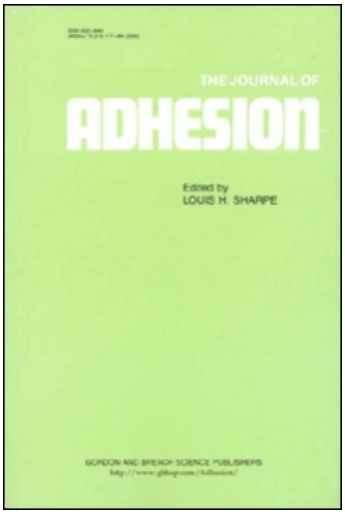

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The Effect of Moisture Content in Epoxy Film Adhesives on their Performance. II. T-Peel and 105°C Lap Shear Strength

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INTRODUCTION

The benefits of adhesively bonded structures are well known. However, the most significant factor limiting the extensive application of metal bonding in primary aerospace structures is the prevailing lack of confidence in its long term durability under hostile environmental conditions.[1,2]

Furthermore, prepregs and adhesive films are B-stage products consisting of a partially reacted mixture of monomers impregnated into a reinforcement. Consequently, during shipping and storage prior to use, reaction may continue. The extent of curing or "age" of the prepreg will depend upon the conditions (temperature, humidity and time) to which it has been exposed.[3–10]

As shown earlier,[10] an uncured epoxy film adhesive absorbs moisture during storage with a resulting reduction in bond shear strength. However, preconditioning of B-staged adhesives under 3-5 mmHg vacuum for a controlled period of time at room temperature was found to remove moisture and, consequently, shear bond strength was regained. The recommended method was effective when the absorbed moisture content was below ~0.3% (weight). Above this threshold value, irreversible

deterioration occurred and drying resulted only in partial recovery of the adhesive bond shear strength.

The objective of the present study was to determine the effect of the recommended preconditioning method on the bond peel strength and the high temperature—(105°C) lap shear strength of aged epoxy film adhesives, FM-73 and FM-300K.

FTIR analysis of the fracture surface, thermal neutron radiography and mechanical testing were used to evaluate the effect of absorbed and desorbed moisture in the uncured film adhesive on the ultimate T-peel and 105°C lap shear strength and bond line porosity.

EXPERIMENTAL

Materials and processes

Two commerical film adhesives were studied: FM-73 and FM-300K, supported epoxy film adhesives, and primer BR-127 (Bloomingdale Divisions of American Cyanamid). Details of the curing conditions, adherends, primer application, and surface treatment are given in Table 1. Storage period or "age" of the adhesives was 6–42 months (refrigerated at −18°C and sealed in polyethylene bags).

TABLE I

Adhesive	Curing conditions T(°C), P (MPa), t (hours)	Adherends and primer
FM-73	120°C, 0.25 MPa, 1½ hours	Adherends were 2024-T351 bare aluminium, etched by the FPL (Forest Products Laboratory) method. A thin layer of BR-127 primer was applied by spraying and cured for 30 minutes at room temperature followed by 1 hour 120°C
FM-300K	177°C, 0.25 MPa, 2 hours	"

The film adhesives under investigation were passed through various humidifying (100% R.H.) and drying (3-5 mmHg gauge vacuum) cycles. In each cycle the moisture gain or loss was determined by weighing. T-peel and lap shear strength were determinded as a function of moisture lost or gained.

The drying and humidifying processes were performed as described in Part I[10]; a schematic description of the experimental procedures is also given there.

Mechanical tests

Tensile lap shear specimens were prepared according to ASTM D-1002-72. T-peel specimens were prepared according to ASTM D-3167-73T. Five specimens were fabricated for each test using a special mold under compression. Bondline thickness for all specimens was 0.10 ± 0.03 mm.

The bond strength was measured by mean of an Instron Mechanical Tester (crosshead speed 2 mm/min (Lap Shear Strength—L.S.S) and 200 mm/min (T-peel) at 25°C and 105°C. The mode of failure (adhesive or cohesive) was evaluated by visual inspection.

Spectroscopic analysis

Infrared spectra of the aluminium adherend surfaces after fracture of the adhesively bonded samples were obtained in a FTIR Nicolet 5DX. The External Specular Reflectance mode was used. In addition, it was equipped with horizontal stage in near to normal incidence, with a gold mirror for reference.

Thermal neutron radiographs of the bonded specimens with FM-73 (stored for $1\frac{1}{2}$ years), before and after preconditioning (2 and 4 hours of vacuum drying), were taken at Sorek Nuclear Research Center. The analysis was performed by the method described in Ref. 11.

Void content (visually, by count) was calculated by the following equation:

Void (area) (%) = total area of voids × 100%/area of specimen.

RESULTS AND DISCUSSION

T-peel strength values (Table II) of FM-300K have shown conclusively that it has degraded markedly during storage (24 and 42 months at − 18°C). The reduction found was in the range of 50%. T-peel strengths of FM-73 have exhibited no change when the adhesive was subjected to long term storage, although the lap-shear strength exhibited a significant reduction.[10]

Weight change during preconditioning (drying) of the uncured film adhesive and the effect on T-peel and 105°C lap shear strengths

Weight changes (the percentage weight loss based on initial film weight as

TABLE II
The effect of drying on T-peel strength and weight change of FM-73 and FM-300K film adhesives

Adhesive type	FM-73 (1½ years)		FM-73 (1 year)		FM-300K (3½ years)		FM-300K (2 years)	
Drying time (hours)	T-Peel (a) (Lb/inch)	Weight change (%)	T-Peel (a) (Lb/inch)	Weight change (%)	T-Peel (a) (Lb/inch)	Weight change (%)	T-Peel (a) (Lb/inch)	Weight change (%)
0	$45.6^{\pm 1.3(b)}$	—	$47.1^{\pm 0.0(b)}$	—	$5.4^{\pm 0.0(c)}$	—	$5.6^{\pm 0\ (c)}$	—
1.0	$44.8^{\pm 0.0}$	0.30	$49.7^{\pm 0.6}$	0.04	$6.9^{\pm 0.2}$	0.28	$7.8^{\pm 1.1}$	0.19
2.0	$43.0^{\pm 0.6}$	0.77	$44.8^{\pm 0.0}$	0.02	$12.3^{\pm 1.1}$	0.36	$11.6^{\pm 0.6}$	0.26
2.5	$44.9^{\pm 0.0}$	0.80	$44.8^{\pm 0.0}$	0.05	$14.6^{\pm 0.0}$	0.50	$13.1^{\pm 0.6}$	0.30
3.0	$40.7^{\pm 1.3}$	1.01	$37.7^{\pm 0.6}$	0.05	$13.8^{\pm 0.6}$	0.45	$9.5^{\pm 0.6}$	0.34
3.5	$41.1^{\pm 0.7}$	1.10	$39.2^{\pm 0.0}$	0.10	$12.3^{\pm 0.0}$	0.54	$10.8^{\pm 0.6}$	0.35
4.0	$42.6^{\pm 2.2}$	1.03	$38.5^{\pm 1.7}$	0.12	$11.6^{\pm 0.6}$	0.45	$9.5^{\pm 0.0}$	0.32

(a) T = 25°C, average of 5 test specimens ± standard deviation. (b) Catalog value 45 Lb/inch.
(c) Catalog value 10.8 lb/inch.

TABLE III

The effect of humidifying—drying cycles on lap shear strength of FM-73 and FM-300K film adhesives

Adhesive type	FM-73 (Storage age: 1½ years)		FM-300K (Storage age: 3½ years)	
Specimen type (a)	L.S.S. (psi) (b)		L.S.S. (psi) (b)	
Temperature test °C				
Preconditioning	R.T.	105°C	R.T.	105°C
No preconditioning	$4150^{\pm 100}$	$760^{\pm 60}$	$3420^{\pm 35}$	$2880^{\pm 180}$
1st drying cycle (c)	$4630^{\pm 50}$	$1120^{\pm 20}$	$3790^{\pm 20}$	$3605^{\pm 60}$
1st rehumidifying cycle (d)	$4000^{\pm 50}$	$1060^{\pm 100}$	$3690^{\pm 100}$	$2980^{\pm 90}$
2nd drying cycle (c)	$4520^{\pm 90}$	$1600^{\pm 90}$	$3370^{\pm 140}$	$3075^{\pm 75}$

(a) Average of 5 test specimens ± standard deviation.
The test specimens showed cohesive bond failures in all cases.
(b) L.S.S.—Lap Shear Strength.
(c) 3-5 mmHg 2.5 hours, ~0.3% weight loss.
(d) ~0.3% weight gain.

a function of drying time under vacuum), T-peel and 105°C lap-shear strength are listed in Tables II and III for desiccated (0 to 4 hours) film adhesives. The test specimens show cohesive failures in all cases.

As can be seen in Table II, a significant initial enhancement in bond T-peel strength was achieved for FM-300K, and a smaller or no change for FM-73, by drying before cure. In case of FM-300K, the greater the decrease in sample weight (0.2–0.6%) the larger the increase in T-peel strength. However, following 3–4 hours of drying, there seems to be some inconsistency in the results.

Figure 1 illustrates T-peel and lap-shear strength *vs.* drying time of FM-300K stored for 2 years. Figure 2 shows T-peel strength *vs.* weight change for two batches of FM-300K (stored for 3½ years and for 2 years). It can be observed that, at low levels of volatile removal (~0.3%), the bond strength (T-peel) improved from substantially differing storage age batches to give similar T-peel results. Later, some inconsistency appears.

Generally, longer drying periods (3–5 hours and >0.3% wt. loss) resulted in inconsistent behaviour. This phenomenon may be due to the removal of residual solvent or diluent which reduces flow in the subsequent cure step.[4] Although lap shear strength increased during drying of FM-73[10], T-peel results showed minor or no changes.

The drying method—2.5 hours at 3-5 mmHg (vacuum)—is even more

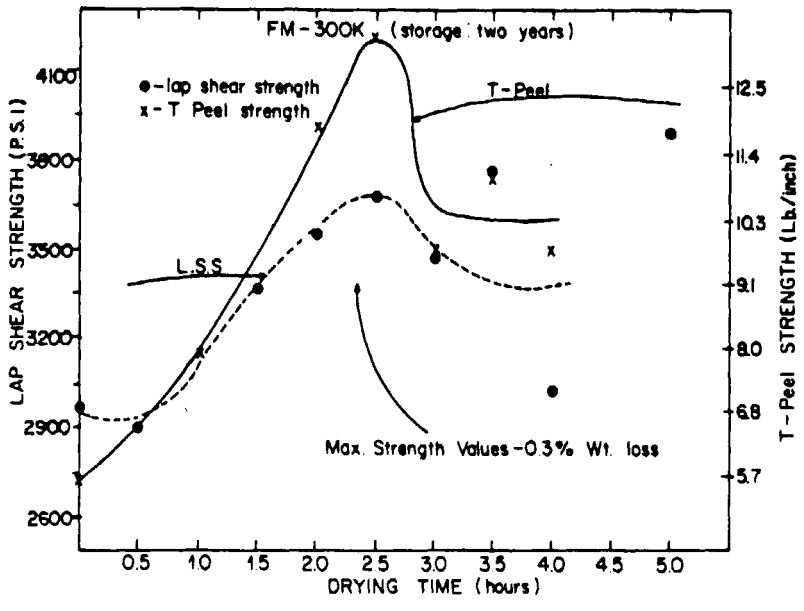

FIGURE 1 Lap shear and T-peel strength *vs.* drying time

effective for elevated temperature (105°C) lap shear strength. The data in Table III shows that while the RT lap shear strength increased by about 11–12%, the 105°C values increased by 47% for FM-73 and 25% for FM-300K. The difference in 105°C shear strength improvement between FM-73 and FM-300K can be explained by the lower high-temperature performance of FM-73.

Porosity

Thermal Neutron Radiography enables the examination of a thin adhesive layer (0.1 mm) through a thick aluminium metal layer (0.5–1 mm)[11] to be made. The results are summarized in Table IV. Figures 3 and 4 show photographs of T-peel fracture surfaces. It was observed that when the film adhesives were subjected to longer drying periods some additional porosity appeared in both FM-73 and FM-300K. However, in case of FM-73 ($1\frac{1}{2}$ years) the pores are larger and more pronounced (Fig. 3, void content $\sim 20\%$) than that in case of FM-300K (2 years) (Fig. 4, void content $< 1\%$) while the bond strength improvement of FM-300K is more pronounced than that of FM-73 (Table II).

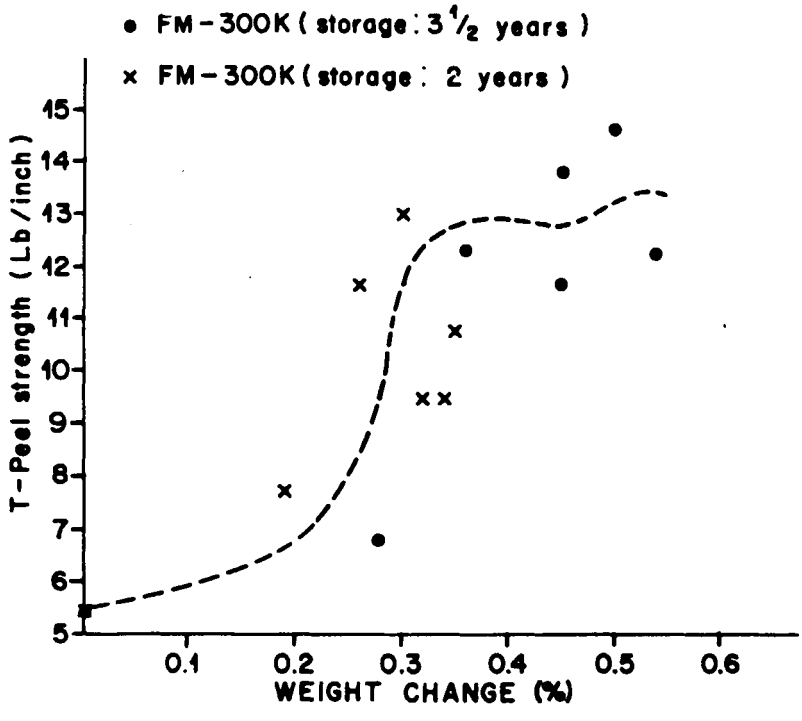

FIGURE 2 T-peel strength *vs.* weight change for FM-300K.

It seems that the strengthening of FM-73 in lap shear[10] in spite of the increased void content is due to the greater effect of water desorption compared to the weakening effect of porosity.

In both cases, longer drying times (4 hour) which caused more porosity did not contribute to bond strength improvement.

FTIR analysis

FTIR spectra of adherend fracture surfaces after bonding with FM-73 and FM-300K, following drying for various durations before cure, were determined. Since the failure was cohesive the two adherend's surfaces exhibited identical IR spectra. The objective of these measurements was to relate the chemical composition and moisture content of cured adhesive systems to weight loss during drying of adhesive before cure.

TABLE IV
Void content in FM-73 and FM-300K film adhesives

Adhesive type	Void content, %	
Drying time (hours)	FM-73 (a) (1½ years)	FM-300K (b) (2 years)
0	0	0
2	8	<1
4	20	<1

(a) Additional large pores.
(b) Additional little pores.

Examination of infrared spectra of the moisture-containing films showed that the marked changes in both adhesives, FM-73 and FM-300K, occur in the 3400–3500cm^{-1} region.

The strong band at 3450 cm^{-1} is assigned mainly to hydroxyl groups of absorbed moisture. The intensity decrease at 3450 cm^{-1} suggests loss of water molecules during drying. Any concurrent changes in the hydroxyl content of the adhesives[12] would probably be minor in comparison with the changes observed in the moisture content.

Since alkyl groups absorb at 2933–2948 cm^{-1} the absorption at 2934 cm^{-1} was chosen as an internal reference for determination of changes in water content. The water content was adequately and conveniently monitored by simply comparing the infra-red bands at 3450 cm^{-1} with the internal standard at 2934 cm^{-1}. The IR absorption ratio, 3450/2934 cm^{-1}, for FM-73 and FM-300K was plotted *vs.* weight changes in Figure 5. It represents, mainly, the moisture loss *vs.* weight loss during drying of precured adhesive.

The results (Fig. 5) clearly indicate a linear relationship between weight loss in the adhesives, before curing, and the reduction of IR water absorbance after curing, up to ~0.3% weight change. At a higher weight loss inconsistency appears, probably because longer drying periods (higher weight changes) caused a removal of volatiles or diluents other than water, which could not be identified clearly in the IR spectra.

These results parallel the trends which were observed by mechanical (RT Shear, RT Peel, 105°C shear) bond strength behavior.[10]

Effect of preconditioning (humidity exposure and redrying cycles) on T-Peel and 105°C lap shear strength

The question which remains to be answered is whether the desiccated adhesive can regain its original performance following a few cycles of precure humidity exposure and drying.

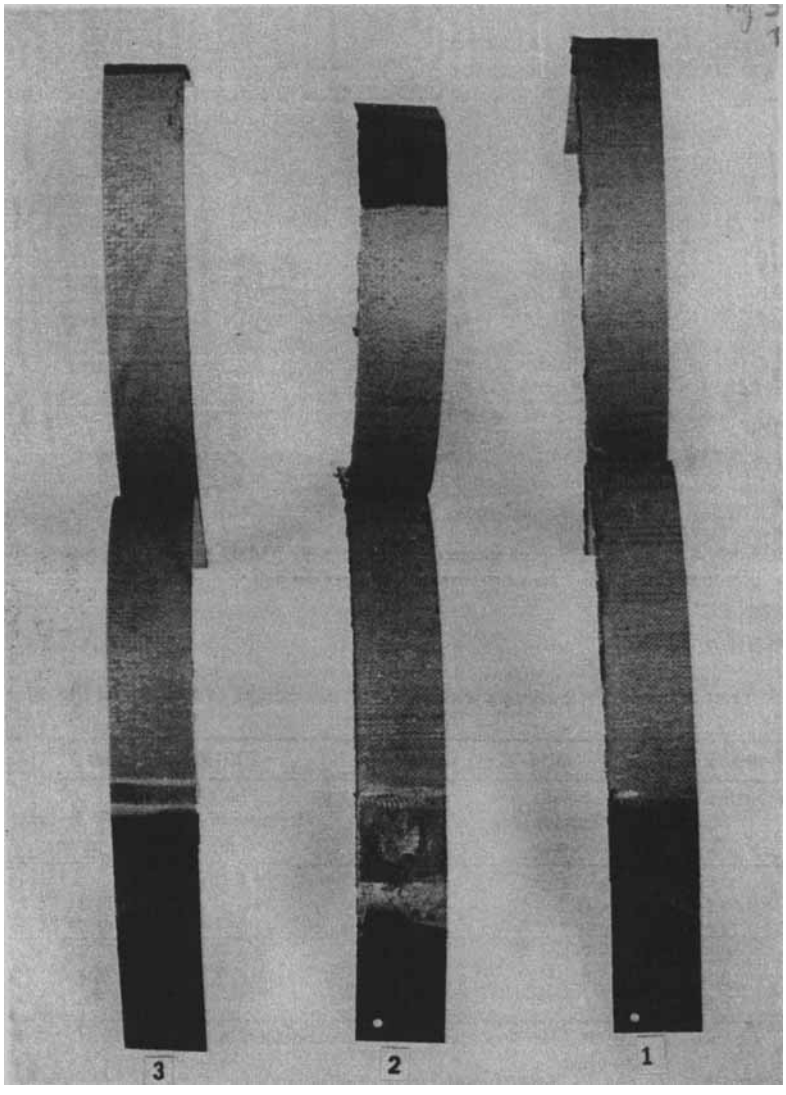

FIGURE 3 Fractured T-peel specimen bonded with FM-300K (storage: 2 years). (1) No preconditioning. (2) 2 hours drying. (3) 4 hours drying.

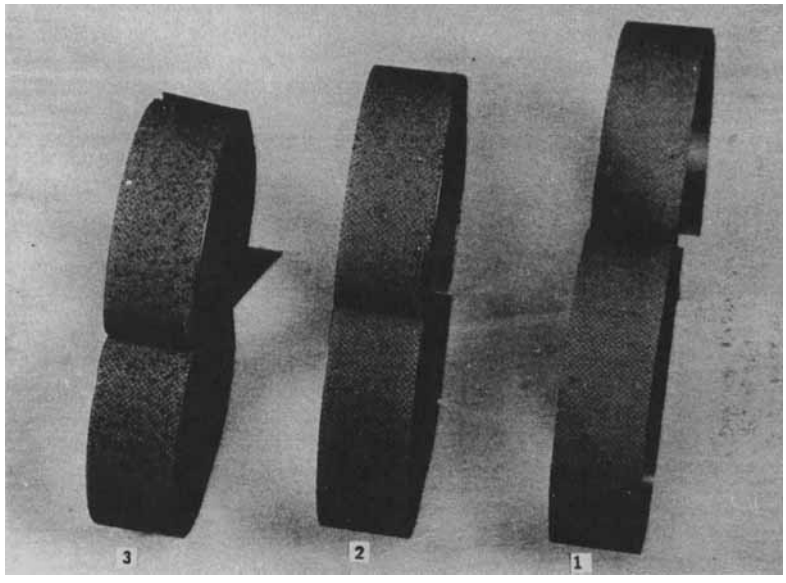

FIGURE 4 Fractured T-peel specimen bonded with FM-73 (storage: 1½ years). (1) No preconditioning. (2) 2 hours drying. (3) 4 hours drying.

TABLE V
The effect of humidifying-drying cycles on T-peel (a) strength of FM-73 and FM-300K film adhesives

Adhesive type	FM-73 (1½ years)		FM-300K (3½ years)	
Moisture added (c) %	1st Rehumidifying cycle	2nd drying cycle	1st Rehumidifying cycle	2nd drying cycle
0.0	43.0 (b)		12.3 (b)	
0.1	$41.7^{\pm 0.5}$	$40.8^{\pm 0.5}$	$11.2^{\pm 0.0}$	$11.3^{\pm 0.0}$
0.2	$38.3^{\pm 0.5}$	$39.3^{\pm 0.0}$	$11.0^{\pm 1.5}$	$11.4^{\pm 0.2}$
0.3	$35.9^{\pm 0.0}$	$35.1^{\pm 0.5}$	$8.3^{\pm 0.5}$	$11.7^{\pm 0.5}$
0.5	$37.0^{\pm 0.0}$	$37.0^{\pm 0.9}$	$6.3^{\pm 0.9}$	$6.4^{\pm 0.4}$
0.6	$31.4^{\pm 0.0}$	$35.5^{\pm 0.6}$	$5.7^{\pm 0.1}$	$7.0^{\pm 1.3}$

(a) Lb/inch, average of 5 test specimens ± standard deviation, RT.
(b) After 1st drying cycle.
(c) Weight gained in 1st rehumidifying cycle.

Tables III and V show the T-peel and 105°C lap shear of FM-73 and FM-300K following drying for 2.5 hours (3.5 mmHg) and exposure to humidity (100% RH) prior to curing. Moisture level was

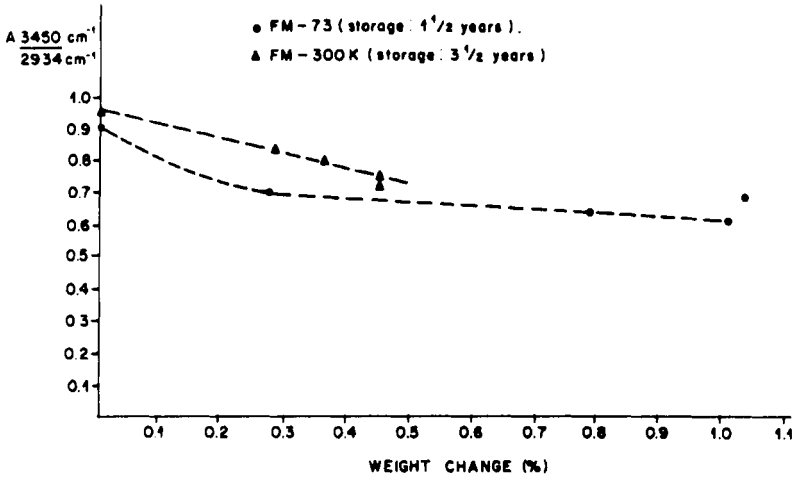

FIGURE 5 A 3450cm^{-1}/2934 cm^{-1} *vs.* weight change for FM-73 and FM-300K.

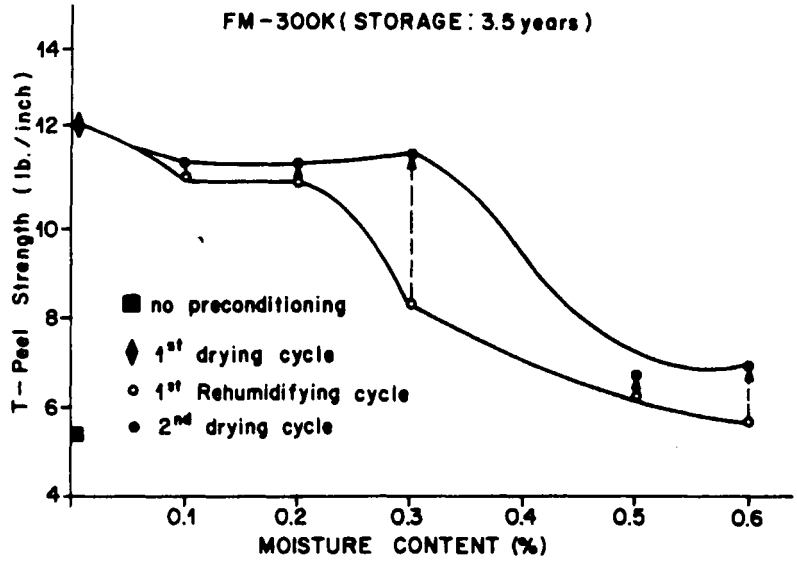

FIGURE 6 T-peel strength *vs.* moisture content for FM-300K after various drying-humidifying cycles.

determined by weight changes of the uncured film adhesive.

As shown in Tables III, and V, the lap shear (RT and 105°C) and T-peel (RT) strengths have deteriorated as the moisture content increases. Redesiccation (after exposure to humidity of the uncured samples) resulted in consistently high bond strength. However, samples which absorbed more than ~0.3% moisture did not regain their original strength. Figure 6 illustrates this phenomenon for FM-300K (T-peel bond strengths). This phenomenon may be attributed to irreversible mechanisms occurring at higher moisture levels such as hydrolysis and homopolymerization. On the other hand, the reversible mechanisms may be the result of plasticization and hydrogen bonding in the matrix phase.[6-10]

Further investigation is planned in order to elucidate these reversible and irreversible mechanisms.

CONCLUSIONS

When the moisture level in FM-73 and FM-300K film adhesives is above some threshold value (~0.3%), strength (T-peel and 105°C lap shear) can only be partially regained by drying. Furthermore, some porosity is generated in the bond line. Above this critical moisture level, irreversible changes occur in the B-stage adhesive which result in a permanent loss of properties.

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