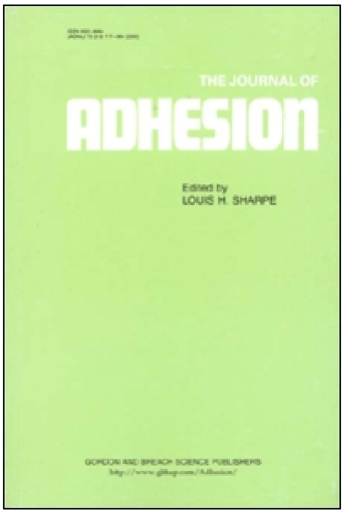

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The Effect of Moisture Content in Epoxy Film Adhesives on their Performance. III: Bulk Properties

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Humidity absorbed by epoxy film adhesives during low temperature storage or exposure to atmosphere may result in reversible changes and irreversible modifications. Vacuum treatment may partially remedy the reversible changes. The consequences of vacuum drying are manifested in enhancement of both the peel and shear properties of bonded joints (Part I and Part II of this series of papers) and the thermal, physical and mechanical properties of the bulk adhesive, characterized in the present study.

Experimental results have shown that the bulk properties of structural epoxy based adhesives are highly correlated with the aging processes caused by water absorption in the prepolymerized adhesive. Applying the vacuum process is harmful to fresh unaged adhesive due to devolatization of low molecular species of the film adhesive.

The characterization of bulk properties for the purpose of following the aging and recovery processes is advantageous, since the bulk is independent of geometrical and interfacial effects which dominate in the case of property evaluation of the adhesive in a bonded joint.

KEY WORDS Epoxy structural adhesives; moisture aging; storage; bulk properties; thermal properties; mechanical properties.

INTRODUCTION

The use of structural adhesives for high performance applications is well known. Most of these film adhesives consist of a B-staged epoxy, impregnated on a carrier cloth. During shipping and storage, prior to use, curing may continue and cause "aging" of the material, and consequently limit its shelf life and the adhesive long term durability.

Various methods[2–7] have been used to follow the aging processes of the adhesive under diverse storage conditions. These methods are mainly related to evaluation of strength after bonding. Limited work has been performed in characterizing the changes in the bulk properties of the adhesive due to aging of the prepolymer prior to curing.

The study of adhesive bulk properties compared to its behaviour in joints has some advantages due to the ease of measuring bulk properties. Moreover, bulk specimens are not affected by the interfacial and geometrical factors which govern the adhesive in bonded joints.[1]

In previous investigations, determination of bulk properties was carried out using Fourier Transform I.R. (FTIR) Spectroscopy,[2] Thermal Mechanical Analysis (TMA),[3] High Pressure Liquid Chromatography (HPLC),[4] Flow,[5] mechanical properties of the bulk adhesive,[7] tackiness, dynamic viscosity, Differential Scanning Calorimetry (DSC) and dielectric studies.

In previous publications of the present series[11,12,13] it was shown that the uncured epoxy adhesive absorbed water during storage resulting in reduction of shear and peel strengths. Morris *et al.*[14] indicated that some moisture is also absorbed during warming prior to use.

In these studies the adhesives were conditioned under humidity and drying cycles. Moisture level was determined after each conditioning step followed by evaluation of the shear and peel strengths.

Experimental results have shown that predrying of the uncured adhesive under vacuum (3–5 mm Hg) for a controlled period of time—($2\frac{1}{2}$ hours for FM-300K) at room temperature, is very effective in removing the absorbed humidity and regaining the bond strength. Predrying was effective when the absorbed moisture content was below ~0.3% (weight). Above this threshold value, irreversible deterioration occurred and drying resulted in only partial recovery of shear and peel strengths. The irreversible drop in properties has been attributed to hydrolysis and homopolymerization of the epoxy resin.

In the present investigation the reversible and irreversible mechanisms were elucidated by direct characterization of the adhesive bulk properties. By this approach, the aging and recovery processes of the bulk adhesive were determined independent of geometrical and interface effects and correlated with the thin adhesive properties.

MATERIALS AND PROCESSES

In the present investigation FM-300K (made by American Cyanamid, U.S.A.) a commercial epoxy-based structural adhesive, reinforced by a nylon fabric, was used. Two types of samples were used: Unaged samples stored at −18°C and samples aged for various periods of time in cold storage (−18°), before curing. Two lots were used for each testing condition.

Aged and unaged samples of the adhesive were vacuum treated in a desiccator at 3–5 mm Hg (absolute) for 2½ hours before polymerization (dried samples). The drying time chosen, 2½ hrs, has been shown to be optimal for FM-300K.[11,12,13] The bulk properties of the aged, unaged and dried adhesive samples were determined prior and following curing in a Teflon®-coated aluminum mold.

The bulk properties were compared with thin bond line joint properties[11,12,13] of aged, unaged and dried adhesive.

Testing periods were 0, 1 and 2 years.

Uncured adhesive prepolymer

Epoxy equivalent Epoxy equivalent of unaged, aged and dried samples was determined by potentiometric titration with methanolic NaOH following dissolution of the prepolymer in dioxane and HCl.[8]

The nylon fabric and the inorganic filler were separated by filtering the solution. Aged prepolymer showed incomplete solubility in dioxane. The amount of insoluable gel was deduced from the initial weight (resulting in a possible error of 1%).

Moisture level

Moisture level was determined by weighing the adhesive prepolymer before and after vacuum treatments.[11,12,13] I.R. measurements have shown that the main contribution to weight loss is water.

Cured adhesive

Tension test Two layers of the aged, unaged or dried adhesive film of 0.2 mm thickness were molded between Teflon coated aluminum plates. The samples were polymerized by heating under 30 psi at a rate of 5°C/min up to 177°C and then heated for 1 hour at 177°C.[5] These curing conditions were used throughout the present work.

The polymerized layers were cut to strips of 1.5 × 10 cm and tested at room temperature in an Instron Tension Machine according to ASTM standard.[9]

Swelling, hardness and density tests Six-mm-thick specimens were prepared by polymerization of 20 layers of the adhesive film for the purpose of determining the density, hardness and swelling. Proper care was taken to insure a void-free and uniformly-heated specimen during curing of the adhesive.

Hardness was measured by a Shore D durometer. Swelling was carried out in an acetone/water solution (1:1 by volume) to equilibrium. Weight percentages of the swollen material was determined and molecular weight between crosslinks (Mc) was calculated according to the Flory–Rehner equation:

$$M_c = \frac{d_p V_1 (V_2^{1/3} - 2V_2 Z)}{V_2 + XV_2^2 + \ln(1 - V_2)}$$

where $V_2 = 1/[(d_p/d_t(M_1/M_p - 1) + 1)]$

d_p = density of the sample
V_1 = specific volume of the solvent (10.6)
X = interaction factor (0.33)
Z = hardener functionality (3)
d_t = density of the solvent (0.868)
M_1 = weight of the sample after swelling until equilibrium
M_p = weight of the sample after drying in vacuum for 24 hrs.

Torsion modulus vs. temperature Two-mm-thick test samples prepared by polymerization of 6 layers of adhesive film were used to determine the torsion modulus in a Gehman apparatus[10] over a temperature interval of +20 to +200°C. Changes in the torsion modulus *vs.* temperature curve including Tg were correlated with changes occurring in the prepolymer during the aging and drying processes.

FTIR spectroscopy The aged, unaged and dried samples were analyzed by means of a Nicolet 5XD FTIR spectrophotometer. The external specular reflectance mode was used. In addition, it was equipped with a horizontal stage in a near normal incidence and a gold-coated mirror as reference.

RESULTS AND DISCUSSION

Prepolymerized adhesive

Figure 1 summarizes the changes of epoxy number with storage time. Results show that the concentration of active epoxy groups decreases with aging. Vacuum treatment of new adhesives causes a relatively large decrease in epoxy number, probably due to volatilization of reactive components from the resin which leads to a marked decrease in its chemical activity.

Vacuum treatment of the aged prepolymer improves its adhesive performance. However, restoration has been found to be incomplete. This phenomenon can be attributed to irreversible effects[11,12,13] such as homopolymerization and partial hydrolysis caused by water.

The polymerized adhesive

Tension test Table I summarizes the mechanical properties of aged samples. As can be noticed, lower strength and elongation are the consequence of the aging process. However, almost no change has been detected in the modulus of elasticity.

Vacuum treatment of aged adhesive markedly improved the mechanical properties but never to their original values. As previously shown, vacuum drying of the unaged adhesive caused a fundamental change of the resin. These changes are demonstrated through a decrease in mechanical properties including the modulus of elasticity and shear and peel strengths of the adhesively bonded joints.[11,12,13]

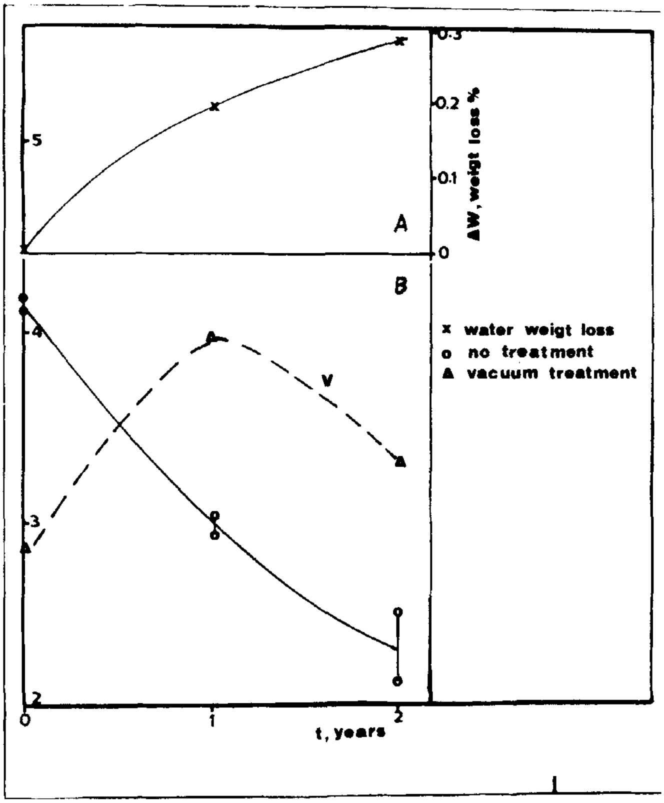

FIGURE 1 Epoxy number of unpolymerized FM-300K adhesive *vs.* time of storage (−18°C) (b), compared to weight loss after preconditioning ($2\frac{1}{2}$ hrs, 3–5 mm Hg) (a).

Swelling, hardness and density tests Table II lists the physical properties of unaged, aged in storage and dried (before polymerization) FM-300K. The results include hardness, density and swelling properties.

No change in hardness has been measured for any of the samples. This indicates that the hardness test is apparently not sensitive to aging as was also the case for the modulus of elasticity.

A decrease in density of samples aged for long periods (over 1 year), before polymerization, seems to agree with the appearance of

TABLE I
Mechanical properties of FM-300K before and after preconditioning

Property				
Specimen[a]	Storage period (year)	σ Kg/cm^2	ε_b %	$E \times 10^2$ Kg/cm^2
New	0	523 ± 41	3.74 ± 0.50	233 ± 19
New—v^b	0	296 ± 23	2.23 ± 0.10	147 ± 8
1	1 Year	350 ± 25	3.70 ± 0.40	216 ± 15
1—v^b	1 Year	408 ± 31	5.08 ± 0.27	237 ± 17
2	2 Years	234 ± 37	1.57 ± 0.07	239 ± 17
2—v^b	2 Years	335 ± 37	2.56 ± 0.50	228 ± 15

[a] 6 specimens.
[b] After preconditioning in vacuum 3–5 mm Hg for $2\frac{1}{2}$ hours.

voids in the cured polymer as can be seen in Figure 2. In an unaged or short time aged prepolymer no porosity has been detected.

Vacuum treatment increased the density and reduced the concentration and size of the voids. It should be noted that foaming occurred during the vacuum treatment. Furthermore, vacuum treatment of an unaged prepolymer caused a vast reduction in the density of the cured adhesive.

The swelling curve (weight change *vs.* time of swelling) is

TABLE II
Physical properties of FM-300K before and after preconditioning

Property					
Specimen[a]	Storage period (year)	Hardness shore D	Density gr/cm^3	ΔW_t^c %	M_c^d
New	0	73.0 ± 2.0	1.247 ± 0.020	3.47 ± 0.08	149
New—v^b	0	73.0 ± 2.5	1.194 ± 0.020	6.98 ± 0.20	256
1	1 Year	73.0 ± 2.5	1.252 ± 0.020	3.09 ± 0.40	153
1—v^b	1 Year	73.4 ± 2.0	1.237 ± 0.015	3.38 ± 0.20	194
2	2 Years	73.2 ± 1.7	1.113 ± 0.010	5.59 ± 0.02	237
2—v^b	2 Years	73.0 ± 3.4	1.218 ± 0.020	2.74 ± 0.01	188

[a] 2 specimens 5 measurements on each.
[b] After preconditioning in vacuum 3–5 mm Hg for $2\frac{1}{2}$ hours.
[c] Swelling ratio.
[d] Molecular weight between cross-links.

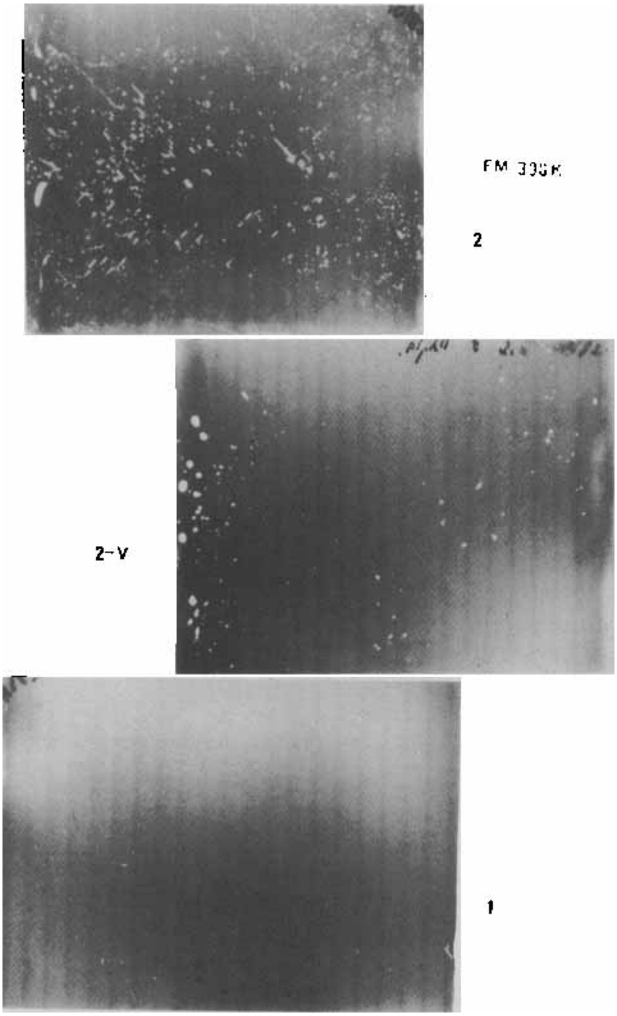

FIGURE 2 FM-300K adhesive polymerized between Teflon-coated aluminum plates, after storage of 1 (1) and 2 (2) years and drying by preconditioning (2-v).

depicted in Figure 3. An increase in swelling and hence in Mc of samples aged for long duration (2 years) indicates a lower degree of crosslinking of the cured resin compared to unaged adhesives (Table II). This is attributed to the affinity of water for the polar reactive sites which may be blocked, lowering crosslinking density.

Vacuum treatment prior to cure, which desorbs part of the water, has increased the crosslinking density of aged samples and, on the contrary, decreased that of the unaged prepolymer by turning it into a spongy material which readily absorbed the solvent.

Torsion modulus vs. temperature The rheological properties of FM-300K, as determined from the Gehman apparatus, are summarized in Table III.

The glass transition temperature (Tg) and the torsion modulus in the glassy and rubbery regions of the aged, unaged and dried adhesive after polymerization, derived from measurements of the 10 sec. torsion modulus (G) *vs.* temperature (T), are shown in Figure 4 and Table III.

An increase in the aging duration of the prepolymer leads to a decrease in the Tg of the polymer and to attenuation of the torsion modulus of both regions.

Vacuum treatment has a constructive effect on the prepolymer rheological properties by raising values to levels close to those of an unaged prepolymer. However, at long duration of aging the aged prepolymers never reach their original properties after the drying process. Moreover, drying the unaged prepolymer causes deterioration of the polymerized adhesive properties ($G_{25°C}$, $G_{180°C}$, Tg).

FTIR spectroscopy

Figure 5 depicts the FTIR spectra of polymerized, untreated, aged adhesive and a prepolymerized, dried, aged sample.

The intensities of the various absorption bands were normalized with respect to the reference aromatic phenyl band intensity at 1515 cm^{-1}. The latter group is not affected by the aging processes. The normalized spectral data for various functional groups with aging and preconditioning is given in Table IV.[2]

The spectra results (Figure 6) show that the aging phenomenon is

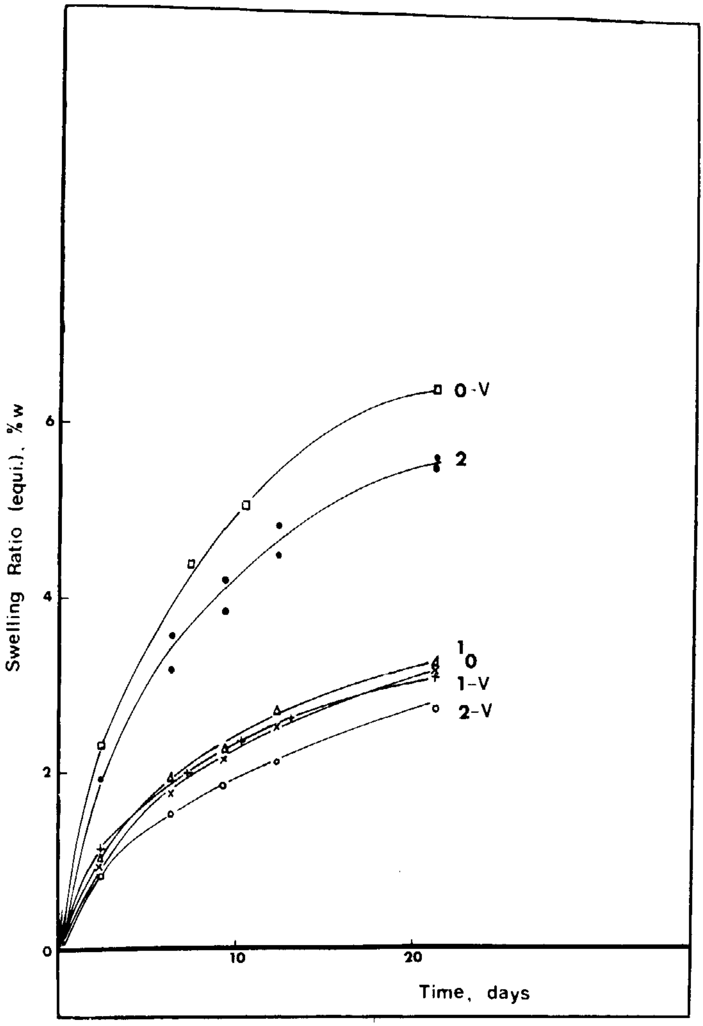

FIGURE 3 Swelling curves (weight changes *vs.* time of immersion) of FM-300K adhesive after various storage periods before and after preconditioning.

TABLE III
Rheological properties of FM-300K before and after preconditioning

Property				
Specimen[a]	Storage period (year)	$G_{25^\circ C}$ dyne/cm^2 (average)	T_g^c °C (average)	$G_{180^\circ C}$ dyne/cm^2 (average)
New	0	$9.9 \cdot 10^9$	148.5	$8.2 \cdot 10^7$
New—*v*[b]	0	$7.8 \cdot 10^9$	146	$6.5 \cdot 10^7$
1	1 Year	$5.2 \cdot 10^9$	140	$3.2 \cdot 10^7$
1—*v*[b]	1 Year	$1.2 \cdot 10^{10}$	144	$3.5 \cdot 10^7$
2	2 Years	$4.6 \cdot 10^9$	140	$4.5 \cdot 10^7$
2—*v*[b]	2 Years	$7.7 \cdot 10^9$	143	$4.4 \cdot 10^7$

[a] 2 specimens.
[b] After preconditioning in vacuum 3–5 mm Hg for $2\frac{1}{2}$ hours.
[c] Calculated from T_i ($T_g = T_i - 4.4$°C).

complicated and includes simultaneous hydrolysis and water absorption (increase in water and hydroxyl absorption group bands—3600, 3314 cm^{-1}), crosslinking and polymerization (decrease in free epoxy group band, 920 cm^{-1}) and scission of C—C bonds which is apparent from the decrease in the C—C absorption band at 1187 cm^{-1}, is unexplained at this stage.

The drying process can restore only the reversible aging processes (physical water sorption).

CONCLUSIONS

In Parts I and II of the present investigation, film adhesives in bonded joints show considerable aging as a result of prepolymer storage prior to curing. In the present study, where the bulk properties are of concern, the same consequences were characterized. Changes in properties as a result of aging are mostly reversible with partial irreversibility depending on the amount of water absorbed by the adhesive during storage.

The adhesive stored at low temperature (−18°C) demonstrates a certain amount of brittleness after polymerization as indicated by its low strain to failure (ε_b), and increase in its void content. Hydrolysis and premature crosslinking of the prepolymer cause a

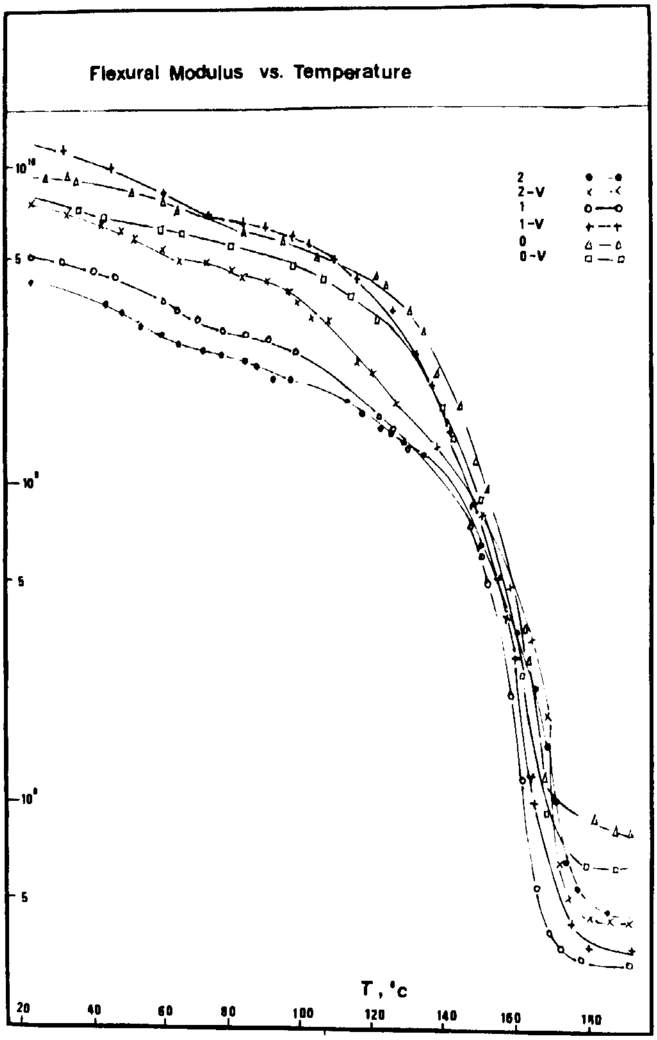

FIGURE 4 Torsional modulus *vs.* temperature of FM-300K adhesive for various storage periods before and after preconditioning.

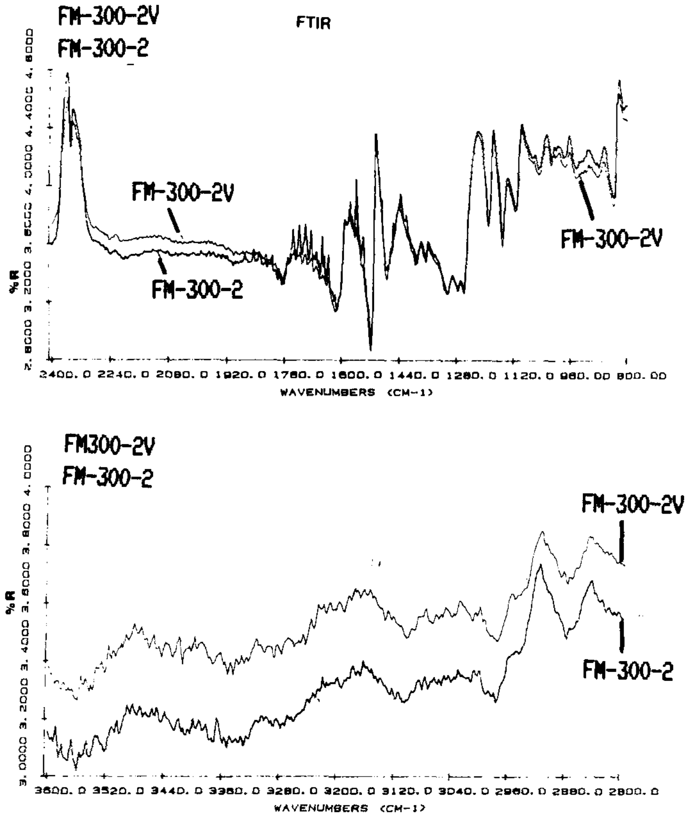

FIGURE 5 FTIR spectra of FM-300K polymerized adhesive stored (−18°C) for a 2-year period before and after preconditioning.

decrease in epoxy equivalent and density, an increase in the swelling ratio and a lower crosslinking density (higher Mc). Aging of the prepolymerized adhesive is reflected also in the decrease in the Tg of the polymerized adhesive, shear modulus (G) at 25°C and 180°C, σ_b, ε_b and smaller changes in E.

Vacuum treatment of the aged adhesive markedly enhance the mechanical properties and extend the shelf life of the polymerized adhesive. However, the properties never regain their original values. On the other hand, vacuum treatment of the unaged adhesive caused degradation of adhesive properties, probably due

TABLE IV
Relative FTIR intensities for FM-300K before and after preconditioning

Property		$\frac{3600\ cm^{-1}}{1515\ cm^{-1}}$	$\frac{3314\ cm^{-1}}{1515\ cm^{-1}}$	$\frac{920\ cm^{-1}}{1515\ cm^{-1}}$	$\frac{1187\ cm^{-1}}{1515\ cm^{-1}}$
Specimen[a]	Storage period (year)	H_2O	OH	C—C \ / O	C—C
New	0	0.27	0.22	0.46	0.45
New—v[b]	0	0.25	0.21	0.49	0.45
1	1 Year	0.57	0.52	0.43	0.38
1—v[b]	1 Year	0.52	0.47	0.44	0.44
2	2 Years	0.76	0.69	0.38	0.28
2—v[b]	2 Years	0.58	0.47	0.42	0.33

[a] 2 specimens.
[b] After preconditioning in vacuum 3–5 mm Hg for 2½ hours.

to evaporation of residual solvents and/or diluents. These phenomena conform with the results obtained by the adhesively-bonded joints as manifested in peel and shear samples.[11,12,13]

The general aging process is composed of reversible plasticization and creation of hydrogen bonds and irreversible hydrolysis and homopolymerization caused by the absorbed water molecules.

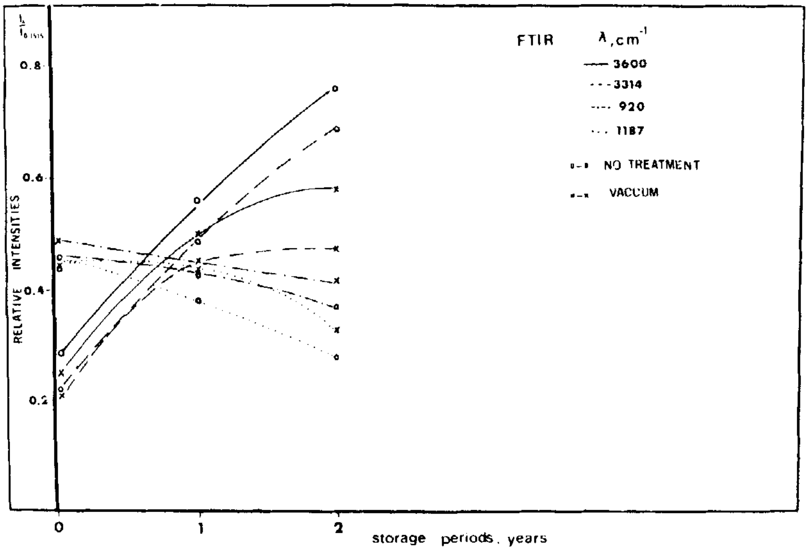

FIGURE 6 Normalized intensity of FTIR bands of polymerized FM-300K following various storage periods before and after preconditioning.

Since bulk properties are directly related to the adhesive performance, it is recommended that these characteristics should be used in the evaluation of the aging processes and other phenomena in addition to the properties of adhesives in bonded joints, where factors such as adherend properties, joint geometry and interfacial effects play a major role in the overall behaviour.

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