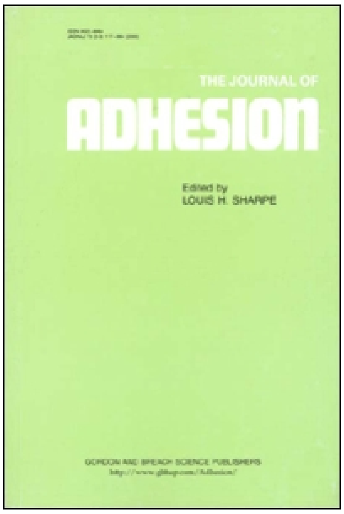

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The Effect of Moisture Content on the Performance of Epoxy Film Adhesives. Part IV. Aluminum-Filled Epoxy

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The effects of moisture content in a B-staged, aluminum-filled epoxy film adhesive on the final shear and peel strengths of the fully cured system were studied.

The effects of moisture pick-up were first characterized with respect to the optimal drying time of the B-staged, filled epoxy adhesive. Pre-drying was followed by remoisturizing to various levels and subsequent dehumidifying (re-drying), with the objective of investigating the effect of reversible and irreversible changes on the cured adhesive shear and peel properties.

Mechanical test results, as well as electron microscopy and infra-red spectroscopy of the fracture surfaces, have indicated that pre-drying of unpacked adhesive for 3.5 hours, which has been stored at low temperature (−18°C), is very effective in upgrading mechanical properties, especially peel strength. Moisturizing pre-dried samples, at increasing levels, resulted in degradation of properties. However, a subsequent drying treatment of the uncured adhesive was demonstrated to enhance recovery of properties, provided the moisture level did not exceed 0.3% (of the total material). The adverse consequences of high moisture pick-up were manifested in matrix porosity and debonding of the aluminum filler and nylon carrier from the epoxy matrix. Dehumidifying from moisture levels above 0.3% had the same consequences. FTIR (Fourier Transform I.R.) absorption peaks corresponding to water, hydrogen bonding and Dicy (dicyandiamide), have been correlated with the moisture level in the pre-cured adhesive. The possible chemical hydrolysis of Dicy was identified as one of the main mechanisms contributing to degradation of mechanical properties.

KEY WORDS Moisture effect; B-staged epoxy adhesives; aluminum-filled epoxy; drying; dicyandiamide; FTIR; SEM.

INTRODUCTION

Adhesives are commonly employed in the aerospace industry in some of the most critical areas of primary structures exposed to highly demanding environments. To meet the high performance requirements structural adhesives are evaluated thoroughly in their uncured as well as the cured state, using a variety of testing methods.

Epoxy-based film adhesives contain in their uncured state both the base epoxy prepolymer and the appropriate curing agents as well as toughening agents and, in most cases, a carrier. Consequently, film adhesives, such as composite prepregs, require storage in below-freezing temperatures (−18°C) in order to prevent premature curing.

It has been shown that, besides elevated temperatures, moisture in uncured film adhesives degrades the quality of the cured adhesive.[1,2,3,4] Several mechanisms have been suggested to explain the decline in properties, among them hydrogen bonding between water molecules and the polar epoxy moieties, hydrolysis of the epoxide group and homopolymerization in the presence of water. Systematic studies carried out by the authors have shown[1,2,3,4] that vacuum drying of the uncured epoxy adhesive system may reverse some of the adverse effects of the moisture to the point of regaining properties equivalent to those of moisture-free adhesives, provided that the moisture level is below a certain threshold value (~0.3%). In the above-mentioned studies, the investigation was limited to 250°F and 350°F curing film adhesives, formulated to meet performance requirements in service at 250°F (121°C) and 350°F (177°C), respectively. To enhance further the thermal performance of structural adhesives, aluminum powder is commonly added to the 350°F curing epoxy system, resulting in acceptable properties at 400°F (204°C). In addition to the thermal benefit, the aluminum filler increases the rigidity as well as the thermal conductivity of the epoxy adhesives. The inclusion of the fine metallic fillers, such as aluminum, may introduce into the adhesive some deficiences, due to their relatively large surface area, such as increased moisture absorption prior to cure. Furthermore, as a result of the large differences in rigidity and thermal expansion coefficient between the aluminum and the polymeric constituents, thermal stresses may develop in the cured adhesive. The presence of aluminum filler in the epoxy network turns the polymer adhesive into a particulate composite with characteristics that determine the final properties of the composite adhesive. Among the most important ones are the interfacial interactions between the filler and the polymer.

The objective of the present study is to elucidate the effects of absorbed and desorbed moisture in B-staged, aluminum-filled, structural epoxies on their cured peel and lap shear properties. The methodology used has been described in previous publications,[1,2,3] using moisturizing steps to various levels followed by vacuum drying. In each step the adhesives were cured and characterized with respect to their mechanical properties. FTIR was used to study chemical changes due to moisture presence during cure and, finally, microstructural analysis was performed, in the particulate composite adhesive, using electron microscopy.

EXPERIMENTAL

Methodology

Prior to the study concerning the effects of moisture level in uncured adhesives on the mechanical properties of the resulting joints, a detailed analysis was performed to determine the composition of the composite film adhesive. In the preliminary investigation, the epoxy resin system was separated from the aluminum filler and thermoplastic carrier by means of a centrifuge, using chloroform as a solvent. Following drying of the filler and carrier, their weights were determined and the morphology and structure examined using a scanning electron microscope. The residual solution was filtered and the solid part was identified by infra-red analysis. The volatile portion of the filtrate was then evaporated and the solid residue analysed once more by infra-red.

Following completion of the preliminary study, two samples of the aluminum-filled adhesive, one and six years old, respectively, were vacuum dried at intervals of half-an-hour for up to 4.5 hours (1st drying cycle). Subsequently, the mechanical properties of cured joints in shear and peel were evaluated, the weight change determined, and the fracture surfaces analysed using electron microscopy and infra-red spectroscopy. Finally, the uncured adhesive was exposed to moisture followed by vacuum drying to determine the threshold point for reversible-irreversible effects of humidity. Consequently, the 1- and 6-year samples were moisturized to various levels (1st rehumidifying cycle) and the respective cured properties evaluated. Uncured samples were then vacuum dried (2nd drying cycle), and the properties re-evaluated. The sequential drying, humidifying and re-drying was followed by a rigorous microstructural analysis by means of electron microscopy and FTIR.

MATERIALS AND CONDITIONING

A commercial aluminum-filled epoxy film adhesive—FM 400, and the corresponding primer—BR 400 (American Cyanamid), were used throughout the present investigation. Curing was carried out at 350°F and 45 psi. Heating time to 350°F was 1 hour followed by 1 hour at the curing temperature. The primer was applied by spraying, followed by drying at room temperature for 30 minutes and curing for 1 hour at 225°F.

The adherends were bare aluminum 2024-T351, etched by the conventional FPL (Forest Products Laboratory) method.[1,2,3]

The adhesive used was stored at −18°C in sealed polyethylene bags; one batch had been stored for 1 year and the second for 6 years prior to commencement of the study. Drying of the adhesive samples was caried out in 3–5 mm Hg vacuum and humidifying by exposure to 100% relative humidity at ambient temperature for various periods of time (1–5 hours). Following each conditioning step the weight loss (drying) or weight gain (humidifying) was determined.

MECHANICAL TESTS

Tensile lap shear specimens were prepared according to ASTM D-1002-72. T-peel specimens were prepared according to ASTM D-1876-72. Five specimens were fabricated for each test, using a special compression fixture. Bondline thickness for all specimens was 0.10 ± 0.03 mm.

The bond strength was measured by means of an Instron Mechanical Tester using a cross-head speed of 2 mm/min (Lap Shear Strength—LSS) and 200 mm/min (T-peel) at 25°C. The mode of failure (adhesive or cohesive) was evaluated by visual inspection.

SPECTROSCOPIC ANALYSIS

Infra-red spectra of the fractured T-peel surfaces were obtained by FTIR using a Nicolet 5DX spectrophotometer. The external specular reflectance mode, with a horizontal stage in near-to-normal incidence, was used. A gold mirror served as a reference.

SEM/EDAX

The surfaces of the fractured T-peel specimens were examined in a Jeol SEM Model JSM 840 connected to an Energy Dispersive Analyser—Link Systems Model 860.

The specimens were Au–Pd coated prior to examination to suppress charging of the surfaces. It was assured that the EDAX operation conditions were such that only the Al filler was detected and no Al signal due to the Al adherend could interfere with measurements.

RESULTS AND DISCUSSION

Adhesive composition

Since FM-400 is a composite adhesive that contains aluminum particulates and a carrier, the first step of the investigation comprised a detailed compositional analysis.

Following the experimental procedures described earlier, dissolving of the uncured adhesive revealed the carrier and aluminum particulates. Figure 1 is an electron micrograph of the special knitted carrier that has been identified as nylon comprising 4% of the adhesive weight. Figure 2 depicts the aluminum particulates which were determined to constitute 55% of the adhesive weight.

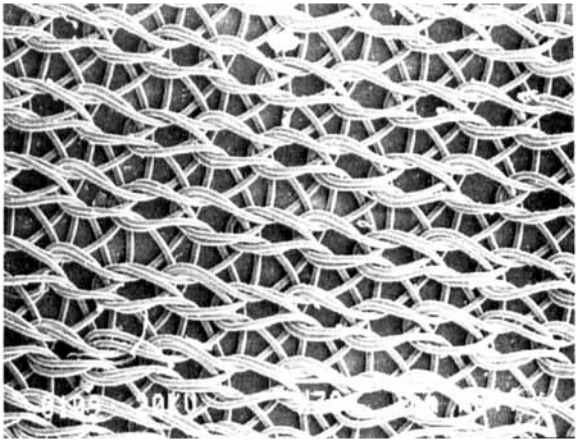

FIGURE 1 Electron micrograph of adhesive carrier (×30).

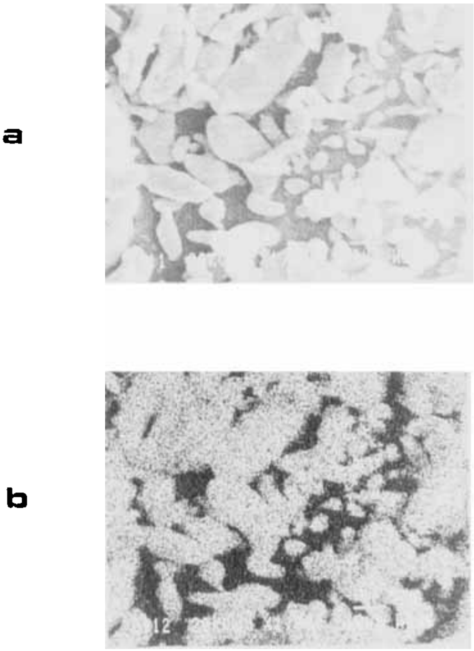

FIGURE 2 Electron micrograph (a) and EDAX imaging (b) of the aluminum filler (×1000).

As can be seen in Figure 2a, the size distribution of the filler is wide, from a few microns to more than 40 microns. The particulates were positively idenfied as aluminum using the EDAX technique, as shown in Figure 2b.

Filtration of the residual turbid solution separated the solid organic material from the dissolved one. The solid phase was characterized by FTIR and the results are given in Figure 3. The infra-red spectrum of the solid residue was identified to be typical of dicyandiamide (Dicy). The filtrate was further analysed by FTIR and was found to be tetraglycidyl-4-4′-diamino diphenyl methane (TGGDM), as shown in Figure 4. In short, the base epoxy (TGGDM) and the curing agent (Dicy), as identified, constitute the resin system in FM-400.

The effect of drying on mechanical properties

Following the compositional study, the next stage of the study included vacuum drying and the characterization of its effect on the lap shear and peel strengths of the aluminum-filled adhesive. Table 1 summarizes the results for the 1- and 6-year-old samples following vacuum drying of the pre-cured adhesive, for different time periods.

The experimental results demonstrate that the storage of the adhesive for 1 or 6 years (at −18°C) resulted in degraded shear properties compared to the catalog values −3780 psi, while no reduction and even increase in peel properties was obtained compared to the catalog value of 8 lb/inch. FM-73[1,2,3] gave a similar response to long term storage, while FM-300[1,2,3] exhibited a decline in T-peel strength following storage. Figure 5 depicts the variation of shear and peel strengths with drying time for the 1 (5a) and 6 (5b) year old adhesive specimens. Generally, at the initial stages of drying properties increased, followed by a decrease at longer drying times. This was also the case for another Dicy cured adhesive (FM-300) compared to the non Dicy curing system (FM-73) which did not exhibit a pronounced enhancement in properties with increasing drying duration. It is interesting to note that the T-peel strength of the dried adhesive almost doubled compared to the non-dried sample and, even more importantly, compared to the reported catalog value of 8 lb/inch.

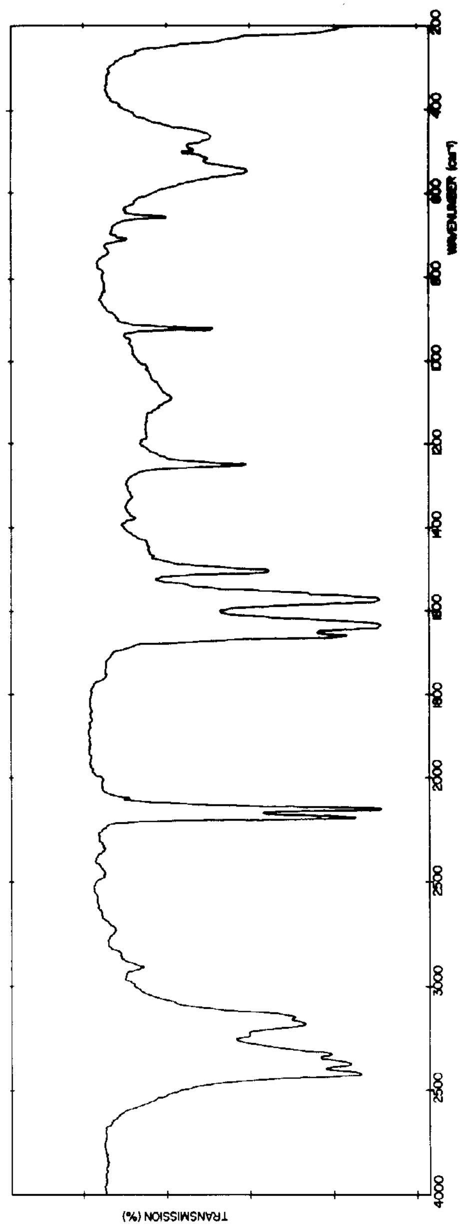

FIGURE 3 FTIR spectrum of the organic solid phase identified as dicyandiamide (Dicy).

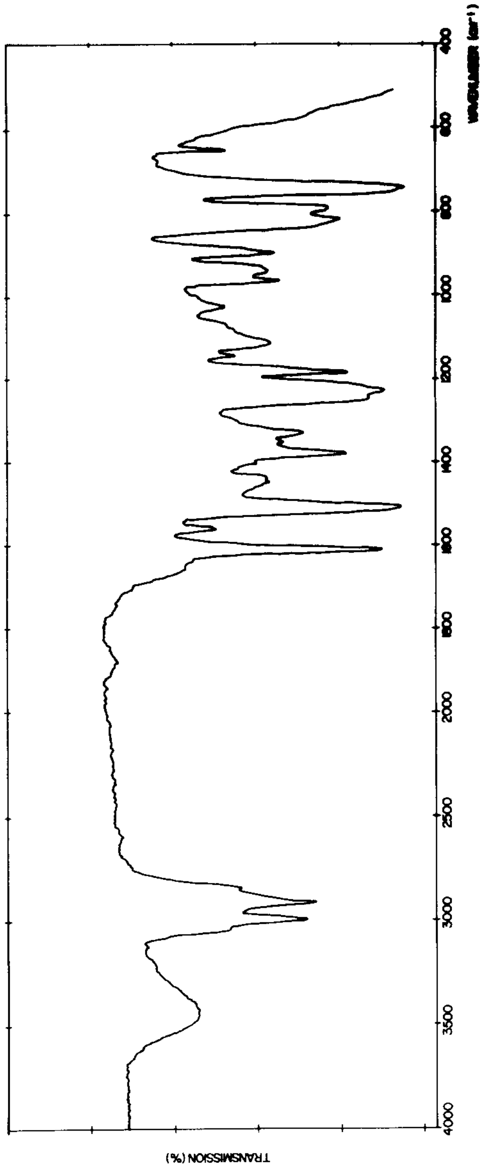

FIGURE 4 FTIR spectrum of the organic dissolved phase identified as TGGDM.

TABLE I

The effect of drying time on the strength and weight change of FM-400 film adhesive

	FM-400[b] (1 year)		FM-400[b] (6 years)		FM-400[d] (1 year)		FM-400[d] (6 years)	
Drying time (hours)	L.S.S. (psi)[a]	Weight change (%)[e]	L.S.S. (psi)[a]	Weight change (%)[e]	T-Peel (lb/inch)[c]	Weight change (%)[e]	T-peel (lb/inch)[c]	Weight change (%)[e]
0	2920 ± 52	—	3080 ± 28	—	9.4 ± 0.6	—	9.6 ± 0.1	—
1.0	3150 ± 26	0.26	3164 ± 40	0.26	7.0 ± 0.4	0.08	10.9 ± 0.5	0.50
2.0	3104 ± 34	0.28	3262 ± 43	0.43	12.8 ± 0.8	0.10	11.0 ± 0.7	0.56
2.5	3170 ± 38	0.29	3188 ± 57	0.78	8.5 ± 0.4	0.26	9.8 ± 0.7	0.42
3.0	3100 ± 50	0.29	3110 ± 32	0.78	16.2 ± 0.5	0.25	11.4 ± 0.3	0.69
3.5	3104 ± 26	0.32	3651 ± 21	0.55	16.3 ± 0.1	0.28	16.6 ± 0.8	0.40
4.0	3084 ± 19	0.32	3577 ± 142	0.73	7.8 ± 0.6	0.23	22.9 ± 0.6	0.56
4.5			3436 ± 30	0.56				

[a] Lap shear strength at 25°C, average of 5 test specimens ± standard deviation.

[b] Catalog value 3780 psi.

[c] $T = 25°\text{C}$, average of 5 test specimens ± standard deviation.

[d] Catalog value 8 lb/inch.

[e] ±0.01.

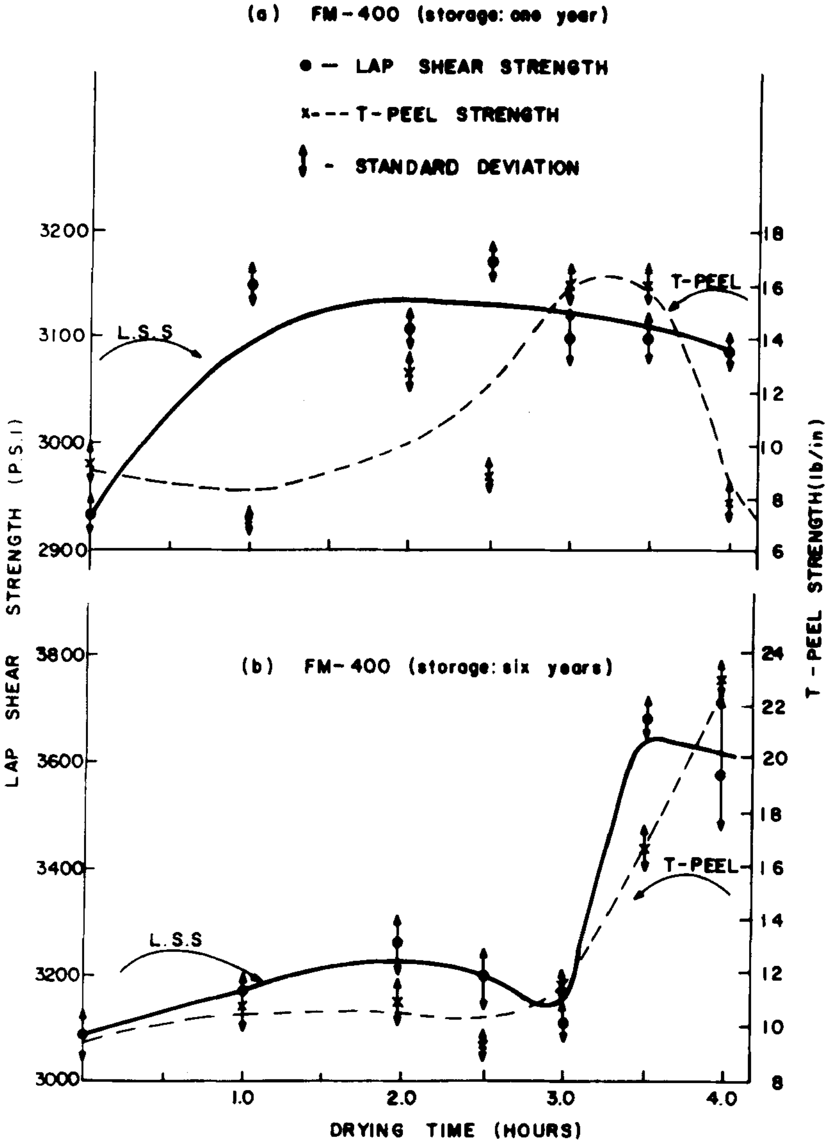

FIGURE 5 The effect of drying time on lap shear and T-peel strengths of FM-400 adhesive: (a) 1-year stored adhesive. (b) 6-year stored adhesive.

TABLE II
The effect of humidifying—drying cycles on lap shear and T-peel strengths of FM-400 film adhesive

	Lap Shear Strengths (psi)[a]				T-Peel Strengths (lb/inch)[a]			
Adhesive (age)	FM-400 (1 year)		FM-400 (6 years)		FM-400 (1 year)		FM-400 (6 years)	
Moisture Added (%)[c]	1st Rehumidifying Cycle	2nd Drying Cycle	1st Rehumidifying Cycle	2nd Drying Cycle	1st Rehumidifying Cycle	2nd Drying Cycle	1st Rehumidifying Cycle	2nd Drying Cycle
0.0	3170 ± 38[b]		3651 ± 21[b]		16.3[b]		16.6[b]	
0.1	3005 ± 69	3026 ± 36	2933 ± 10	3500 ± 81	11.1 ± 0.2	8.9 ± 0.4	15.6 ± 1.0	18.5 ± 0.4
0.2	2827 ± 13	2892 ± 35	3040 ± 39	3475 ± 52	12.1 ± 0.4	11.8 ± 1.4	13.6 ± 0.2	18.0 ± 0.7
0.3	2885 ± 80	2980 ± 60	3061 ± 34	3537 ± 55	11.9 ± 0.3	6.7 ± 0.0	13.9 ± 1.5	13.4 ± 1.2
0.4	2538 ± 24	3068 ± 24	3069 ± 45	3328 ± 38	10.9 ± 0.4	11.9 ± 1.3	13.3 ± 1.5	13.8 ± 1.5
0.6	2518 ± 11	2951 ± 46	3226 ± 31	3257 ± 35	10.9 ± 0.5	12.9 ± 0.7	15.2 ± 1.5	17.0 ± 1.0

[a] Average of 5 test specimens ± standard deviation.
[b] 1st drying cycle ($3\frac{1}{2}$ hours, 3–5 mm Hg).
[c] Weight gained in 1st re-humidifying cycle.

As illustrated in Table I, the enhancement in mechanical properties was accompanied by weight loss of the adhesive. Some inconsistancy was observed following 3.5 to 4.5 hours of dehumidifying. As reported for the other adhesives (FM-73, FM-300),[1,2,3] it was suggested that during prolonged drying solvents could be removed which, in turn, might reduce the flow properties of the adhesives during cure.[5] In summary of this part of the investigation, results indicated that the optimal drying time was 3 to 3.5 hours. This demoisturizing period was used in the next stage of the study.

The effect of moisture content and subsequent drying on mechanical properties

The detrimental effects of water on uncured epoxy systems have been shown to be comprised of reversible and irreversible phenomena.[1,2,3] To characterize the reversible-irreversible transition range, pre-dried (before cure) adhesive samples were exposed to humidity for various periods resulting in increased moisture levels with conditioning time. After moisturizing, the wet adhesive specimens were dehumidified for $3\frac{1}{2}$ hours, cured into joints and their properties evaluated in shear as well as peel modes.

Table II and Figure 6 summarize the experimental results obtained with the 1- and 6-year-old adhesive samples. As is evident, the shear and peel strengths declined with increasing moisture content followed by recovery of properties upon dehumidifying. Furthermore, above a threshold value of ~0.3% moisture the recovery was incomplete, indicating that damage was irreversible at high moisture levels. A similar response was previously found in unfilled epoxy film adhesives.[1,2,3] At low moisture content resin plasticization and hydogen bonding are believed to be the main mechanisms associated with reversible changes, as opposed to hydrolysis and homopolymerization reactions related to irreversible, permanent modifications at high moisture content.

Fractography

The objective of the fractographic study was to identify the moisture effects associated with the aluminum filler at the micro-

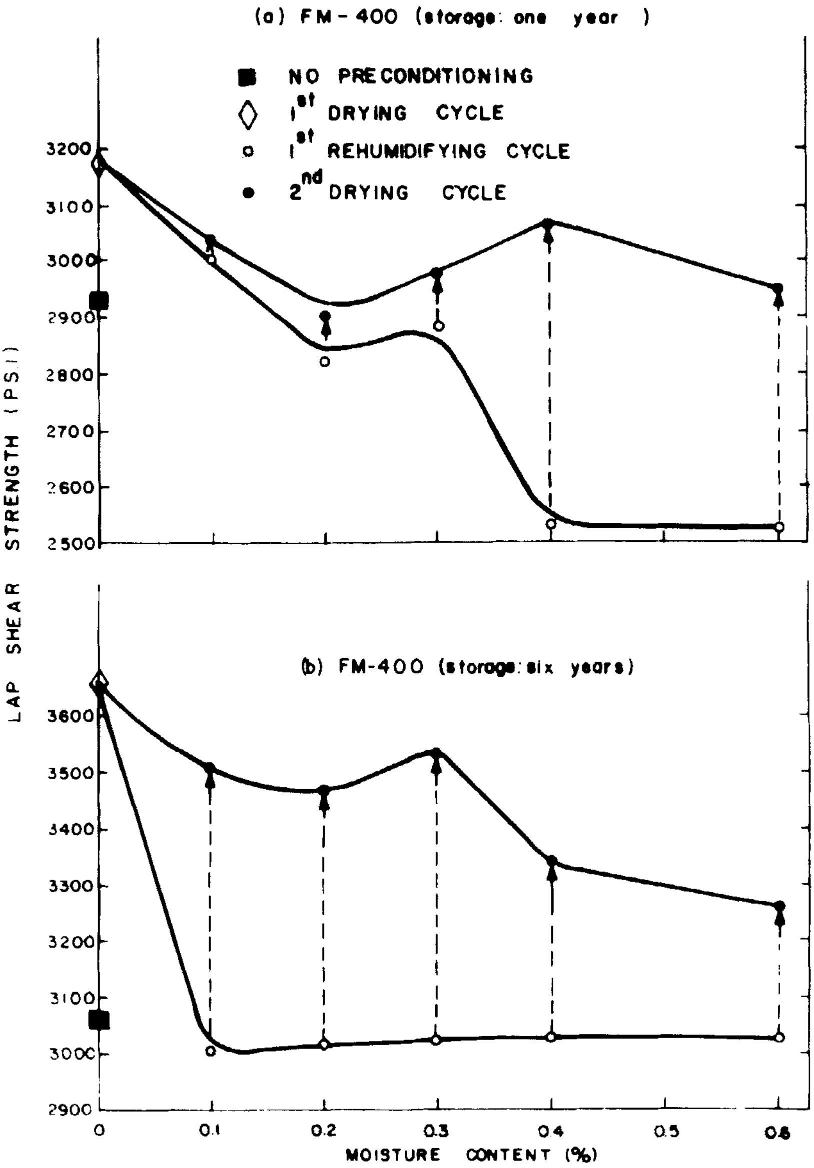

FIGURE 6 The effect of controlled humidification (of pre-dried adhesive) and subsequent drying on the shear strength of FM-400: (a) 1-year stored adhesive. (b) 6-year stored adhesive.

FIGURE 7 Fracture topography of untreated cured adhesive after 6-year storage: (a) General view of adhesive (×30). (b) Magnified view of carrier and matrix (×100). (c) Aluminum filler and epoxy matrix (×1000).

level and to provide, if possible, a correlation with the macro-mechanical properties.

Figure 7 illustrates the fracture surface of the as-received 6-year-old FM-400 adhesive following peel loading. Generally, fracture occurs at the carrier plane, with some porosity present (see Fig. 7a).

The polyamide fibers of the carrier are almost bare, indicating low interfacial strength between the carrier and adhesive matrix (7b). The apparent low interfacial strength and porosity are also manifested in the appearance of the failure surface at high magnifications (7c) where the aluminum filler either seems to debond from the surrounding matrix or to be bare.

FIGURE 8 Fracture surface of 6-year-stored adhesive after drying for 2.5 hours: (a) General view of carrier and matrix (×100). (b) Magnified view of fiber and surrounding matrix (×1000). (c) Aluminum filler and matrix (×1000).

Following drying for 2.5 hours prior to bonding the topography of the fracture surface changes. As seen in Figure 8, drying results in lower porosity (8a), improved interfacial adhesion between the carrier and the epoxy adhesive (8b) as well as between the aluminum particles and the polymeric matrix (8c).

When the 6-year-old adhesive was dehumidified and subsequently moisturized to 0.4% level, the fracture surfaces of the cured adhesive were found to be highly porous (see Fig. 9a). Porosity was accompanied by massive debonding between the carrier fibers and the epoxy (9b), as also observed in Figure 9c. As seen, some of the aluminum particles seem to either debond from the epoxy matrix or leave empty craters where, prior to fracture, the particles nested.

Following a drying step, the 0.4% moisture-containing adhesive system still shows a porous fracture surface—Figure 10a, with improved surface bonding between the carrier and adhesive (10b) as well as enhanced interfacial bonding between the filler and matrix (10c).

Comparison between these fractographs and the results given earlier, indicates that a correlation may exist between the microstructural changes that have been observed in the fracture surfaces and the corresponding mechanical properties. Generally, the relatively large-area aluminum particulates may provide high energy surfaces for attracting water which, in turn, has to be removed prior to bonding for development of a high quality bond.

FTIR analysis

To complement the study of the moisture effects, the chemical changes that took place in the cured adhesive joints were followed by means of FTIR. FTIR was performed on the fractured peel specimens after initial drying, successive re-humidifying and final demoisturizing. Table 3 summarizes the main absorption peaks for the epoxy system studied. Figure 11 shows the FTIR spectra for as-received, 0.1%, 0.2% and 0.4% water-containing samples and for the corresponding dried samples. The spectra are typical of epoxy with characteristic absorptions of the Dicy moiety (2150 cm^{-1}, 2200 cm^{-1}) and hydroxyl group (3000–3600 cm^{-1}). The intensity of the hydroxyl group transmittance was assumed to be proportional to water content in the cured adhesive. Since the

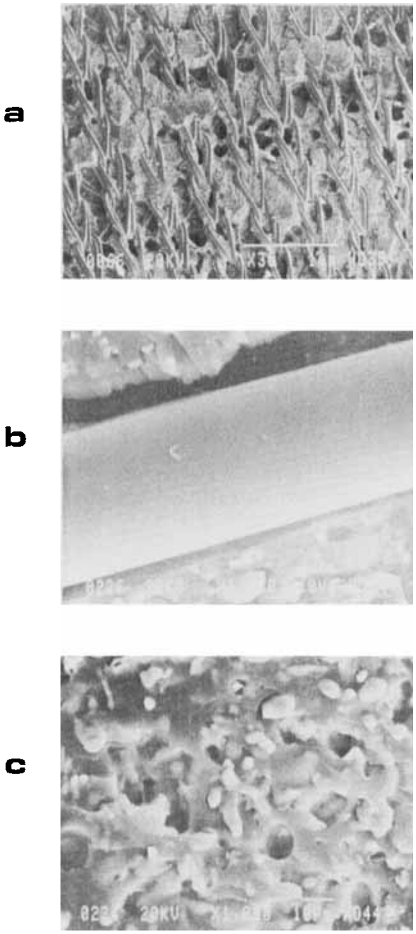

FIGURE 9 Fracture surface of 6-year-stored adhesive after re-humidifying to 0.4% moisture: (a) General view of failure surface (×30). (b) Debonded fiber and surrounding matrix (×1000). (c) Debonded aluminum particles (×1000).

unaffected aromatic peak at 1515 cm^{-1} was obscured by the aluminum filler, it could not serve as a reference for quantitative analysis, as carried out for unfilled epoxy systems.[2] Consequently, the results are discussed qualitatively. As indicated in Figure 11, an increase in moisture content in the adhesive after humidifying was

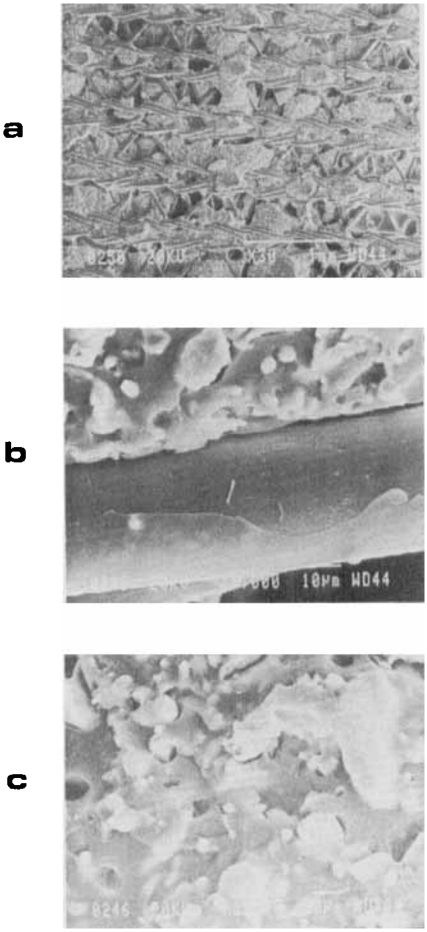

FIGURE 10 Fracture surface of 6-year-stored adhesive after drying from 0.4% moisture level: (a) General view of failure surface (×30). (b) Magnified view of fiber and matrix (×1000). (c) Aluminum particles and surrounding matrix (×1000).

accompanied by widening of the absorption band at 3000–3600 cm^{-1} on the lower frequency side, characteristic of a higher level of hydrogen bonding. Furthermore, high moisture levels in the uncured adhesive could be correlated with intensification of the 1600 cm^{-1} band, typical of water.

TABLE III
The main absorptions in FTIR spectra of FM-400[a]

Frequency cm^{-1}	Functional group
3000–3600	A broad absorption band of hydroxyl groups and water.
3400–3200	N–H band.
3000–2800	Alkyl C–H band.
2200–2150	Doublet of the dicyandiamide group originates from the curing agent. The high frequency absorption is attributed to –CN, the lower frequency absorption to C=N—H functional group.
≈1600	Absorption band results from absorbed water.
1515	Absorption band of aromatic rings.

[a] The spectra are unclear as a result of interference caused by the aluminum filler.

Following drying of the moisturized, B-staged adhesive, the characteristic absorption bands at 3000–3600 cm^{-1} and 1600 cm^{-1} decreased in intensity, but were still larger relative to the intensity of the same peaks after the initial drying step. This result suggests that drying after humidifying cannot completely remove the absorbed/adsorbed moisture.

The Dicy polar moiety is known to be sensitive to hydrolysis.[6] This affinity could be substantiated, in the present study, from the intensities of the typical doublets in the 2150 to 2200 cm^{-1} range.

Generally, increased moisture content in the uncured adhesive resulted in widening of the characteristic bands (Fig. 11g) while dehumidifying resulted in sharpening of the absorption peak at 2174–2180 cm^{-1} (Figure 11b, 11f, 11h).

The hydrolysis reaction between Dicy and absorbed moisture may give rise to irreversible degradation of the adhesive strength, due to possible partial curing of the base epoxy, especially at high levels of moisture content. The above results suggest that in the Dicy-cured TGGDM epoxy system, used in this study, hydrolysis of the cyano groups is one of the decisive mechanisms that affect the final properties of the adhesive in the presence of moisture.

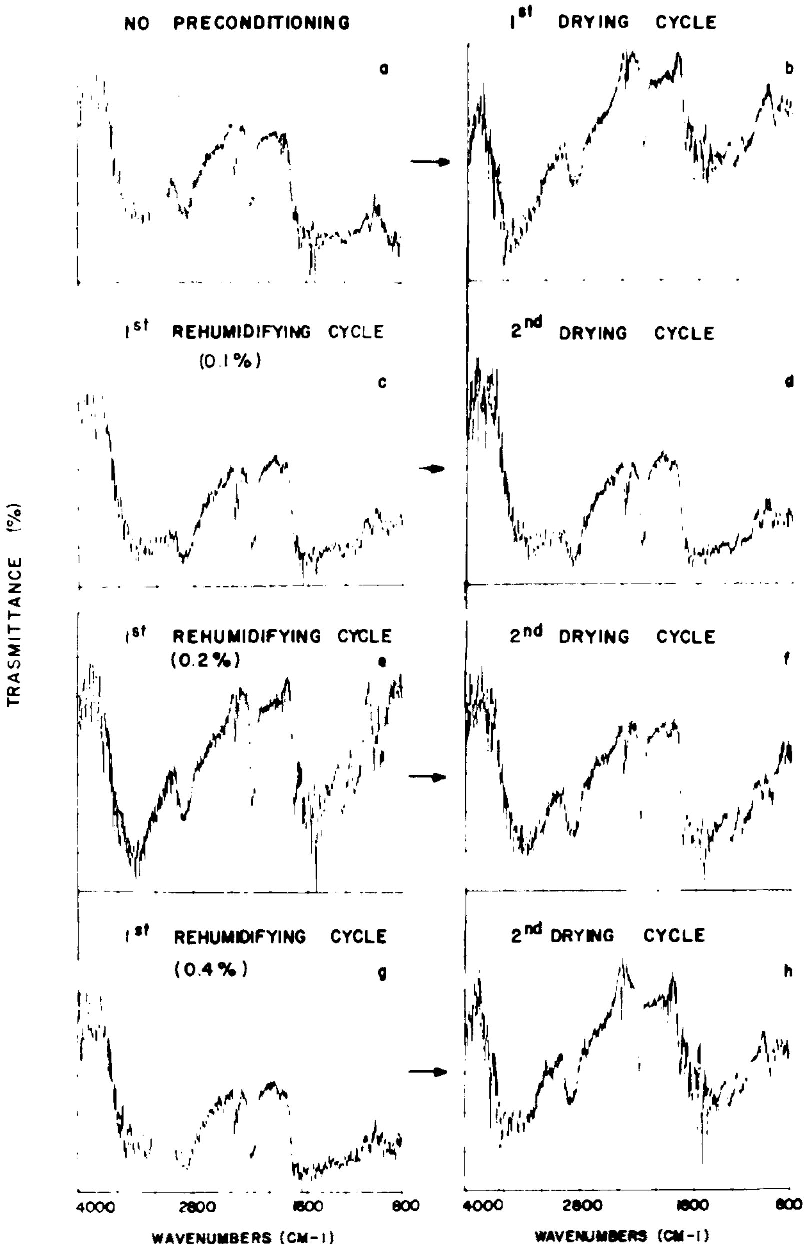

FIGURE 11 FTIR spectrum of cured adhesive after various humidifying and drying cycles.

CONCLUSIONS

Aluminum-filled, composite film adhesives, like the previously studied filler-free adhesives (FM-73, FM-300) are sensitive to moisture in their uncured state. Moisture in the adhesives may be traced to their storage period, or to moisture pick-up when exposed to the working atmosphere prior to cure. Moisture has been shown to have adverse effects on the adhesive shear and peel strengths. Furthermore, de-humidifying the as-received or exposed adhesives is very effective in removing the absorbed moisture, with subsequent regain in strength almost to the initial values. Irreversible changes due to humidity absorbed in uncured adhesive occurs when the initial moisture content is above 0.3% or after prolonged drying (>4 hrs).

Electron microscopy of the fracture surfaces of peel specimens as well as FTIR have been shown to be effective techniques to characterize changes in the composite adhesive. Moreover, a correlation has been established between the macro-mechanical properties and the micro-analysis comprising failure morphology and infra-red spectroscopy.

Acknowledgment

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