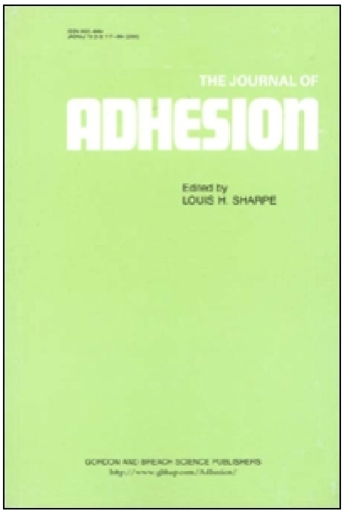

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

The Effect of Moisture in Epoxy Film Adhesives on their Performance: I. Lap Shear Strength

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Online publication date: 02 December 2010

To cite this Article Dodiuk, H. , Drori, L. and Miller, J.(1984) 'The Effect of Moisture in Epoxy Film Adhesives on their Performance: I. Lap Shear Strength', The Journal of Adhesion, 17: 1, 33 — 43
To link to this Article: DOI: 10.1080/00218468408078428
URL: http://dx.doi.org/10.1080/00218468408078428

J. Adhesion, 1984, Vol. 17, pp. 33–44
0021-8464/84/1701-0033 $18.50/0

The Effect of Moisture in Epoxy Film Adhesives on their Performance: I. Lap Shear Strength

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(Received June 7, 1983, in final form October 17, 1983)

The effect of moisture content in four commercial epoxy film adhesives on their performance was studied.

The investigation included conditioning of the adhesives under humidity and drying cycles, determination of moisture level following each conditioning step, and evaluation of the shear strength of the conditioned adhesive.

Experimental results have shown that absorbed moisture caused reduction in adhesive shear strength. Predrying of the uncured adhesive under vacuum (3–5 mm Hg), for 3–4 hours at room temperature, was very effective in removing the absorbed humidity and consequently bond strength was regained, provided that the absorbed moisture was below the 0.3% level.

Above this threshold value, irreversible deterioration occurred and drying resulted in only partial recovery of adhesive bond strength.

1. INTRODUCTION

The use of film adhesives and composites based on epoxy resin have become an industry standard for high performance aerospace structures. Consequently, the specifications for these material systems are very demanding. Adhesion quality and the reproducibility of curing are of major importance for high performance aerospace bonded structures. These two factors are decisive as far as their reliability in service is concerned. Furthermore, the experience among end users has indicated that some difficulties are inherent in these B-staged epoxy based materials due to the existence of the curing agent in the prepregged fibers and adhesive films. (The curing reaction proceeds in the B-staged epoxy even at low temperatures to the point where the material is eventually rendered unusable).

Moreover, a great deal of effort has been directed toward the study of the thermal history on the curing state of the B-stage epoxy and its consequences on the final cured material[1]. However, little attention has been given to the effect of the moisture on the uncured epoxy.

As some recent investigations show[2,7], the moisture level in epoxy film adhesives (FM-123-5[2], FM-73 (American Cyanamid), and EA-9628 NW (Hysol/Dexter)[3]), is of major importance as far as the adhesive response to the fabrication process and the final adhesive properties. The 3M Company offers new adhesives (AF-163, and AF-163-2), the peel properties of which are almost unaffected by exposure to humidity[6] prior to curing.

The suggested mechanisms causing the degradation of adhesion quality due to the penetration of water into the precured polymer network were:

(a) Moisture absorbed by the adhesive tends to plasticise the adhesive[6]. As the moisture level increases, the moisture deteriorates the bond integrity, and can cause phase separation of rubber modifiers, a decrease in the particle size of the rubber toughener domains, and formation of voids in the cured adhesive bondline.
(b) Hydrogen bonding interactions between water molecules and the polar epoxy group in the resins could influence the adhesive properties. This effect has been studied by infrared spectroscopy[4].
(c) It has been shown that some epoxy resins can undergo hydrolysis. Consequently, the loss of epoxide could affect the performance of the adhesive as has been reported[5].
(d) Epoxy resin could undergo a homopolymerization reaction in some cases[5]. This could also lead to the reduction of the epoxide group in the uncured material.

The understanding of the reversible or irreversible effects of moisture is a critical issue. Irreversible losses in properties during moisture exposure may be attributed to hydrolysis and homopolymerization and could not be remedied. On the other hand, the reversible behaviour in the matrix phase may be the result of plasticization and hydrogen bonding and can be remedied.

In the present investigation four commercially available film adhesives were used following storage for different durations in a deep freezer (−18°C).

The moisture level of the adhesives was controlled by drying under vacuum and/or exposure to humid atmosphere. Shear strengths of the conditioned adhesives were evaluated in order to determine the effect of absorbed or desorbed moisture (in uncured film adhesive) on the ultimate bond shear strength and its reversibility.

2. EXPERIMENTAL

Materials

Four commercial film adhesives were studied:

FM-73 and FM-300K, supported film epoxy adhesives, and primer BR-127 (Bloomingdale Department of American Cyanamid), Redux 319, supported film epoxy adhesive (Ciba Geigy), AF-126 (3M, U.S.A.). Table I summarizes the curing conditions for the above mentioned adhesives.

TABLE I

Adhesive (storage period—a)	Curing conditions T(°C), P(psi), t (hours)	Adherends and primer	Prebond surface treatments
FM-73 (new, half a year, one year)	120°C, 35 psi, 1½ hours	2024-T351 bare aluminium and thin layer of BR-127 primer was spray applied and cured (½ hour at R.T. and 1 hour at 120°).	Etched by the FPL (Forest Product Laboratory) method
FM-300K (half a year, two years)	177°C, 35 psi, 2 hours		"
AF-126 (two years)	120°C, 35 psi, 1½ hours	"	"
Redux 319 (two years)	175°C, 35 psi, 1½ hours	"	"

a—Refrigerator storage period or age of adhesives used.

The adhesives under investigation were taken through various humidifying-drying steps. At each step the moisture level was determined, and the effect of sorbed moisture was quantified by measurement of lap shear strength. A schematic representation of the experimental procedures is given in Figure 1.

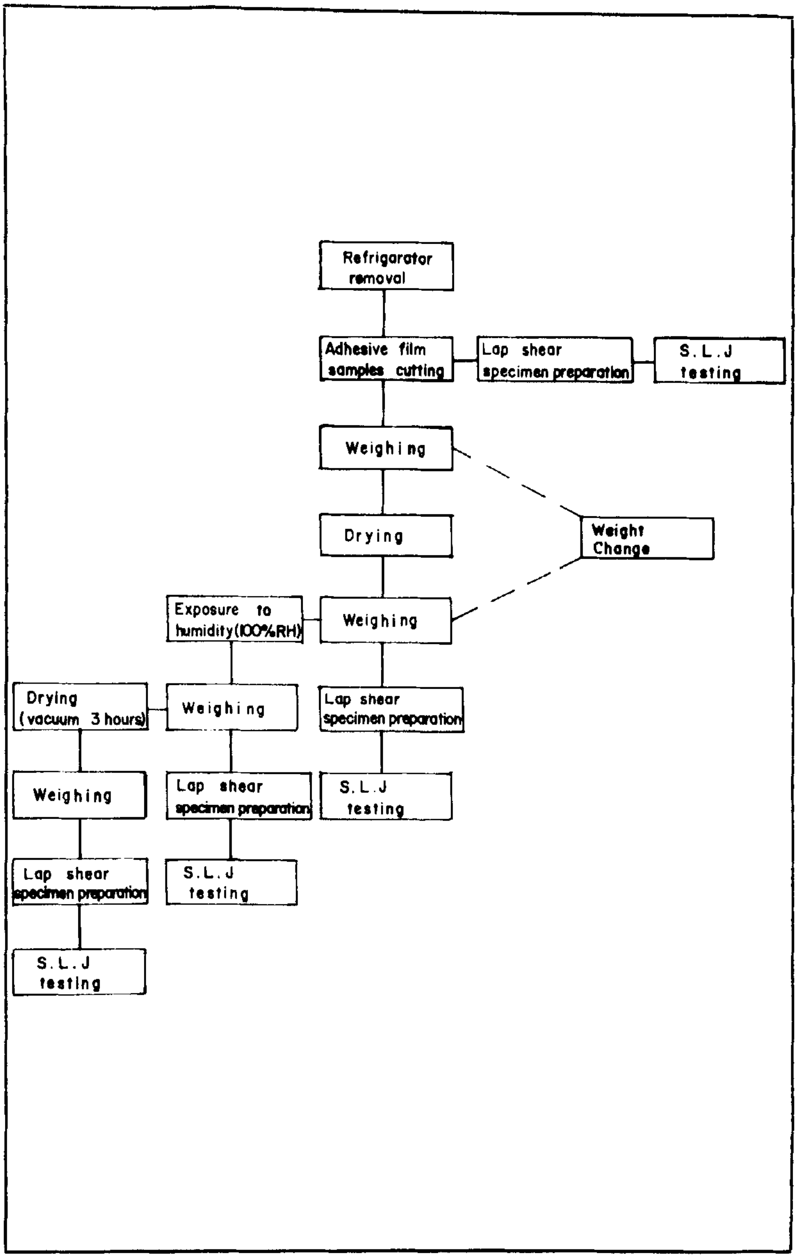

FIGURE 1 Test Plan.

Tensile Tests

Tensile Lap Shear specimens were prepared according to ASTM D-1002-72. Bondline thickness was 0.10 ± 0.03 mm. Five specimens were fabricated in each cycle using a special mold under compression. The tests were carried out at room temperature. (Table I summarizes selected materials and processes).

Drying Procedure

The film adhesives were removed from the refrigerator (-18°C) after various "storage periods"—"age" of adhesives as given in Table I—and then allowed to warm up for 2 hours at room temperature while sealed in polyethylene bags. The polyethylene cover was removed and samples of 12.7 mm × 150 mm were cut and weighed. Lap Shear specimens from each batch were prepared, cured and tested. The rest of the film sample was placed in a desiccator, and desiccated at 3–5 mm Hg (absolute) for various periods (1–5 hours). Then they were immediately weighed and an additional lap-shear series of specimens were prepared, cured and tested respectively. Each sample was preconditioned in a desiccator for different durations.

Exposure Procedure

A series of film adhesive samples were desiccated for 3 hours according to the drying procedure described above, then weighed and exposed to 100% RH for different periods. The amount of moisture absorbed was determined by weighing.

Following exposure, the samples were weighed and divided into two groups. From one batch, a series of L.S.J. specimens were prepared, cured and tested. The other groups of samples were redesiccated for 3 hours, weighed, L.S.J. (Lap Shear Joint) specimens were prepared, cured and tested.

Outgassing Products

During drying of the film adhesive, the outgassing products were trapped using an appropriate setup (Figure 2), then dissolved in methylene chloride and identified using an Infra-red spectrophotometer (Perkin–Elmer 283B).

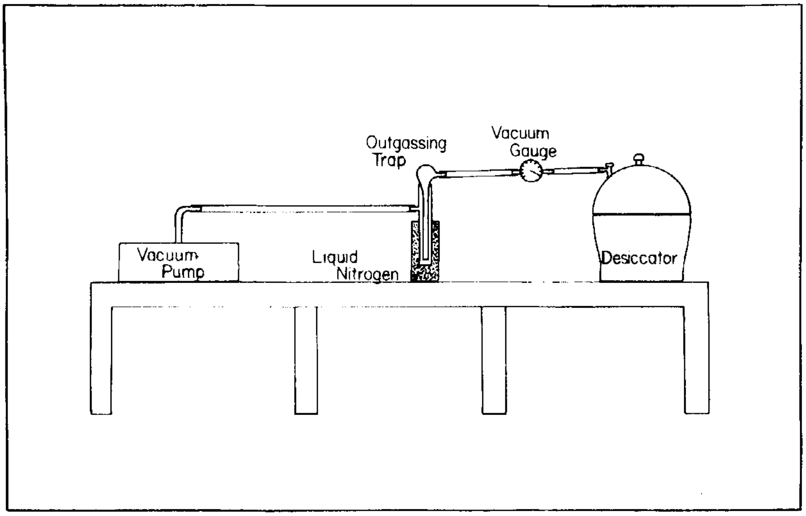

FIGURE 2 Schematic description of the experimental system.

3. RESULTS AND DISCUSSIONS

The initial lap-shear strength values (Table II) of the epoxy adhesives studied here (manufactured by 3 different companies) have shown conclusively that the lap shear strengths have degraded markedly (from the catalog values) after storage (3–24 months) at −18°C. The reduction found was in the range of 8–30% and decreased further when the adhesive was subjected to long term storage. It has been suggested by some authors[2-7] that this may be due to moisture which permeates into the B-staged epoxy adhesive.

Weight Change During Preconditioning (Drying) of the Uncured Film Adhesive and the Effect on Lap Shear Strengths

Weight changes (the percentage weight loss based on initial resin weight as a function of drying under vacuum) and lap-shear strengths at ambient temperature are listed in Table II for the desiccated (for the period of 0–5 hours) film adhesives.

The test specimens showed cohesive bond failures in all cases.

As can be seen in Table II, a significant initial enhancement in the

TABLE II

The effect of drying on the strength and weight change of various film adhesives

Adhesive Type	b FM-73 (half a year)		b FM-73 (one year)		c FM-300K (half a year)		c FM-300K (two years)		d Redux 319 (two years)		e AF-126 (two years)	
Drying time (hours)	a L.S.S(psi)	weight change (%)	L.S.S(psi)	weight change (%)	L.S.S(psi)	weight change	L.S.S(psi)	weight change (%)	L.S.S(psi)	weight change (%)	L.S.S(psi)	weight change (%)
0	$4710^{\pm 50}$	—	$4700^{\pm 15}$	—	$2940^{\pm 20}$	—	$2970^{\pm 40}$	—	$4090^{\pm 90}$	—	$4340^{\pm 20}$	—
0.5	$4780^{\pm 20}$	0.08	$4670^{\pm 20}$	0.05	$3280^{\pm 70}$	0.08	$2910^{\pm 60}$	0.05	$4100^{\pm 80}$	0.04	$4320^{\pm 30}$	0.18
1.0	$4690^{\pm 5}$	0.11	$4720^{\pm 70}$	0.05	$3260^{\pm 30}$	0.17	$3640^{\pm 40}$	0.19	$3710^{\pm 5}$	0.07	$4140^{\pm 20}$	0.40
1.5	$4740^{\pm 15}$	0.08	$4690^{\pm 10}$	0.06	$3270^{\pm 90}$	0.08	$3360^{\pm 20}$	0.09	$4310^{\pm 40}$	0.13	$4300^{\pm 60}$	0.46
2.0	$4830^{\pm 20}$	0.14	$4720^{\pm 220}$	0.03	$3410^{\pm 60}$	0.22	$3550^{\pm 40}$	0.30	$4580^{\pm 320}$	0.14	$4300^{\pm 50}$	0.70
2.5	$4820^{\pm 30}$	0.39	$4730^{\pm 40}$	0.24	$3540^{\pm 30}$	0.25	$3680^{\pm 105}$	0.30	$4130^{\pm 40}$	0.20	$4540^{\pm 70}$	0.60
3.0	$5000^{\pm 50}$	0.38	$5040^{\pm 80}$	0.28	$3600^{\pm 60}$	0.24	$3470^{\pm 155}$	0.34	$4080^{\pm 70}$	0.13	$4470^{\pm 50}$	0.46
3.5	$4630^{\pm 70}$	0.30	$4730^{\pm 60}$	0.13	$3360^{\pm 90}$	0.25	$3470^{\pm 130}$	0.30	$4100^{\pm 50}$	0.20	$4980^{\pm 30}$	0.80
4.0	$4450^{\pm 130}$	0.28	$4870^{\pm 60}$	0.20	$3130^{\pm 60}$	0.27	$3030^{\pm 80}$	0.32	$4330^{\pm 60}$	0.20	$4840^{\pm 10}$	0.68
4.5	$4540^{\pm 100}$	0.30	$4640^{\pm 40}$	0.20	$3380^{\pm 70}$	0.42	$3090^{\pm 250}$	0.45	$4320^{\pm 110}$	0.20	$4770^{\pm 50}$	0.69
5.0	$4570^{\pm 60}$	0.40	$4960^{\pm 50}$	0.27	$3530^{\pm 30}$	0.38	$3890^{\pm 45}$	0.45	$4400^{\pm 90}$	0.13	$4800^{\pm 30}$	0.90

a: Lap Shear Strength at 25°C R.T. average of 5 test specimens $\pm$ standard Deviation.
b: Catalog value; 6400 P.S.I.
c: Catalog value; 6780 P.S.I.
d: Catalog value; 5500 P.S.I.
e: Catalog value; 5580 P.S.I.

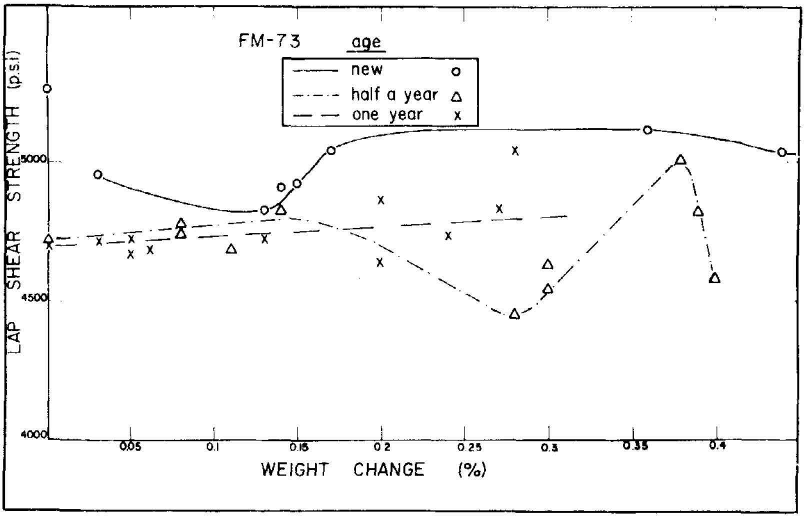

FIGURE 3 Lap shear strength *vs.* weight changes for FM-73.

bond strength was achieved by drying before cure. The greater the decrease in sample weight (0.1–0.8%) the larger the increase in shear strengths (8–25%). However, following 2–3 hours of drying, there seems to be some inconsistency in the results.

Figure 3 describes the lap shear strengths *versus* weight changes for a few batches of FM-73 (new, half a year, one year). It could be observed that, at the beginning, the shear strengths increase, but later some inconsistency appears.

Generally, longer drying periods (3–5 hours) result in inconsistent behaviour. This phenomenon may be due to the removal of residual solvent or diluent which reduces flow in the subsequent cure step[2].

Outgassing Products Identification

The I.R. spectra of the outgassing products of the FM-73 and FM-300K are given in Figure 4.

The main peaks (absorptions) in both spectra are at $\nu = 3400$–3500 cm^{-1} (broad), 2150 cm^{-1}, 1600 cm^{-1}, which indicate that water is the main product for both uncured adhesives, FM-73 and FM-300K.

Minor concentration of other residual volatiles which might be present cannot be detected in the I.R. spectra. Hence, the weight losses measured in the present study were due mainly to the removal of

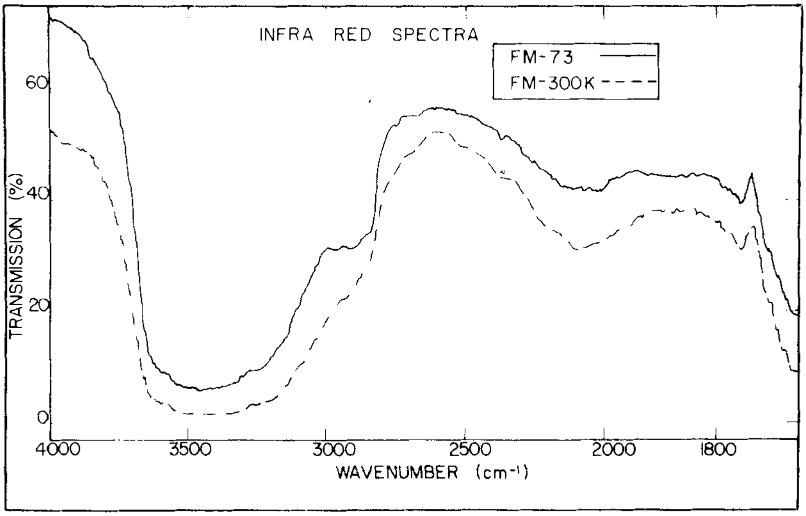

FIGURE 4 I.R. spectra of FM-73 and FM-300K outgassing products.

absorbed water from the uncured film adhesives.

Effect of Preconditioning (humidity exposure and redrying) on Lap Shear Strength

The problem which remains is whether the desiccated adhesive can return to its original performance following precure humidity exposure for a few cycles.

To clarify this issue, a set of experiments were designed where

TABLE III

The effect of humidity—drying cycles on the strength of various film adhesives

Adhesive Type	FM-73 (one year)		FM-300K (half a year)	
Moisture added (%)	L.S.S(psi)[a] after exposure to Humidity	L.S.S(psi)[a] after additional Drying	L.S.S(psi)[a] after exposure to humidity	L.S.S(psi)[a] after additional Drying
0.0	$4910^{\pm 30}$		$3990^{\pm 30}$	
0.3	$4855^{\pm 50}$	$4833^{\pm 40}$	$3540^{\pm 30}$	$4020^{\pm 20}$
0.4	$4550^{\pm 30}$	$4670^{\pm 20}$	$3450^{\pm 40}$	$3910^{\pm 60}$
0.6	$4510^{\pm 60}$	$4700^{\pm 20}$	$3460^{\pm 50}$	$3850^{\pm 20}$
0.7			$2950^{\pm 40}$	$3790^{\pm 40}$
0.8	$4450^{\pm 40}$	$4620^{\pm 50}$	$3050^{\pm 30}$	$3680^{\pm 55}$
0.9	$3370^{\pm 30}$	$3740^{\pm 30}$		

[a] average of 5 test specimens ± standard deviation

desiccated adhesives were exposed to humidity and redesiccated.

Table III correlates the lap shear strengths of FM-73 and FM-300K, following drying for 3 hours and exposure to humidity (100% RH) prior to curing. Moisture level was measured by weight gained by the uncured film adhesive.

As shown in Table III, the shear strength has significantly deteriorated as the moisture content increased. Redesiccation for 3 hours (after exposure to humidity of the uncured samples) resulted in consistently higher lap shear strengths. However, samples which absorbed more than 0.25–0.3% moisture did not return to their original strength level. This may be attributed to the irreversible mechanisms occurring at higher moisture levels. Figure 5 demonstrates, for example, this phenomenon for FM-300K.

Thus it may be concluded that preconditioning of uncured film adhesive is effective in enhancing performance as long as the moisture content is below 0.3%. Higher moisture levels result in irreversible damage and permanent loss in properties.

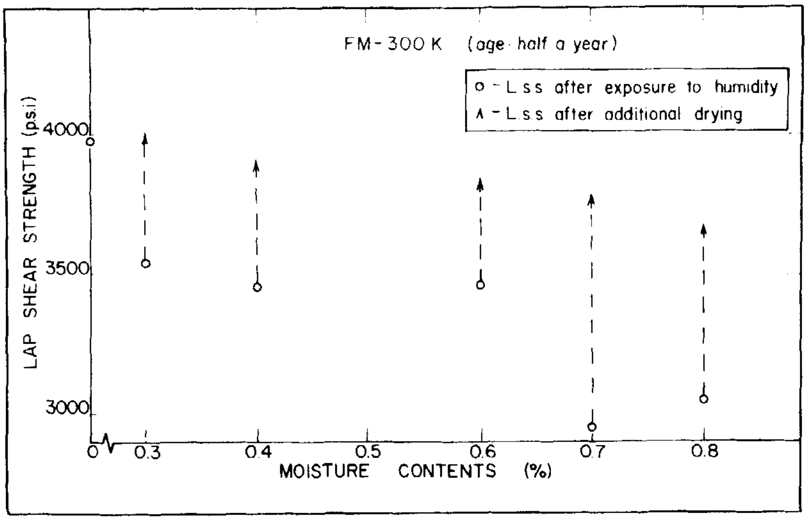

FIGURE 5 Lap shear strength *vs.* moisture contents for FM-300K.

4. SUMMARY AND CONCLUSIONS

An uncured film adhesive absorbs moisture during storage which ultimately can affect the bond strength (of a bonded joint). Preconditioning of B-staged adhesives under 3–5 mm Hg vacuum for 3–4 hours is recommended in order to remove moisture and consequently bond strength is regained.

The recommended method is effective when the absorbed moisture content is below 0.3%, and for 3–4 hours only. When the initial moisture content increases above this level, or when drying is carried out for longer periods, deterioration of properties takes place.

Further study is planned concerning the effect of moisture in the uncured film on other properties of the cured structural adhesives (such as peel strength and high temperature shear strength).

Aknowledgment

We are grateful for helpful discussions with Dr. S. Kenig.

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