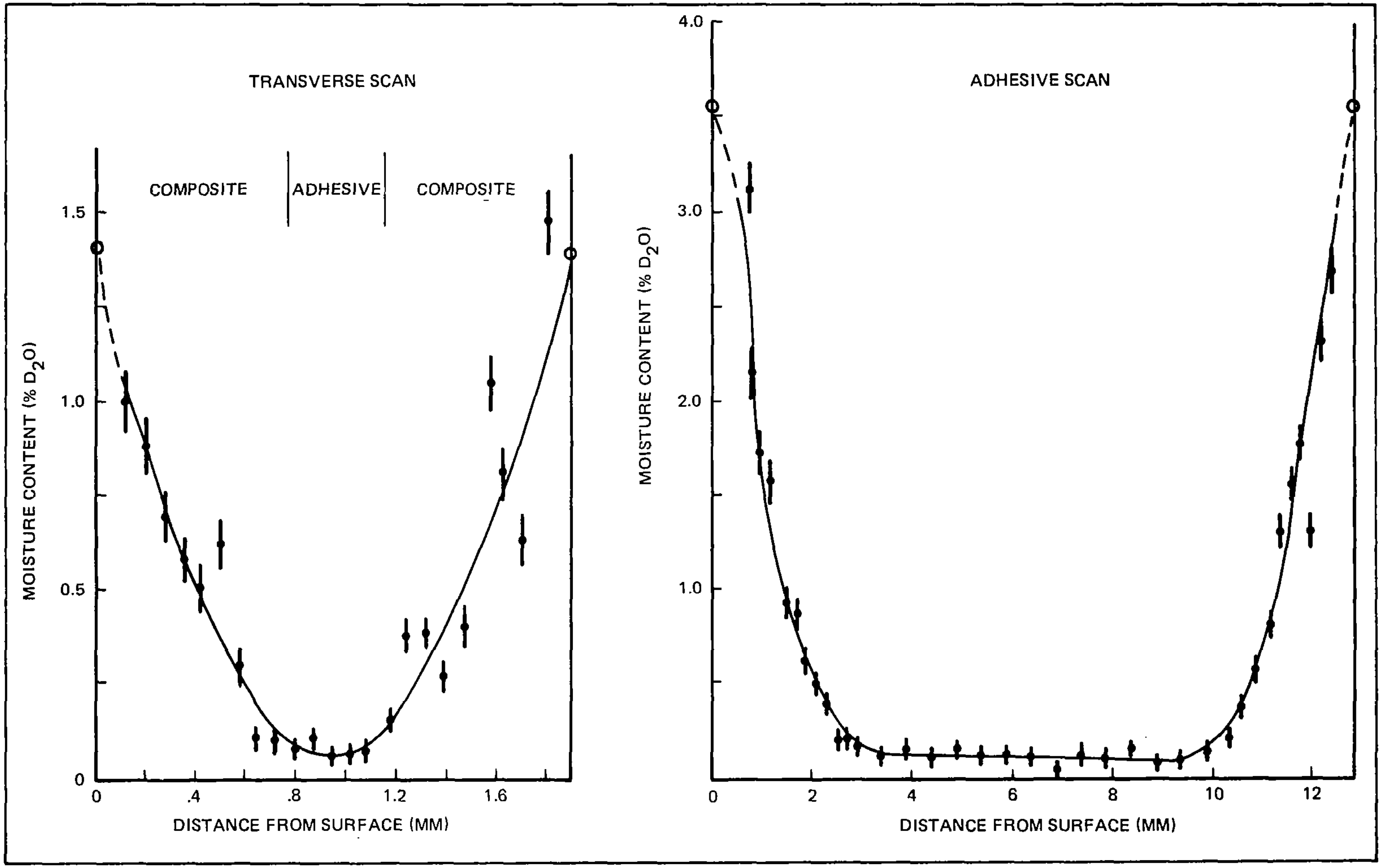


Fig. 19 Moisture Profiles for FM-300 Bonded Specimen Conditioned at 49°C, 90% RH for 23 Days

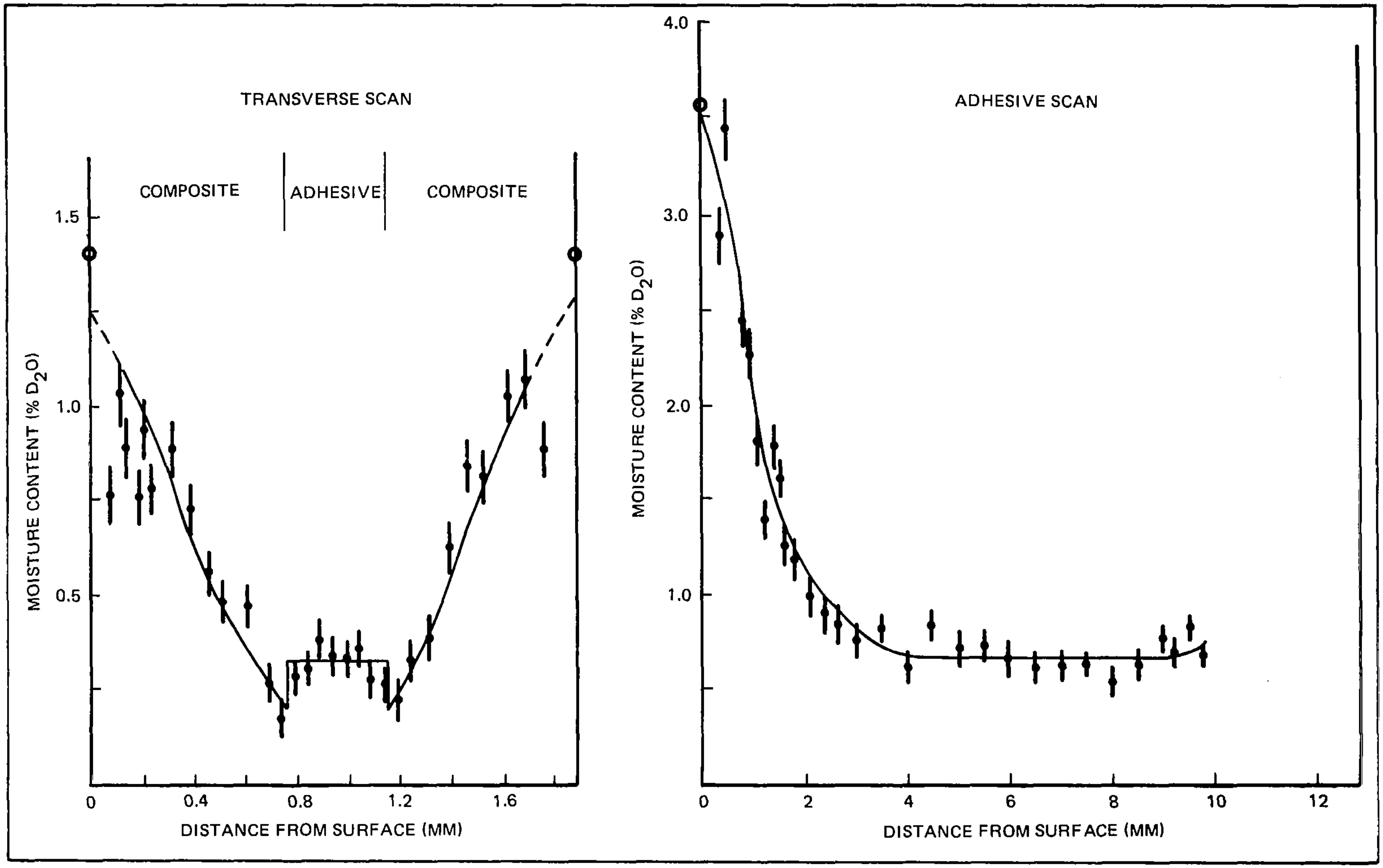


Fig. 20 Moisture Profiles for FM-300 Bonded Specimen Conditioned at 49°C, 90% RH for 40 Days

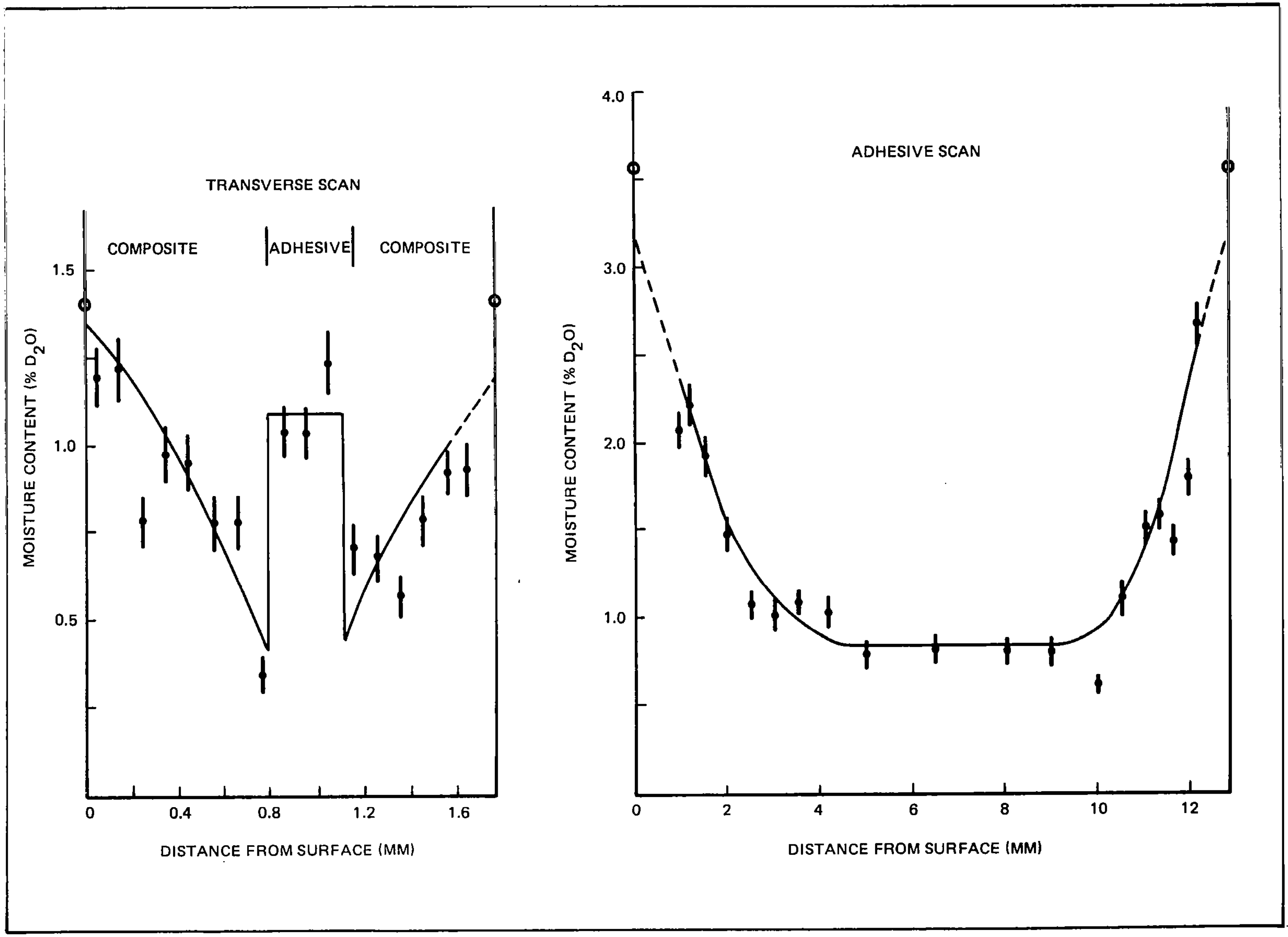


Fig. 21 Moisture Profiles for FM-300 Bonded Specimen Conditioned at 49°C, 90% RH for 70 Days

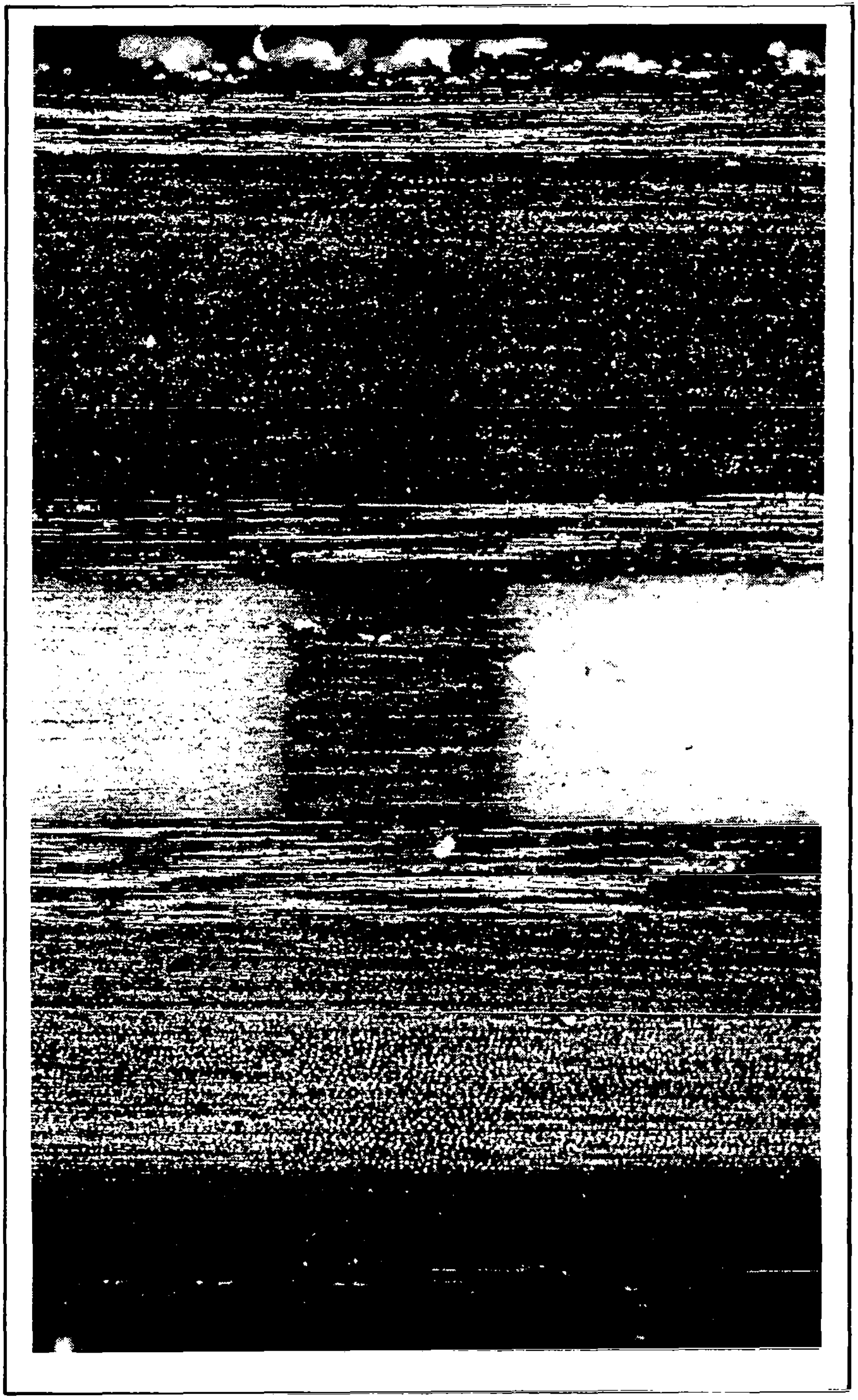


Fig. 22 Beam Spots on Bonded Specimen, Typical Transverse Scan

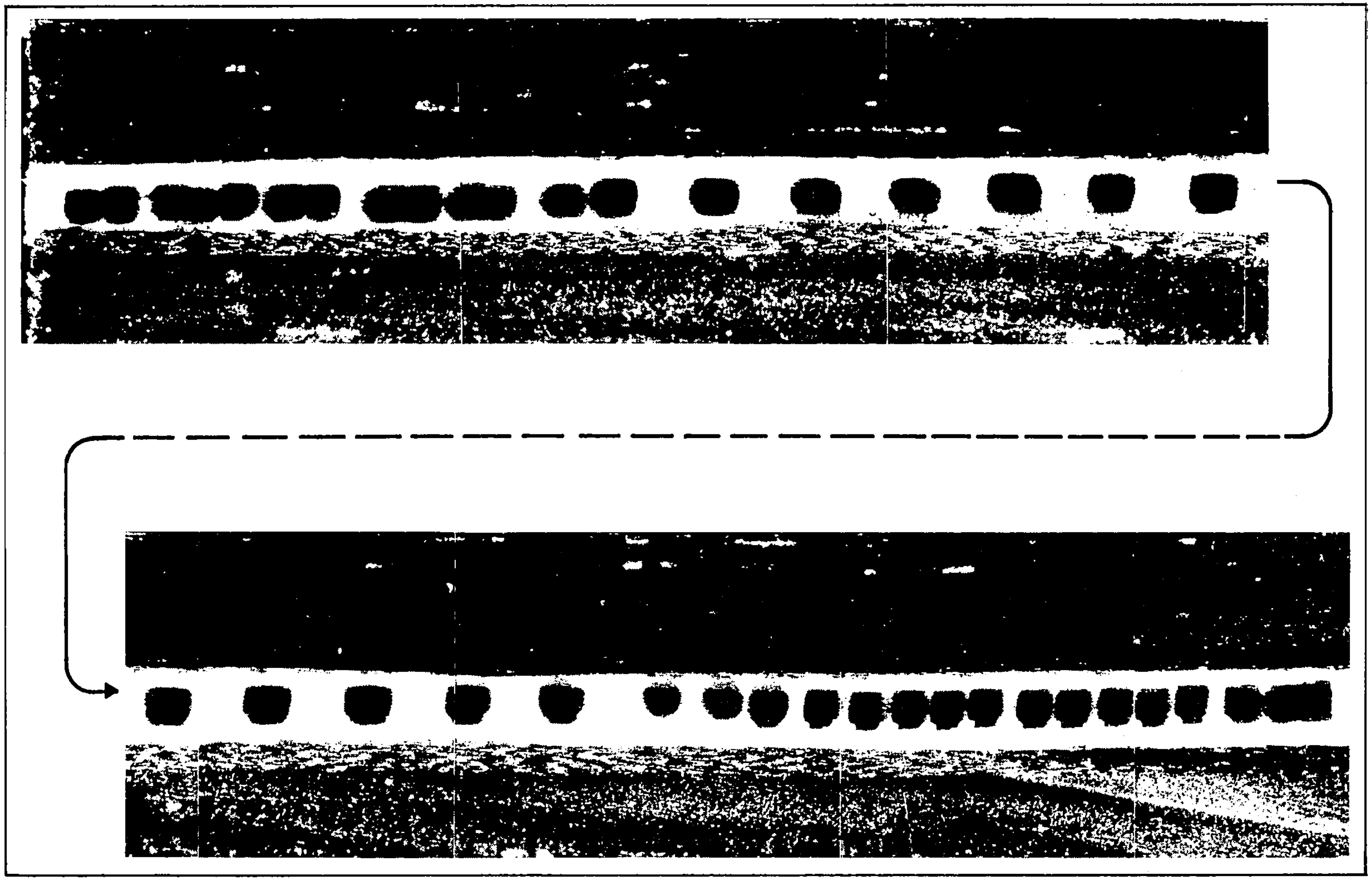


Fig. 23 Beam Spots on Bonded Specimen, Typical Adhesive Scan

TABLE 4 - MEASURED MOISTURE CONTENTS IN BONDED SPECIMENS

	Moisture	Conditioning		Nuclear Reaction Analysis			Gravimetric Analysis
Adhesive	T(°C),	RH(%),	t(day)	Composite (%)	Adhesive (%)	Total (%)	Bulk (%)
FM-300	77,	90,	6	0.75	0.91	0.78	0.88 ± 0.07
	77,	90,	12	0.81	1.79	1.00	1.24 ± 0.05
	77,	90,	70	1.16	3.50	1.70	2.04 ± 0.19
	77,	70,	6	0.54	0.55	0.54	0.69 ± 0.12
	77,	70,	12	0.78	1.04	0.84	0.97 ± 0.12
	77,	70,	70	1.12	2.80	1.50	1.36 ± 0.10
	49,	90,	23	0.63	0.69	0.65	0.88 ± 0.05
	49,	90,	40	0.78	1.00	0.82	1.05 ± 0.02
	49,	90,	70	0.93	1.33	1.02	1.37 ± 0.02
	49,	70,	23	0.39	0.57	0.42	0.61 ± 0.02
	49,	70,	40	0.69	0.74	0.70	0.72 ± 0.02
	49,	70,	70	0.71	0.95	0.77	0.92 ± 0.06
EA-9601	77,	90,	6	0.93	1.28	0.99	1.11 ± 0.15
	77,	90,	12	0.96	1.82	1.10	1.54 ± 0.06
	77,	90,	70	1.15	4.40	1.64	2.80 ± 0.33
	77,	70,	6	0.68	1.06	0.73	0.78 ± 0.13
	77,	70,	12	1.05	1.70	1.15	1.13 ± 0.20
	77,	70,	70	1.16	2.80	1.44	1.51 ± 0.05
	49,	90,	23	0.74	0.94	0.77	0.97 ± 0.08
	49,	90,	40	0.88	1.84	1.03	1.18 ± 0.03
	49,	90,	70	0.95	2.07	1.12	1.49 ± 0.06
	49,	70,	23	0.46	0.73	0.50	0.64 ± 0.03
	49,	70,	40	0.70	0.74	0.71	0.76 ± 0.01
	49,	70,	70	0.74	0.85	0.76	0.91 ± 0.06

The scatter in the data is more pronounced within the composite in the transverse scan and is due to the local variation of fiber density throughout the composite, especially at ply interfaces, as well as the variation in moisture content. As the spatial resolution (determined by the beam dimensions) is made finer, the effect of the varying fiber density produces an even greater degree of scatter in the data. A compromise was reached between a suitable spatial resolution and an acceptable degree of scatter. The data obtained for the adhesive scan indicate a smoother variation of moisture content but in this case the adhesive is far more homogeneous and the beam dimensions are larger so that the local moisture content is measured (and, therefore, averaged) over a greater surface area.

The reason for the general inability to measure the fully saturated value at the edges of the specimens is twofold. First, the edges of the samples are susceptible to damage during the cutting procedure. The fine polishing procedure improves the surface condition but does not completely eliminate the edge damage. Secondly, the finite beam width and the limited ability to locate the beam precisely means that the probability of making a measurement sufficiently close to the edge is diminished. For the adhesive scans, the specimen is mounted in such a way that a small part of at least one or both edges of the exposed surface is shadowed by a supporting frame which precludes a measurement very close to the edge (see first and last beam spots in Fig. 23). For a few of the specimens the thickness of the adhesive was slightly non-uniform. In the event that the adhesive narrowed to the extent that the 125 µm wide beam partially overlapped the composite, a correction factor was applied to those data based on the degree of overlap determined from the photomicrograph and the measured moisture content in the innermost composite ply.

The solid curves drawn through the transverse and adhesives scans in Figs. 10 - 21 were integrated to obtain the average nuclear reaction analysis moisture contents listed in Table 4. The average moisture content in the composite was obtained by integrating the area under the curves from the exterior surface to the composite-adhesive interface. Generally, the tabulated value is the average of two composite scans in the same sample. The maximum number of scans for any set of environmental conditions was four. In some cases, such as FM-300 bonded specimens conditioned for 6 days at 77°C, 70% RH (see Fig. 10), the measured moisture content is approximately 35% lower in one composite adherend than in the second. The photomicrograph of the probed specimen revealed that one side of the cut surface was extremely irregular. Thus the measured moisture content from this adherend was considered to be nonrepresentative of the true moisture content. In cases of this type the tabulated average composite moisture content is based on only one scan.

The adhesive scans were integrated to obtain the average moisture content in the adhesives. Generally, these data were extremely reproducible from one edge of the specimen to the other and the moisture content in the center is consistent with that of the transverse scan. Saturation was measured at 77°C, 70% and 90% RH for each adhesive by scanning across the cut interior adhesive surface of specimens conditioned for 70 days (see Figs. 12 and 15). It was assumed that these same equilibrium levels would be reached for specimens conditioned at 49°C although time limitations did not permit verification of this level during this program. The moisture profile data for unsaturated specimens were extrapolated to the surface and the surface level was generally in agreement with the measured saturation value.

The total moisture content in the specimens was computed from the measured composite and adhesive moisture contents and the volume fraction of composite and adhesive. The actual composite and adhesive volume fraction for each specimen was measured from the photomicrographs of the specimens. The average composite volume fraction for all FM-300 and EA-9601 bonded specimens was 0.79 and 0.85, respectively. Figures 10 - 21 clearly show that the fully cured EA-9601 adhesive is approximately 35% thinner than the FM-300 adhesive.

The bulk moisture content obtained from gravimetric analysis was corrected for both surface adsorption and edge diffusion in order to compare it with the total moisture content measured with the nuclear probe. The nuclear probe measures the moisture content in a reaction volume within 2 μm of the surface and since the water adsorbed on the surface would be expected to evaporate in the high vacuum chamber prior to analysis, no surface correction factor need be applied to these data. On the other hand, the gravimetric analysis will include a measureable contribution from the water adsorbed on the textured surfaces. The edge correction factor is required because the transverse scan was made through the center of the specimens where the effects of composite edge diffusion are not observed. Since we measured the moisture profile along the length of adhesive (adhesive scan) no correction for adhesive edge diffusion was required for the gravimetric measurements.

The surface adsorption correction factor was calculated in the following manner. Extrapolation of diffusion curves (Figs. 3 and 8) to zero time showed an average instantaneous moisture pickup of approximately 0.14% and 0.30% for composite and adhesive, respectively. These results were combined with the specimen weights and the surface area to compute a surface moisture content (gD_2O/cm^2-sample). We assumed that to a first approximation the surface texture of the bonded specimens could be calculated from that of pure composite and adhesive. The results of this analysis indicate that the bulk gravimetric moisture content contains a surface contribution of 0.10% D_2O. The bulk moisture contents listed in Table 4 have all been corrected by this amount.

The edge diffusion correction factor was computed using the method of Springer (Ref. 12). The relative enhancement of the moisture absorption due to edge diffusion is greater for shorter times and lower temperatures, thus a different correction factor was applied to each bulk measurement. These ranged from a factor of 1.2 at 49°C-23 days and 77°C-6 days to 1.0 at 77°C-70 days. The data in Table 4 also reflect this correction factor.

Comparison between the corrected bulk moisture content and the total moisture content using the NPD show good agreement with the exception of the EA-9601 bonded specimens conditioned at 77°C-90% RH-70 days. Since all other specimens conditioned at 77°C for 70 days show agreement, we must assume that there is an anomaly associated with this material for the prolonged exposure at both high temperature and high relative humidity. Based on the equilibrium moisture content of the composite and adhesive and their volume fractions, the equilibrium moisture content in EA-9601 bonded specimens should be approximately 1.9%. We suggest that the additional water may be held as water clusters at sites in the adhesive or at the composite/adhesive interface and is driven out of the near surface region of the sample during cutting, polishing, or while the sample is maintained under high vacuum during moisture profiling.

Comparison of the remainder of the data shows better agreement between NPD and gravimetric results for specimens conditioned at 70% RH than at 90% RH with the difference in measured moisture content being 0.08% and 0.25%, respectively. Several explanations are proposed to account for this difference. First, the correction factor for surface adsorption as applied to the gravimetric results may have been too small. This is possible because the surfaces of all bonded specimens were coarsely polished to facilitate location of the edge with the ^{3}He beam. This polishing may have loosened surface fiber in the outermost plies creating cavities for moisture clustering. Secondly, the integrated moisture content was computed from the curve through the NPD data points, and, as shown in Fig. 10-21, this curve is often below the expected saturation level in the vicinity of the composite surface. This inconsistency has been ascribed to composite damage during cutting. The larger difference between NPD and gravimetric results at 90% RH than at 70% RH may be due to the greater concentration of unbound water in low density regions or voids in the specimen. Such unbound water is not unlikely since the equilibrium moisture content of epoxy resins and composites as a function of relative humidity exhibits positive deviations from Henry's Law above approximately 65% RH, indicative of water clustering. These clusters would be preferentially broken and lost during cutting, polishing and while held in high vacuum because they are not tightly bound in the polymer network and it is unlikely that they would be reformed by the water reservoir which exists in the bulk of the specimen.

Four samples were selected for the investigation of the extent of back-diffusion into the composite from the adhesive in a region near the edge of a specimen. Each specimen was scanned across the composite-adhesive interface at various distances from the edge of the specimen. The moisture distribution data obtained in these measurements are shown in Fig. 24 through

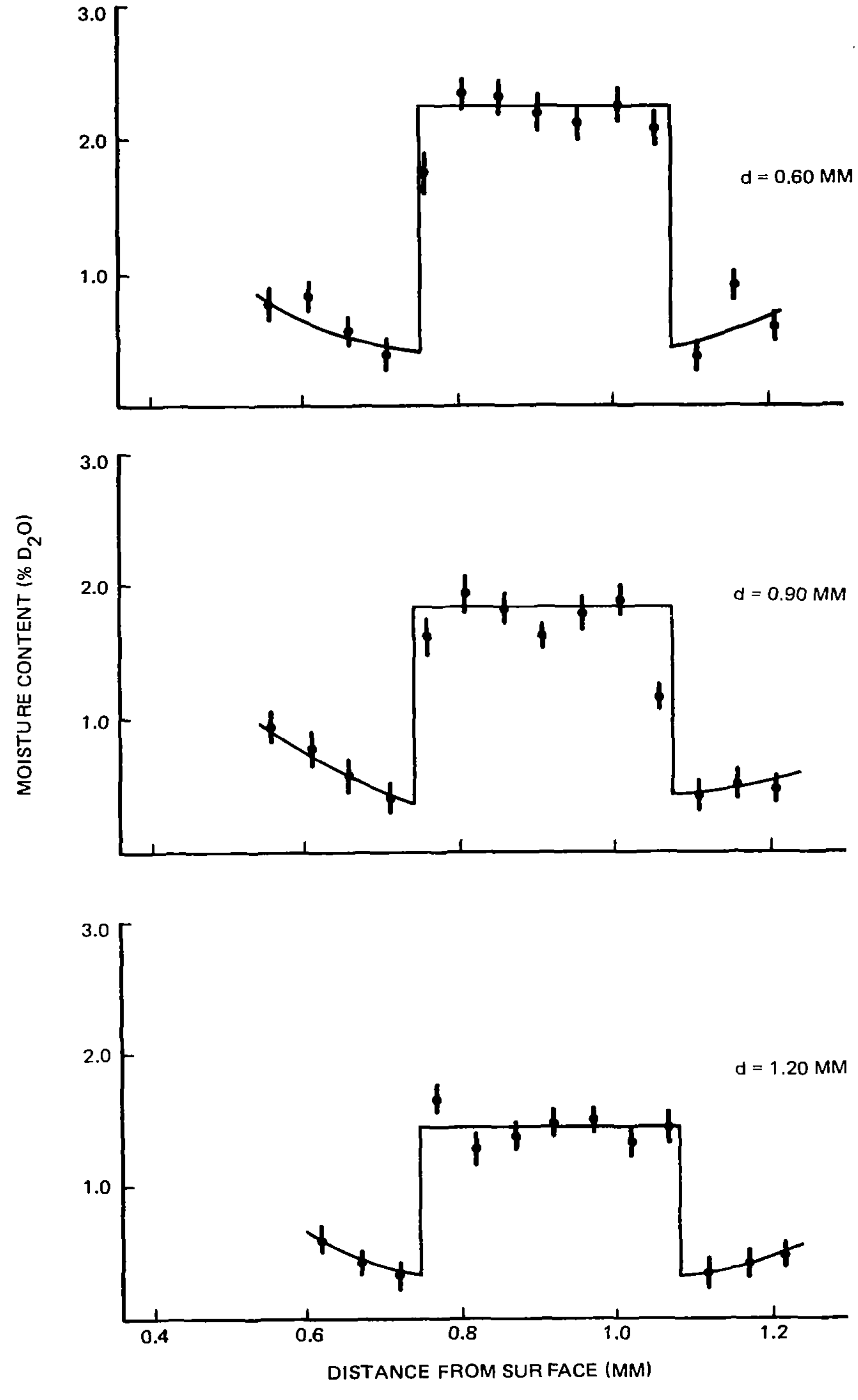


Fig. 24 Moisture Profile in Vicinity of Composite – Adhesive Interface at Various Distances, d, from Edge of FM-300 Bonded Specimen. (Exposure Conditions: 77°C, 70% RH, 12 Days)

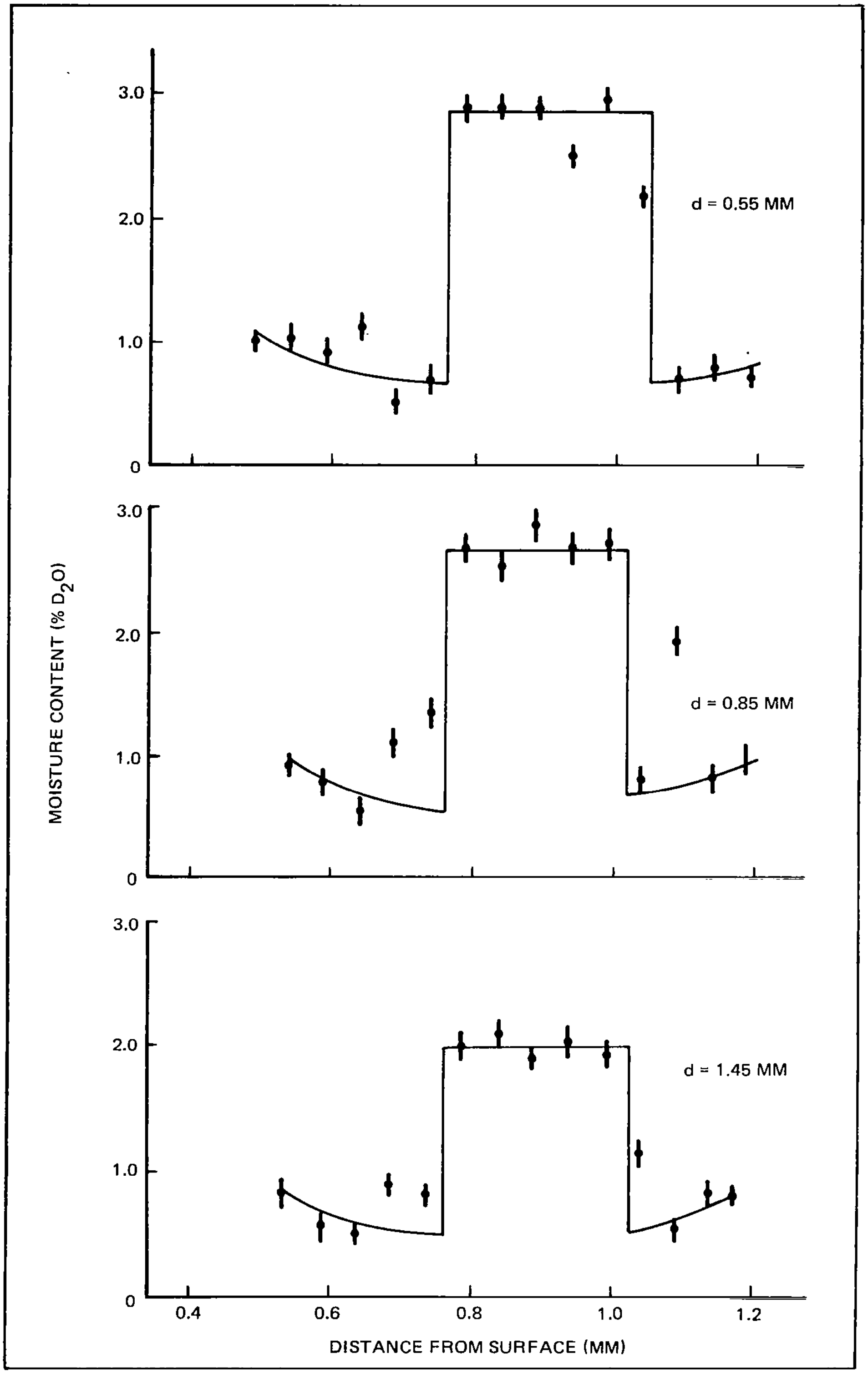


Fig. 25 Moisture Profile in Vicinity of Composite – Adhesive Interface at Various Distances, d, from Edge of FM-300 Bonded Specimen. (Exposure Conditions: 77°C, 90% RH, 12 Days)

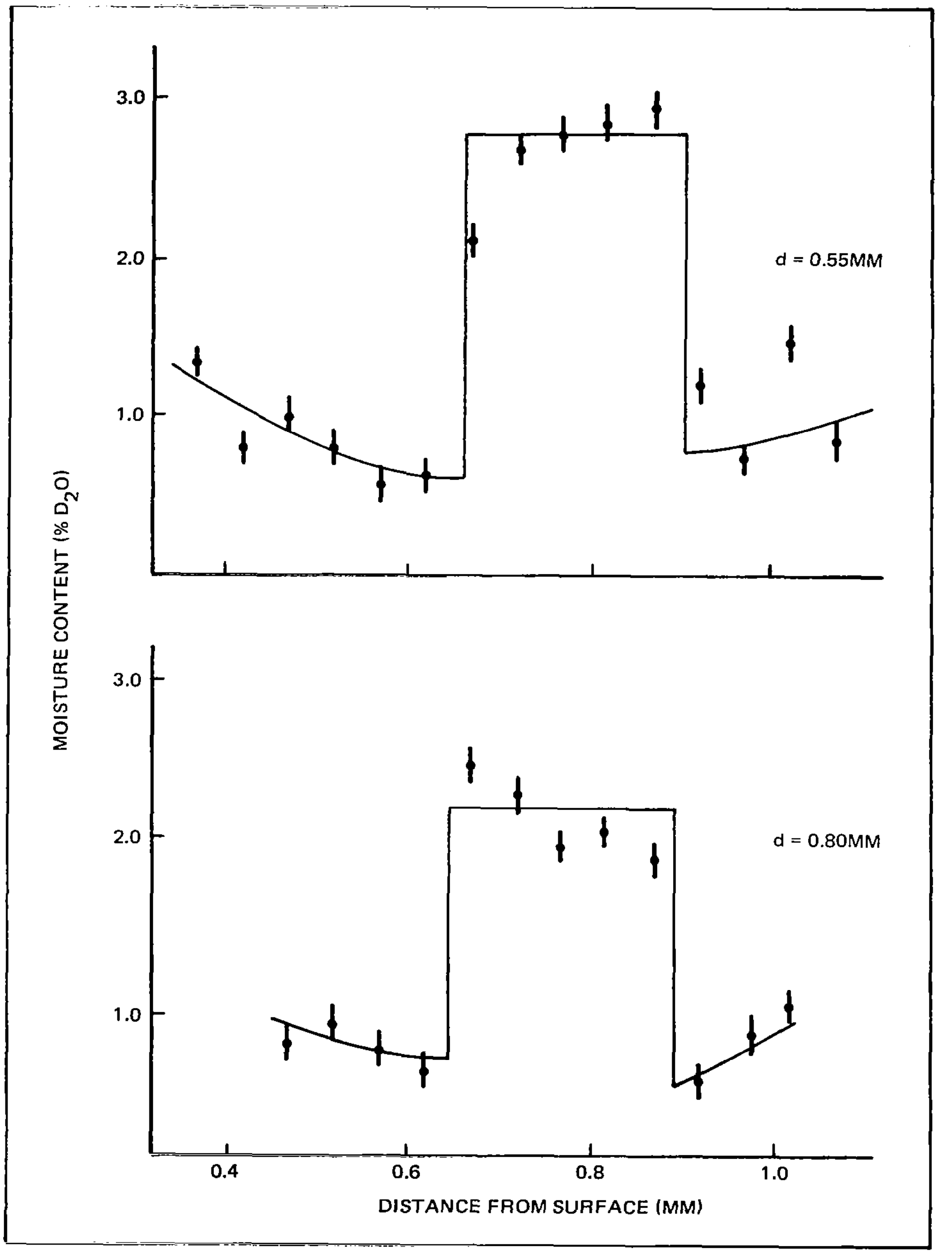


Fig. 26 Moisture Profile in Vicinity of Composite — Adhesive Interface at Various Distances, d, from Edge of EA-9601 Bonded Specimen (Exposure Conditions: 77°C, 90% RH, 12 Days)

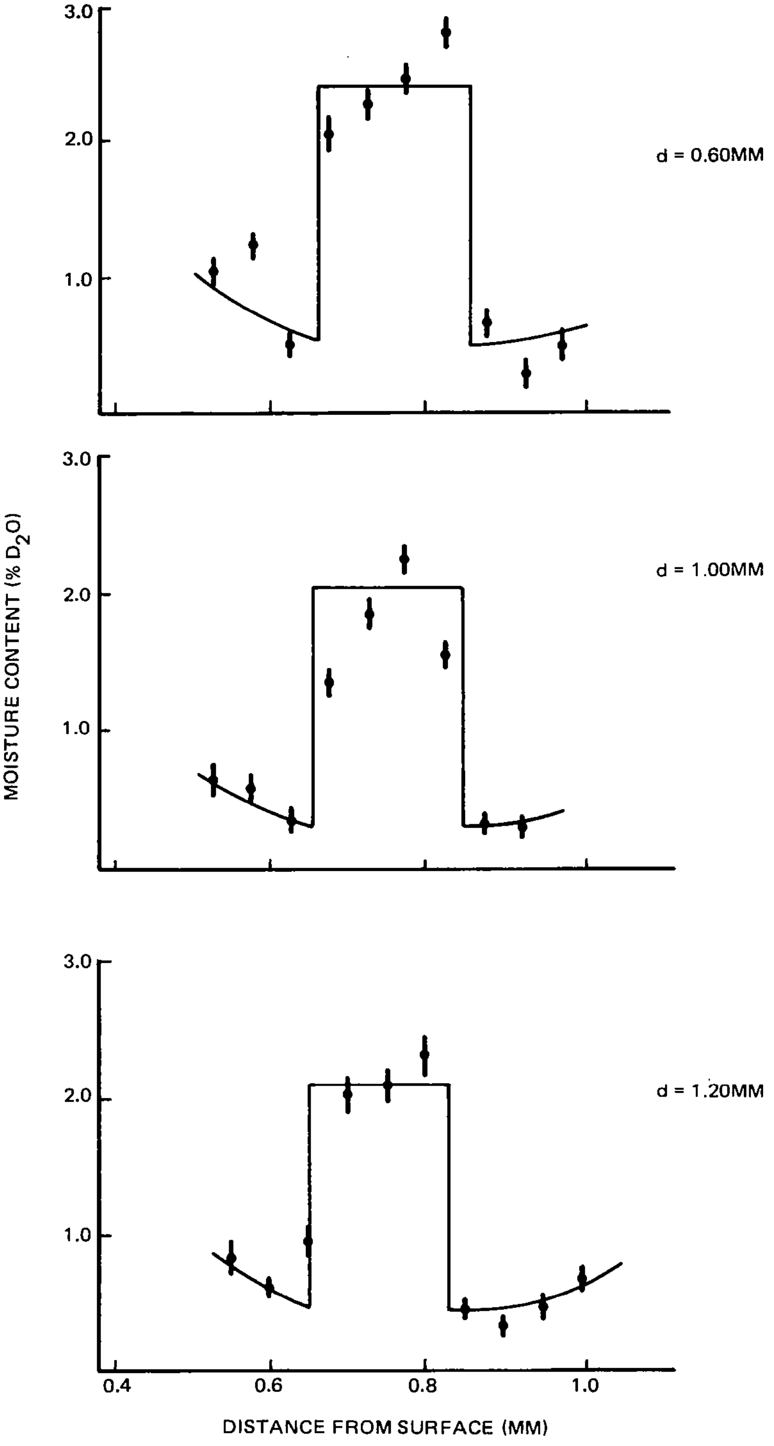


Fig. 27 Moisture Profile in Vicinity of Composite — Adhesive Interface at Various Distances, d, from Edge of EA-9601 Bonded Specimen. (Exposure Conditions: 77°C, 70% RH, 12 Days)

27. The four specimens were exposed to the D_2O environment at 77°C for 12 days at two levels of relative humidity (70% and 90%). The data points lying wholly within the adhesive, the region of constant moisture content, were used to obtain the average adhesive moisture content. The curve through the data points measured within the composite indicate the trend of the moisture profile within that region. The results of the measurements are compiled in Table 5 where the average moisture content within the adhesive is listed as well as the average moisture content within the composite integrated over the first 0.15 mm on each side of the composite-adhesive interface. Also included in Table 5 is the average moisture content obtained in like manner from other samples exposed under identical conditions but scanned at approximately 6.3 mm from the edge for the moisture profiling described earlier. Two features of these results are noteworthy: (1) in spite of the rather large changes in the average moisture content within the adhesive as a function of distance from the edge, there is no appreciable change in the average integrated moisture content within the composite, and (2) the average moisture content in the composite for samples identically conditioned but probed at a distance of 6.3 mm from the edge is comparable in all cases to the average moisture content very near the edge of the specimens. The consistency of these results indicate that the moisture observed within the composite is due chiefly to diffusion through the outer faces of the specimens and substantiate the fact that back-diffusion of D_2O is insignificant even at the edges where the moisture content in the adhesive approaches saturation.

A one-dimensional diffusion model was used to predict the moisture profile along the 12.8 mm length of adhesive. The solution was based on the measured diffusivity from the gravimetric analysis and the adhesive equilibrium moisture content measured from the NPD method. Comparison between predicted and observed profiles was made for all combinations of temperature, relative humidity, exposure time and adhesive. Figures 28 - 31 contain some of these comparisons which are representative of the observed trends. Figure 28 illustrates the comparison for specimens of each adhesive conditioned for 70 days at 49°C, 70% RH. The deviation can be ascribed to diffusion through the composite which is not accounted for in the model. Similar results were

TABLE 5 - MOISTURE CONTENT IN VICINITY OF COMPOSITE ADHESIVE INTERFACE AT 77°C FOR 12 DAYS

Type of Adhesive	Relative Humidity 70%			Relative Humidity 90%		
	Distance from Edge (mm)	Avg Moisture Content (% D_2O) In Adhesive	Avg Moisture Content (% D_2O) In Composite	Distance from Edge (mm)	Avg Moisture Content (% D_2O) In Adhesive	Avg Moisture Content (% D_2O) In Composite
FM-300	0.60	2.24	0.59	0.55	2.84	0.71
	0.90	1.83	0.56	0.85	2.65	0.75
	1.20	1.43	0.46	1.45	2.00	0.68
	6.3	1.17	0.48	6.3	1.25	0.80
EA-9601	0.60	2.37	0.69	0.55	2.77	0.85
	1.00	2.02	0.43	0.80	2.16	0.74
	1.20	2.09	0.57	6.3	1.11	0.82
	6.3	1.46	0.59			

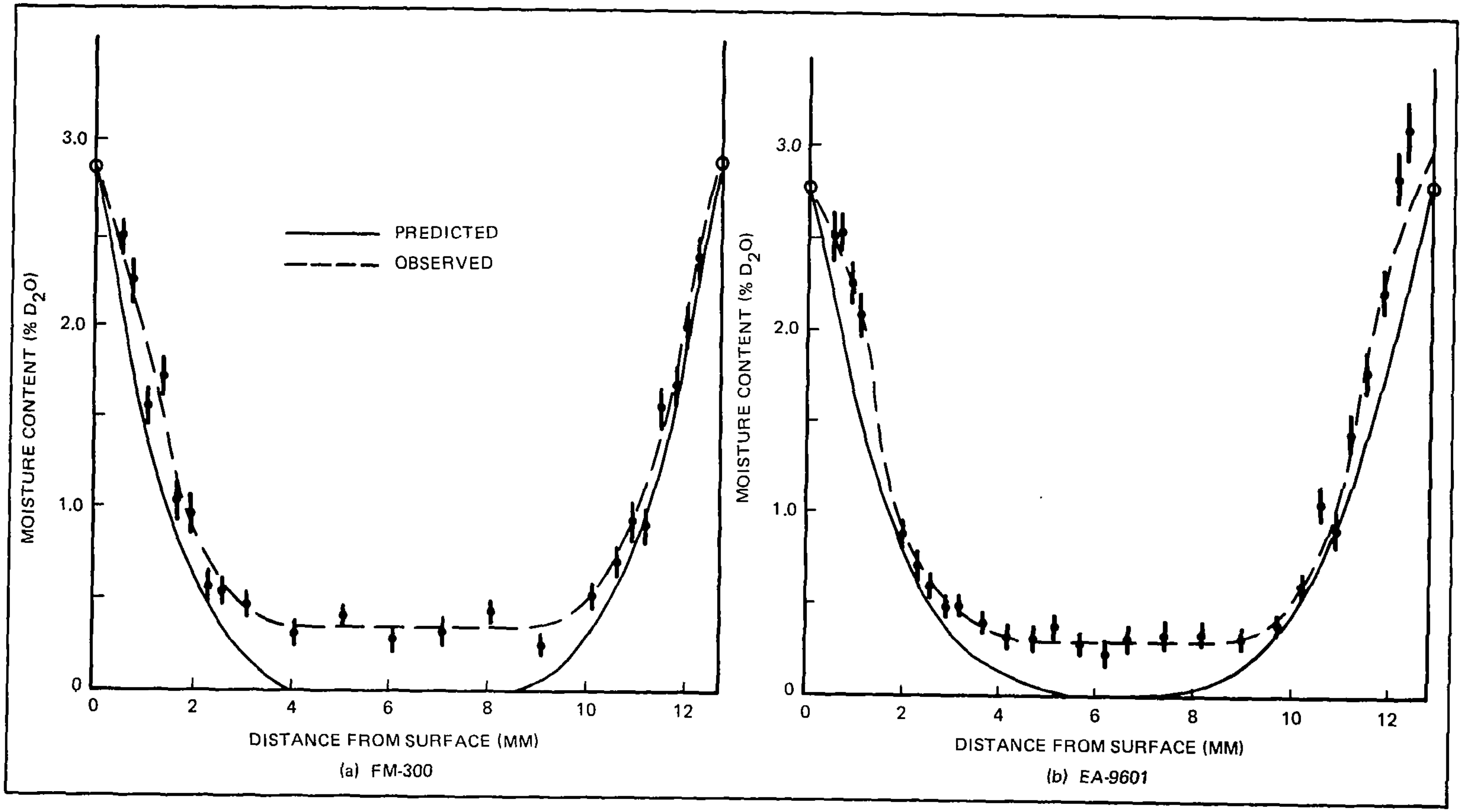
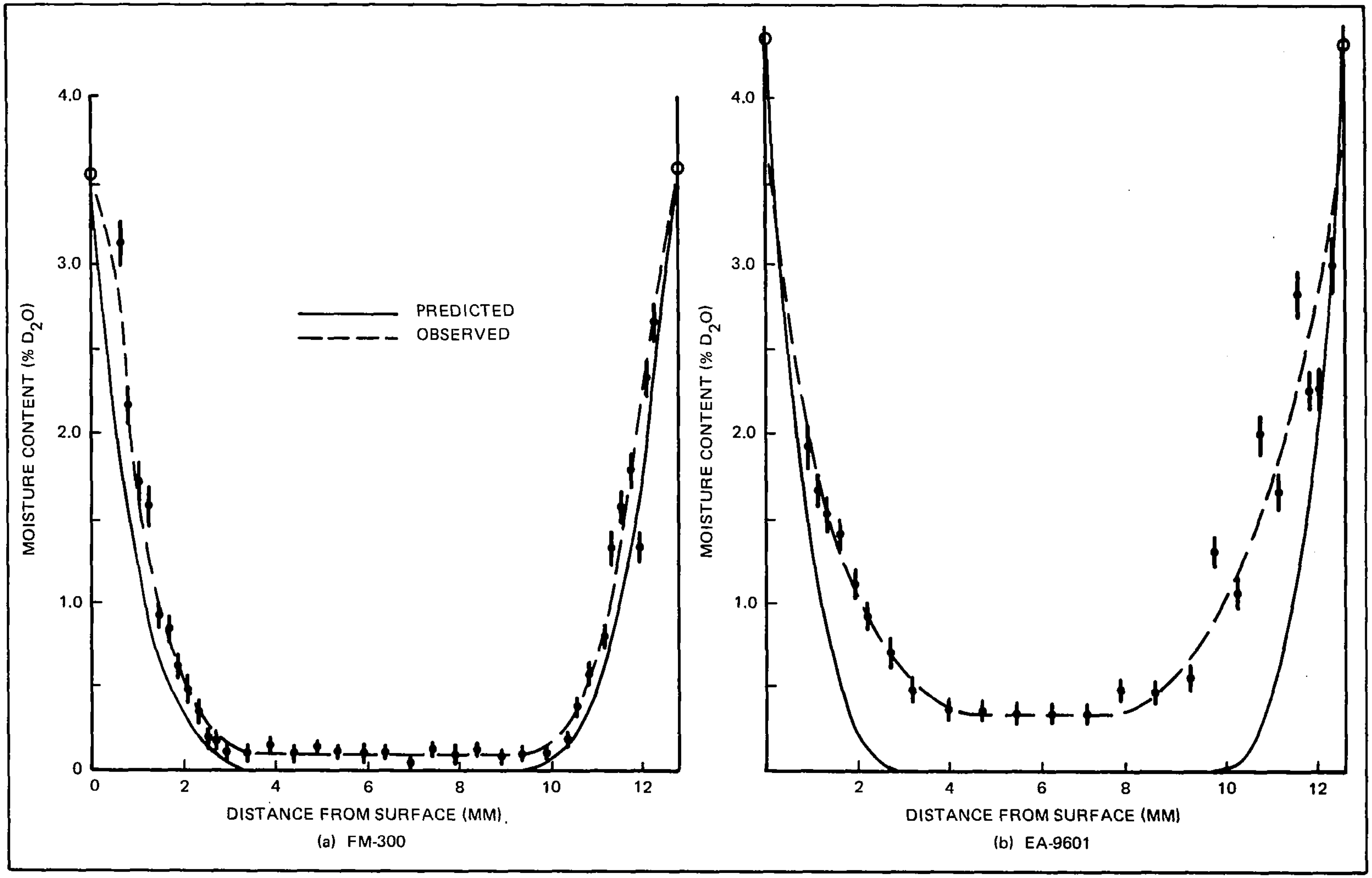


Fig. 28 Comparison Between Predicted and Observed Moisture Profiles in Adhesive for Bonded Specimens Conditioned at 49° C, 70% RH for 70 Days



(a) FM-300

(b) EA-9601

Fig. 29 **Comparison Between Predicted and Observed Moisture Profiles in Adhesive for Bonded Specimens Conditioned at 49°C, 90% RH for 23 Days**

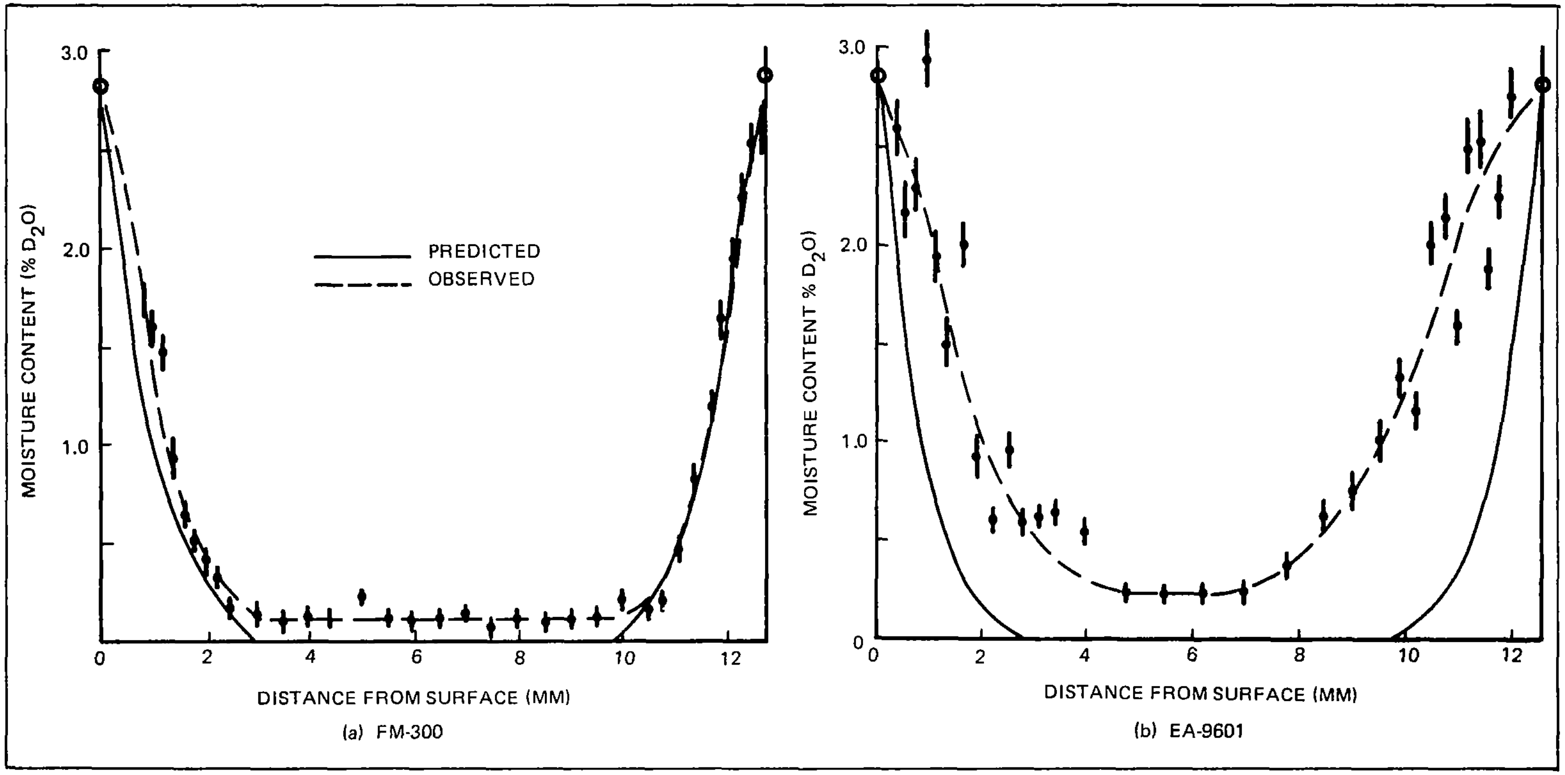
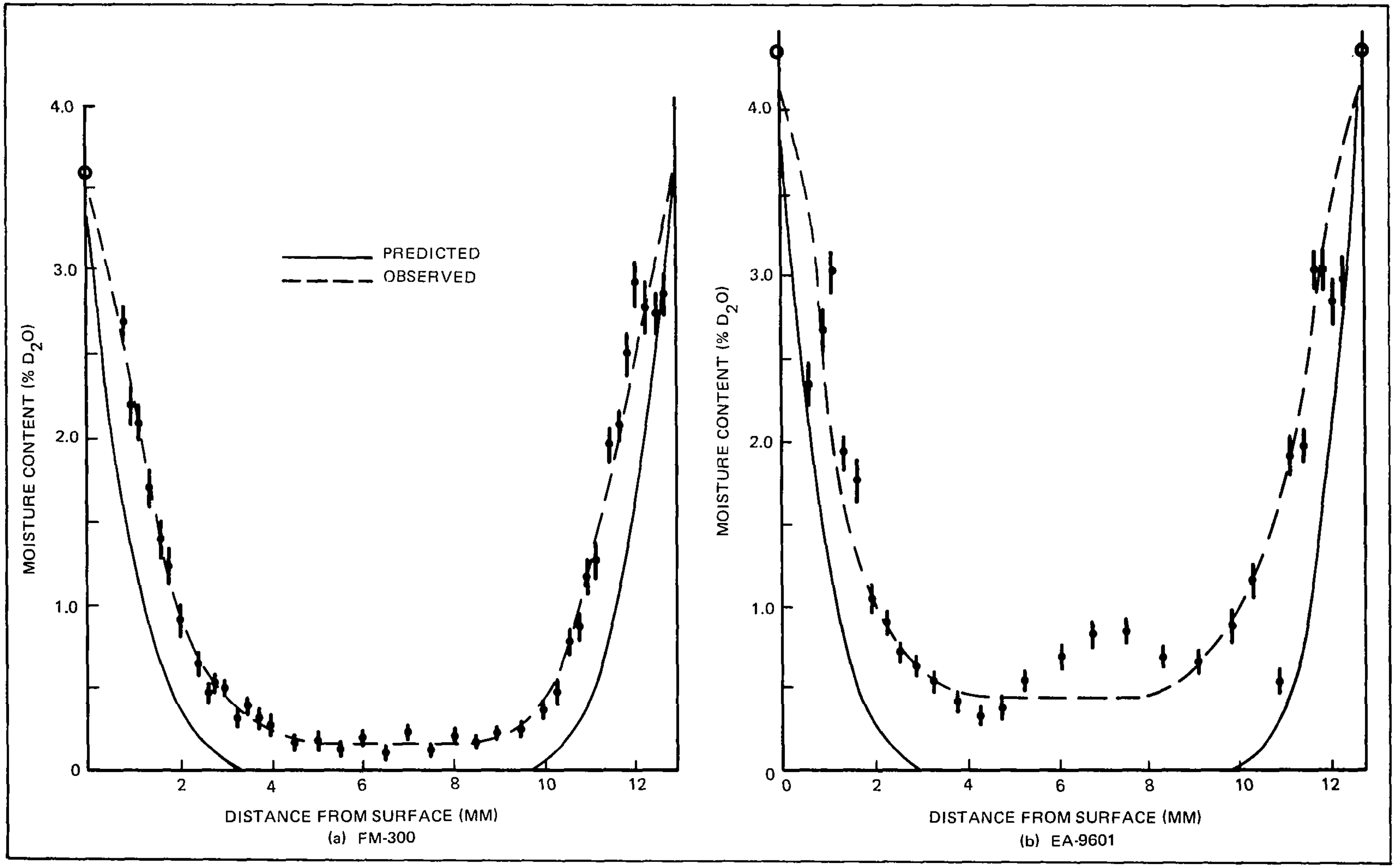


Fig. 30 Comparison Between Predicted and Observed Moisture Profiles in Adhesive for Bonded Specimens Conditioned at 77°C, 70% RH for 6 Days



(a) FM-300

(b) EA-9601

Fig. 31 Comparison Between Predicted and Observed Moisture Profiles in Adhesive for Bonded Specimens Conditioned at 77°C, 90% RH for 6 Days observed for specimens condition for 23 and 40 days at this temperature and relative humidity.

At 49°C, 90% RH the comparison between theory and experiment is also very good at the three moisture levels for the FM-300 bonded specimens. This is illustrated in Fig. 29 for a specimen conditioned for 23 days. The EA-9601 bonded specimens show good agreement at the lowest moisture level (Fig. 29) and fair agreement after 40 and 70 day exposure.

The effect of moisture conditioning at high temperature, 77°C, is illustrated in Figs. 30 and 31. At 70% RH the FM-300 bonded specimen again exhibits good agreement after 6 day (Fig. 30a) and 12 day exposure. The EA-9601 bonded specimens do not agree with the predicted moisture profile at either moisture level (Fig. 30b). The high observed moisture content suggests the occurrence of enhanced edge diffusion. This behavior was also observed for both type specimens conditioned at 77°C, 90% RH (Fig. 31).

These results suggest that FM-300 bonded specimens can be conditioned at 70% RH at temperatures up to 77°C and still exhibit behavior which is predictable from one dimensional diffusion models. At 90% RH the onset of enhanced edge diffusion occurs between 49°C and 77°C. A one dimensional diffusion model is also useful in predicting the behavior of EA-9601 bonded specimens at 49°C at both humidity levels but these specimens exhibit an enhancement in moisture absorption at 77°C at both moisture levels. The observed enhancement appears to be far greater than can be accounted for based on diffusion through the composite.

3.4 MECHANICAL PROPERTIES

The results of mechanical property evaluation at room temperature and 82°C are summarized in Table 6. The bond shear stress is plotted as a function of the total moisture content in the adhesive (Figs. 32 and 33) and as a function of the moisture content in the high stress region (outer 25%) of the joint (Figs. 34 and 35). Both moisture levels were obtained from integration of the adhesive scan moisture content. Each data point represents the average of at least three specimens. The error band represents the spread between the highest and lowest measurement.

TABLE 6 - SHEAR STRESS OF MOISTURE CONDITIONED BONDED SPECIMENS

	T, RH, t	(D 0)	(D 0)	Shear Stress (82°C)		Shear Stress (22°C)	
Adhesive			25%	ksi	MPa	ksi	MPa
FM-300	Control	0	0	(3.50) +.13, -.19	(24.1) +0.9, -1.3	(3.20) +.15, -.16	(22.1) +1.0, -1.1
	77, 90, 6	0.91	1.65	(2.62) +.02, -.02	(18.1) +0.1, -0.1	(4.27) +.14, -.18	(29.4) +1.0, -1.2
	12	1.79	2.10	(2.09) +.22, -.15	(14.4) +1.5, -1.0	(3.27) +.48, -.46	(22.5) +3.3, -3.2
	70	3.5	3.5	(1.59) +.14, -.14	(11.0) +1.0, -1.0	(1.87) +.07, -.09	(12.9) +0.5, -0.6
	77, 70, 6	0.55	1.00	(2.97) +.25, -.30	(20.5) +1.7, -2.1	(3.12) +.35, -.54	(21.5) +2.4, -3.7
	12	1.04	1.56	(2.55) +.04, -.06	(17.6) +0.3, -0.4	(2.40) +.38, -.31	(16.5) +2.6, -2.1
	70	2.8	2.8	(2.16) +.18, -.22	(14.9) +1.2, -1.5	(2.53) +.13, -.26	(17.4) +0.9, -1.8
	49, 90, 23	0.69	1.26	-		(3.26) +.71, -.61	(22.5) +4.9, -4.2
	40	1.00	1.42	-		(3.40) +.30, -.26	(23.4) +2.1, -1.8
	70	1.33	1.82	-		(3.54) +.61, -.66	(24.4) +4.2, -4.6
	49, 70, 23	0.57	1.07	-		(3.62) +.80, -.89	(25.0) +5.5, -6.1
	40	0.74	1.31	-		(3.47) +.90, -.52	(23.9) +6.2, -3.6
	70	0.95	1.58	-		(3.45) +.70, -.68	(23.8) +4.8, -4.7
EA-9601	Control	0	0	(2.44) +.26, -.13	(16.8) +1.8, -0.9	(2.83) +.38, -.35	(19.5) +2.6, -2.4
	77, 90, 6	1.28	2.11	(0.87) +.17, -.13	(6.0) +1.2, -0.9	(3.58) +.37, -.36	(24.7) +2.6, -2.5
	12	1.82	2.45	(0.24) +.01, -.02	(1.7) +0.1, -0.1	(2.91) +.50, -.80	(20.1) +3.4, -5.5
	70	4.4	4.4	-		(2.09) +.28, -.19	(14.4) +1.9, -1.3
	77, 70, 6	1.06	1.77	(1.45) +.19, -.19	(10.0) +1.3, -1.3	(2.87) +.35, -.34	(19.8) +2.4, -2.3
	12	1.70	2.30	(0.79) +.13, -.23	(5.4) +0.9, -1.6	(2.86) +.13, -.13	(19.7) +0.9, -0.9
	70	2.8	2.8	-		(2.76) +.37, -.28	(19.0) +2.6, -1.9
	49, 90, 23	0.94	1.40	-		(3.19) +.25, -.17	(22.0) +1.7, -1.2
	40	1.84	2.79	-		(2.73) +.17, -.18	(18.8) +1.2, -1.2
	70	2.07	2.58	-		(2.59) +.03, -.02	(17.9) +0.2, -0.1
	49, 70, 23	0.73	1.29	-		(3.28) +.23, -.25	(22.6) +1.6, -1.7
	40	0.74	1.29	-		(2.43) +.08, -.08	(16.8) +0.6, -0.6
	70	0.85	1.44	-		(2.99) +.64, -.33	(20.6) +4.4, -2.3

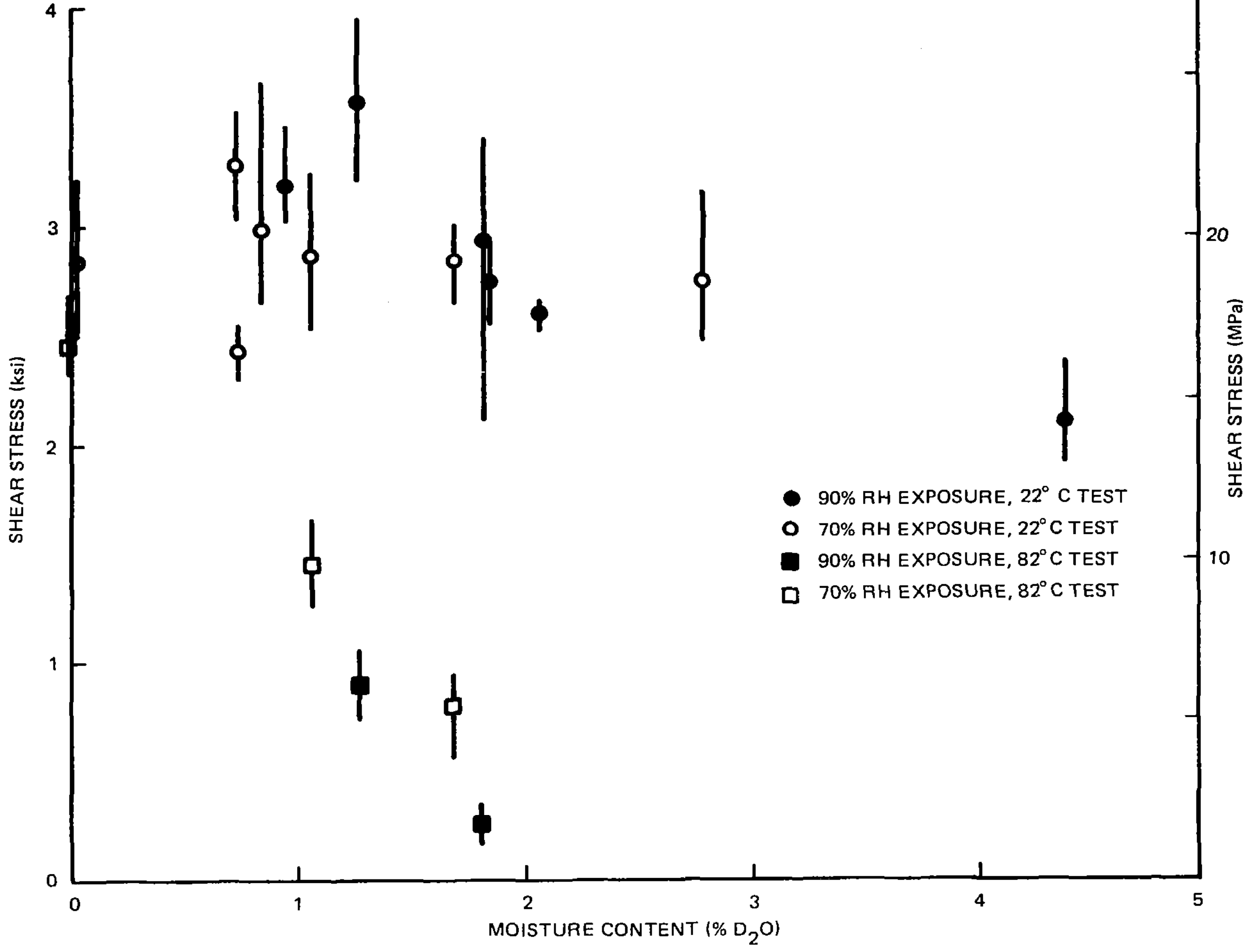


Fig. 32 Effect of Total Adhesive Moisture Content on Shear Stress of EA-9601 Bonded Specimens

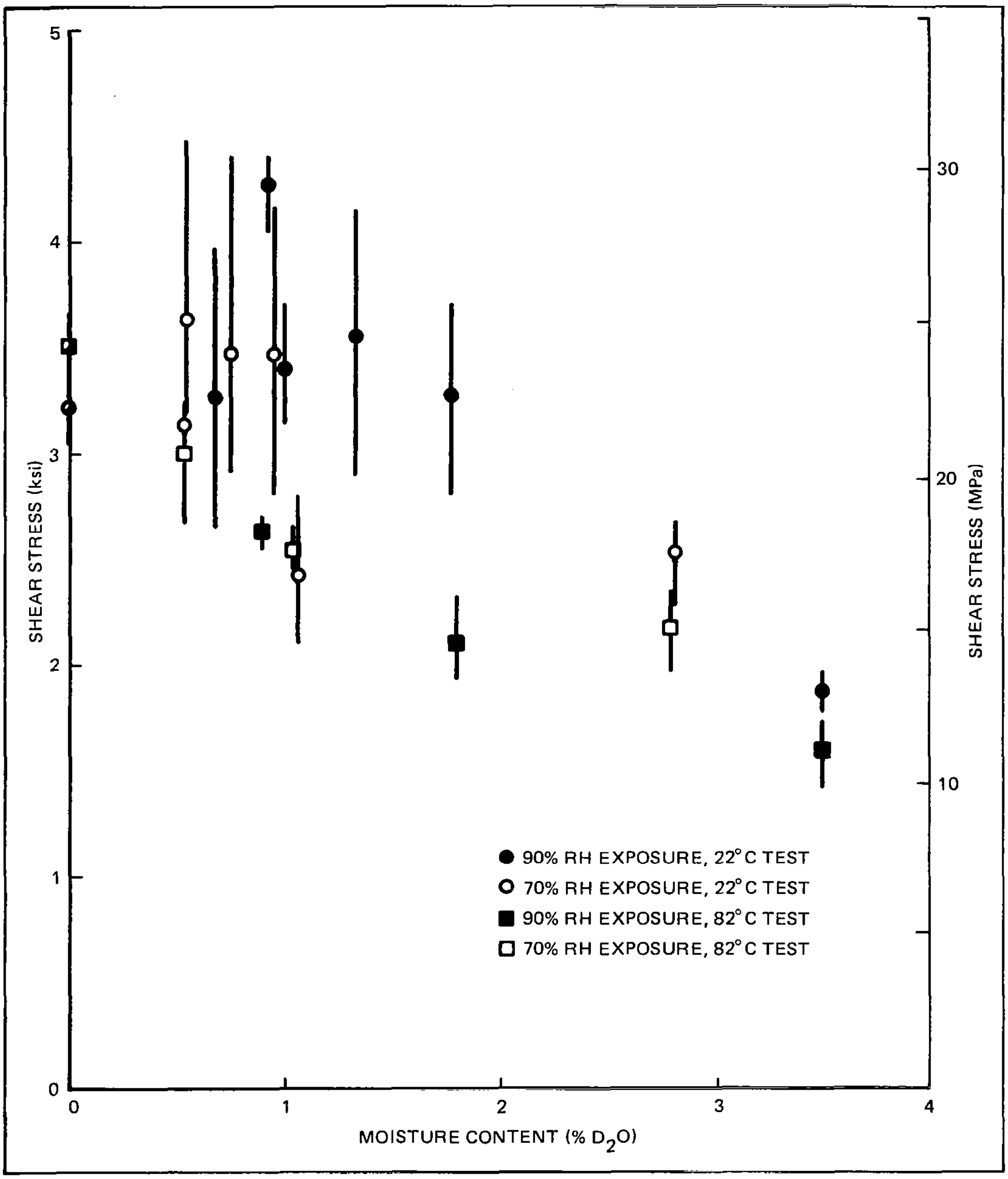


Fig. 33 Effect of Total Adhesive Moisture Content on Shear Stress of FM-300 Bonded Specimens

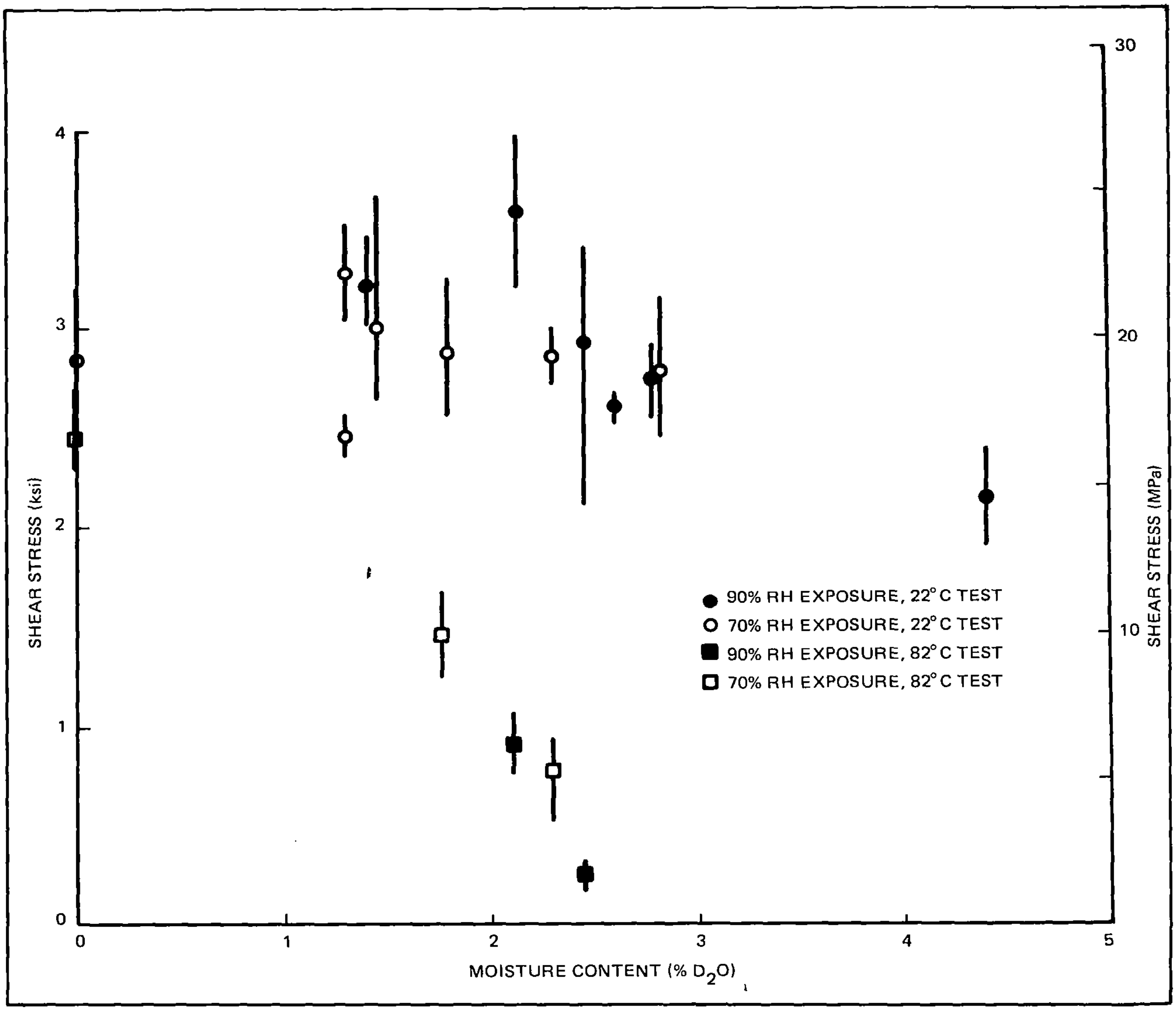


Fig. 34 Effect of Moisture Content in Outer 25% of Adhesive on Shear Stress of EA-9601 Bonded Specimens

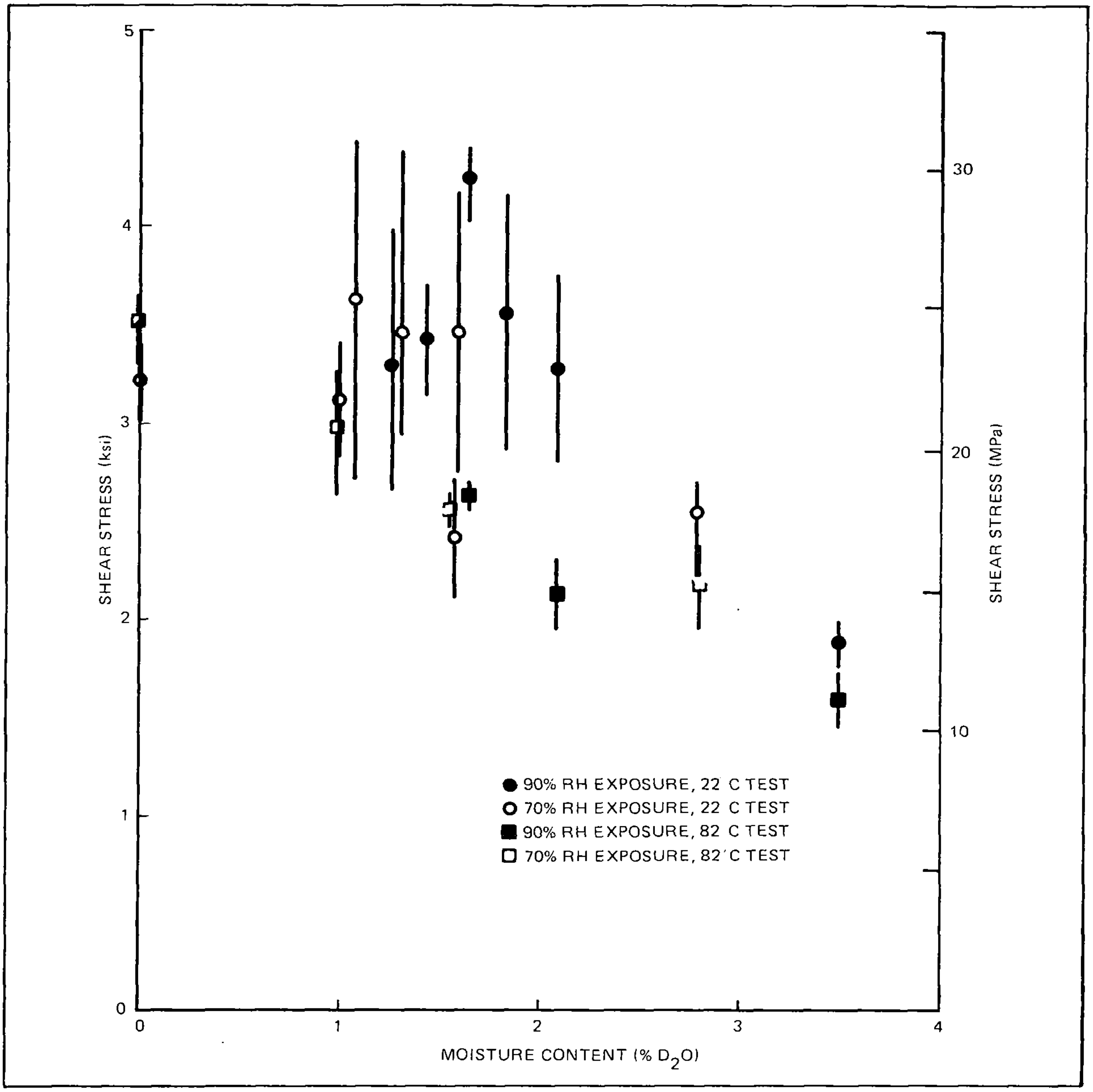


Fig. 35 Effect of Moisture Content in Outer 25% of Adhesive on Shear Stress of FM-300 Bonded Specimens

Overlap shear tests were also performed on specimens conditioned for 12 days at 77°C in H_2O atmosphere (~74% RH). The bulk gravimetric moisture (H_2O) contents are in good agreement with bulk gravimetric D_2O content (see Table 3). The FM-300 and EA-9601 bonded specimens conditioned in H_2O had room temperature shear stresses of 19.7 MPa (2.86 ksi) and 18.9 MPa (2.74 ksi), respectively. These are in good agreement with the shear stresses of the corresponding D_2O conditioned specimens, as listed in Table 6, confirming the equivalence between D_2O and H_2O on mechanical properties.

Considerable scatter is evident in all of the results but the following conclusions can be drawn. The EA-9601 adhesive, at all moisture levels, degraded severely when tested at 82°C. This adhesive is a 121°C curing system and the test temperature is probably at or above the wet glass transition temperature for all moisture levels investigated. Therefore excessive softening, either localized or throughout the adhesive, is likely at the test temperature.

Figures 32-35 show an apparent increase in the shear strength at low nonequilibrium moisture levels (~ 0.5 - 2.0%). These nonequilibrium moisture states are such as to soften the adhesive near the ends of the joint. This tends to make the strain distribution in the joint more uniform and hence enables the joint to work to a higher average stress (total load capacity).

The FM-300 bonded specimens exhibit an improvement in the dry test results at 82°C compared to 22°C results. On the other hand, the EA-9601 bonded specimens show a higher dry shear stress at the lower temperature. This is not inconsistent since a uniform modulus decrease caused by elevated temperature will produce a more favorable stress distribution in both materials. However, this is offset in the EA-9601 specimens by the marked decrease in strength at elevated temperature because of its low glass transition temperature.

4. CONCLUDING REMARKS

The D_2O diffusivity and equilibrium moisture content in AS/3501-5A and FM-300 and EA-9601 adhesives were calculated from gravimetric data at 49° and 77°C, 70% and 90% RH. The composite results are in good agreement with previous results for D_2O and H_2O. The adhesives are well behaved at 49°C but were difficult to characterize accurately at the elevated temperature because the specimens reached equilibrium within 1 day due to their thinness. The EA-9601 adhesive at 77°C, 90% RH exhibited a significant weight loss after 1 day which is ascribed to the exposure temperature exceeding the wet T_g and the resultant loss of lower molecular weight species.

Comparisons between the effect of absorbed D_2O and H_2O environments were in good agreement indicating that the equilibrium moisture content and the moisture diffusivity were unaffected by isotopic substitution in water. The mechanical properties of specimens identically conditioned in D_2O and H_2O are also in agreement and this further substantiates the equivalence of the effects of D_2O and H_2O on the bonded structure.

Nuclear Probe for Deuterium (NPD) measured moisture profiles along the length of the adhesive (adhesive scans) and through the specimen thickness (transverse scan) were integrated to determine the total moisture pickup. A correction for surface adsorption and edge diffusion was applied to the results of the gravimetric measurements and these total moisture absorption results were compared to those from the integrated profiles. Reasonable agreement exists between those results when specimens are exposed at 70% RH but the comparison is less consistent at 90% RH. We believe that the discrepancy occurs because the concentrations of unbound water (water clusters) is substantially larger at the higher relative humidity because of large positive deviations from Henry's Law. These clusters would be disrupted during sectioning and polishing of specimens as well as during the time that the specimens are held under high vacuum prior to nuclear reaction analysis.

The effect of back-diffusion of D_2O from the saturated or nearly saturated adhesive near the edge of the specimen into the innermost plies of the composite was investigated by scanning across the composite-adhesive interface at various distances from the edge of the specimen. In spite of the rather large changes of moisture content along the length of the adhesive, moisture content within the composite was essentially unrelated to the distance from the edge. This would indicate that moisture in the composite is predominantly the result of diffusion occurring through the outer composite faces rather than backdiffusion through the adhesive.

Calculated diffusivities and NPD measured equilibrium moisture contents were used to predict the moisture profiles along the length of the adhesives as a function of exposure time, temperature and relative humidity. These results were compared with the observed moisture profiles to evaluate the extent of enhanced edge diffusion. The FM-300 adhesive exhibits good agreement between measured and predicted profiles at 49°C, 70% and 90% RH, and at 77°C, 70% RH. At 77°C, 90% RH the measured moisture content near the adhesive edge is substantially larger than the predicted level. The EA-9601 adhesive also shows good agreement at 49°C, 70% and 90% RH, but at 77°C, the concentration of D_2O near the edges is enhanced at each humidity level. These results suggest that FM-300 bonded structure cannot be exposed to a combination of high temperature and high relative humidity, and that EA-9601 bonded structure cannot be exposed to high temperature and even moderate humidity without introducing anomalous moisture absorption. These results partially establish a baseline for accelerated moisture conditioning of specimens or structures bonded with typical 121°C and 177°C curing adhesives.

Room temperature mechanical properties of specimens bonded with each of the adhesives are essentially independent of moisture content except near saturation at which point the strength is reduced by 25-40% of the dry strength. However the elevated temperature properties degrade as a function of moisture content. The FM-300 bonded specimens exhibit a slow continuous degradation of strength as a function of moisture content with the fully saturated specimens retaining 45% of the dry elevated temperature shear stress. Degradation of EA-9601 bonded specimens is more severe with the wet strength approaching zero at only one-half of the saturation level for exposure to 90% RH. This is attributed to excessive softening of the adhesive in the high stress region of the joint and the temperature of the test exceeding the local T_g during testing. These results agree with the observed enhancement of edge diffusion in this adhesive and suggest that the upper service temperature in moderate to high humidity environments needs to be reevaluated.

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APPENDIX
SPECIMEN FABRICATION

1. LAYUP OF BASE PANELS

Panels were laid-up as follows, per GM3013 specification. A flat 0.32 x 61 x 91 cm tool plate was buffed and baked at 66°C with release agent Frekote 30, and Tedlar film was held in place on its surface with green mylar tape. The layup was applied to the tool and compacted by warming with an electric iron over TX-1040 release fabric; maximum temperature reached was 54° -60°C as each ply was placed on the stackup. (Plies were cut to size on the layup, using the ply-on-ply technique.) Miltex nylon peel ply was applied to both surfaces of the layup, the first ply being placed directly on the Tedlar, the second ply topmost on the sixth ply of GR/EP.

Corprene dams were applied to the tool plate adjacent to the layup. A ply of porous TX-1040 teflon-coated glass release cloth was placed on top of the upper peel ply, then two plies of style 116 glass cloth bleeder, followed by one ply of Tedlar film cut to fit exactly to the caul plate. Next came the 0.48 cm caul plate, which was taped to the dams with green mylar. Two plies of style 181 glass cloth were next applied and finally a layer of Tedlar film was sealed to Presstite sealant, placed adjacent and peripherally to the Corprene dam.

2. AUTOCLAVE CURE AND POST-CURE CYCLES (per GR-100B)

All panels were placed in a convection autoclave, blanketed on top and cured as follows:

(a) Draw 508 mm Hg (minimum) vacuum on bagged part and place in autoclave.

(b) Apply 0.59 ± 0.03 MPa pressure. Turn vacuum off and check the bag for leakage. The vacuum level shall not fall to 254 mm Hg in 2 minutes or less. If bag fails test, remove part from autoclave, repair bagging defect and repeat steps (a) and (b).

(c) If bag passes leak check, apply 508 mm Hg (minimum) vacuum to part and reduce autoclave pressure to 0.

(d) Heat part from 49°C to 107°C ± 6°C in 45 to 95 minutes maintaining 508 mm Hg minimum vacuum on part.

(e) When part reaches 107°C, pressurize autoclave to 0.59 ± 0.03 MPa.

(f) Hold 107°C + 6°C, - 0°C, 0.59 ± 0.03 MPa, and 508 mm Hg (minimum) vacuum for 50 to 60 minutes.

(g) Reduce vacuum to 51 mm Hg maximum. Raise part temperature to 177 ± 6°C in 45 to 95 minutes.

(h) Hold 177 ± 6°C, 0.59 ± 0.03 MPa, and 51 mm Hg maximum vacuum for 60 ± 5 minutes.

(i) While maintaining 0.59 ± 0.03 MPa and 51 mm Hg maximum vacuum, cool down the laminate as follows:

- From 177°C - 121°C in not less than 100 minutes at a rate of 0.6 ± 0.3°C/minute (maximum).
- From 121°C - 66°C in not less than 80 minutes at a rate of 0.7 ± 0.3°C/minute (maximum).

(j) At 66°C or less part temperature, apply 508 mm Hg (minimum) vacuum to part and reduce autoclave pressure to 0. Remove part from autoclave.

(k) Remove bag and bleeder system and oven post cure as follows:

- Raise the temperature to 93°C and hold for 15 minutes.
- Raise the temperature to 121°C and hold for 15 minutes.
- Raise the temperature to 149°C and hold for 15 minutes.
- Raise the temperature to 177°C and hold for 8 + 0.5,- 0 hours.
- After 8 hours cool down to 66°C at a rate of 0.5 - 1.1°C/minute.

3. ADHESIVE BONDING (per GSS20350)

Bonding cycles were as follows

a. 60 minutes to cure temperature at 0.28 MPa
b. 60 minutes hold at cure temperature at 0.28 MPa
c. cool down to 52°C in 60 minutes at 0.28 MPa