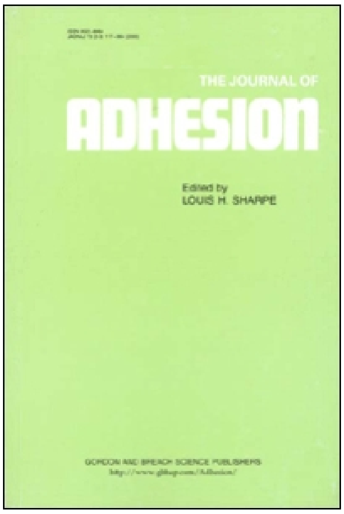

The Journal of Adhesion

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

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To cite this Article Sharon, G. , Dodiuk, H. and Kenig, S.(1989) 'Hygrothermal Properties of Epoxy Film Adhesives', The Journal of Adhesion, 30: 1, 87 — 104

To link to this Article: DOI: 10.1080/00218468908048199

URL: http://dx.doi.org/10.1080/00218468908048199

J. Adhesion, 1989, Vol. 30, pp. 87–104
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Printed in the United Kingdom

Hygrothermal Properties of Epoxy Film Adhesives

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(Received December 23, 1988; in final form April 7, 1989)

The hygrothermal response of high performance epoxy film adhesives, in their bulk state, has been characterized over a wide range of temperatures, following exposure to a combination of humidity (95% R.H.) and heat (50°C).

Experimental results have indicated that the testing temperature has a pronounced effect on both tensile modulus and strength of the adhesives, while the effect of moisture content varies with respect to the adhesive type. The moduli of the film adhesives, which have a wide range of glass transition temperatures (T_g), have been related to both moisture level in the adhesive and testing temperature. This has been accomplished by employing a dimensionless temperature, which incorporates the wet and dry T_g and the testing, as well as a reference, temperature. The strength properties have shown a higher degree of scatter using the abovementioned dimensionless temperature.

Scanning electron microscopy of the fracture surfaces have shown a good agreement between the effects of moisture and the mechanical properties. Adhesives which exhibited good moisture resistance, as manifested by the stability in their tensile properties, showed minor changes in their fracture surfaces regardless of moisture conditioning. Distinctively, the effect on strength properties has been correlated with typical moisture-induced fracture mechanisms.

KEY WORDS Hygrothermal properties; epoxy adhesives; plasticization; moisture; glass transition temperature; SEM.

INTRODUCTION

Structural epoxy adhesives have become a standard joining material for the aircraft and similar industries demanding high performance. Consequently, a great deal of effort has been devoted to evaluating and characterizing epoxy adhesives with respect to their performance in bonded joints under static, dynamic and aggressive environments, simulating actual service conditions. One of the most important requirements of an adhesively bonded joint, and hence of adhesives, is to retain a significant part of their strength and rigidity under elevated temperatures, high humidity and their simultaneous combination for long periods of time.

In bonded joints the exposed surface area of the adhesive in the bondline is usually small. However, under long term exposure, moisture may penetrate the entire adhesive layer and, as a result, may be trapped in the joint with increasing difficulty to diffuse out, as a result of the small exposed surface area of the adhesive. It is well known that moisture attacks the interfacial zones of the joint, causing irreversible damage to the interface and, hence, to the load bearing capability of the whole joint. As far as the adhesive is concerned moisture, in combination with relative high temperatures, may be detrimental to its mechanical properties due to susceptibility of the polymer to hydrolysis and degradation resulting in molecular weight decrease. Apart from the irreversible effect of hydrolysis, the ingressing moisture may have reversible consequences such as plasticization of the adhesive. The affinity for water may be increased due to the polairty of the various additives, hardeners and toughening agents incorporated into epoxy adhesives. Besides a decline in the adhesive rigidity, the absorption of water is manifested in a reduction in the glass transition temperature of the polymer.[1] Similar results, on the hygrothermal response of epoxy systems, have been published with regard to epoxy composites,[2] where reversible as well as irreversible effects are observed.

Even though a variety of epoxy systems have been thoroughly characterized and tested in their bulk form in addition to their performance in bonded joints, a relatively small number of studies have been directed toward structural film adhesives with respect to their hygrothermal bulk properties. Characterization of structural adhesives in the bulk state has a few advantages compared with evaluating their properties as exhibited in bonded joints. Firstly, the cohesive properties of adhesives are directly determined without interference from the interfacial phenomena and adherend type, especially when hygrothermal properties are investigated. Secondly, the specific stress distribution and stress concentrations developed in a particular joint, due to the adherends constraints, result in a nonhomogeneous state of stress in the adhesive studied, with consequences on the resultant elastic behavior as well as failure modes. Finally, preparation of bulk specimens is straightforward, and in most cases cheaper than the equivalent adhesively bonded test specimens. Consequently, investigation of the properties of adhesives in their bulk state has been used as a means to screen initially a series of adhesives for a specific application,[3] for basic studies of their cohesive characteristics,[4] for evaluating the effects of humidity in the pre-cured state,[5] or for investigating their viscoelastic properties.[6]

The present study is concerned with characterizing structual film adhesives in their bulk state, and is aimed at elucidating the hygrothermal response of a series of epoxy film adhesives exposed to a high level of humidity for long periods of time, and tested in a wide range of temperatures from −30°C to 200°C, depending on their glass transition temperature.

EXPERIMENTAL

Adhesives studied

Three classes of adhesives, with regard to their maximum service temperature, have been included in the present study. Table I summarizes the sources of the

TABLE I
Adhesives studied and their curing conditions

Adhesive	Manufacturer	Max. Service temp.[a] [°C]	Curing[a] [°C/h]
FM-73	American-Cyanamid	120	120/1
EA-9628	Hysol	120	120/1
MB-1137	BASF	120	120/1
Redux-319A	Ciba-Geigy	150	175/1
FM-300K	American-Cyanamid	150	175/1
MB-1515	BASF	150	175/2
FM-400	American-Cyanamid	215	175/1

[a] According to the manufacturer's data sheets.

adhesives and their curing conditions. As seen, the three groups of adhesives are categorized into 120, 150 and 215°C maximum service temperatures, respectively.

Specimens preparation

Following storage in low temperature (−18°C), the sealed film adhesives were left to thaw at room temperature. The adhesives were then cut into 200 × 250 mm pieces. Ten pieces, of each respective adhesive, were placed in a special mold and cured in a press under pressure of 0.35 MPa for a duration and temperature defind in Table I. The cured plates, 2 mm thick, were then cut to specimens 12.5 mm wide and 200 mm long.

Testing methods and procedures

A few methods have been used to characterize the bulk properties of the selected film adhesives. Each property was determined at a reference state-room temperature and moisture-free conditions (as received), and then after 30 and 90 days exposure to 50°C and 95% relative humidity.

The properties characterized were:

a) Tensile modulus, strength and elongation, using an Instron mechanical tester, according to ASTM D3039-76.[7] The mechanical properties were determined at −30°C, 25°C and one elevated temperature according to the glass transition temperature of the particular adhesive. Generally, the 120°C maximum service temperature adhesives were tested at 90°C (with the exception of FM-73 which was tested also at 60°C), the 170°C group at 150°C (with the exception of Redux 319 which was tested at 90°C) and the 215°C category at 200°C. Specimens were conditioned at the testing temperature for 30 minutes prior to testing at a rate of 2 mm/min.

b) Glass transition temperature (T_g) was determined, following exposure to the reference and hot/humid environment, by means of Dynamic Mechanical Analysis (DMA) using a 1090 Thermal Analyzer (Du Pont).

c) Density measurements were carried out, using a Mettler analytical balance, according to ASTM D792-86.[8]

d) Fracture surfaces of the tensile specimens were examined, using a Scanning Electron Microscope (SEM), Jeol model JSM 840, equipped with an Energy Dispersive Analyzer Link model 290. Prior to examination, the specimens were Au-Pd coated to suppress charging of the surfaces.

RESULTS AND DISCUSSION

The hygrothermal response of the selected film adhesives was determined following exposure of bulk specimens to humidity (95% R.H.) and moderate temperature (50°C). The response of the conditioned adhesives was characterized by determining the glass transition temperature of the dry and wet specimens, and by evaluating their tensile properties at −30°C, 25°C and one elevated temperature. It should be noted that while the moisture absorbed by the adhesives was little affected following conditioning for 30 minutes at −30 and 25°C prior to tensile loading, it could have changed when the adhesives were tested at the selected elevated temperatures.

Table II presents the basic properties of the tested adhesives, and includes the density at ambient conditions and the measured glass transition temperatures at the reference state and following exposure to 30 and 90 days at 50°C and 95% R.H. In addition, the moisture content of the conditioned adhesives was calculated from the glass transition temperatures, following the empirical relationship suggested by Chamis.[9] Accordingly, the wet glass transition temperature, T_{gw}, the dry one, T_{gd}, and the moisture content, M, of a matrix in epoxy composites are related by:

$$T_{gw} = T_{gd}(0.005M^2 - 0.1\,\mathrm{M} + 1.0) \tag{1}$$

From Eq. (1) the percentage of water absorbed can be estimated as follows:

$$M = 10\left[1 - \left(2 \times \frac{T_{gw}}{T_{gd}} - 1\right)^{1/2}\right] \tag{2}$$

Where T_{gw} and T_{gd} are in °F and M is in weight percent.

TABLE II
Densities, glass transition temperatures and calculated moisture absorption of the adhesives investigated

Adhesive	Density (gr/cm^3)	Tg[°C] Ref.	Dry	after 30 days[a]	after 90 days[a]	Moisture [%w] after 30 days[a]	after 90 day[a]
FM-73	1.16	103[b]	100	90	90	0.89	0.89
EA-9628	1.16	102[b]	100	92	92	0.68	0.68
MB-1137	1.17	—	127	100	98	2.10	2.29
Redux-319A	1.37	—	150	120	110	1.98	3.06
FM-300K	1.33	—	175	140	135	2.02	3.06
MB-1515	1.22	—	170	135	125	2.08	2.78
FM-400	1.76	178[b]	190	180	165	0.52	1.28

[a] At 50°C/95% R.H.
[b] Taken from Ref. 3.

As can be concluded from Table II, the first two adhesives, belonging to the first class of adhesives (120°C maximum service temperature), have similar densities and identical T_g's (dry). From the measured T_g's (dry) it can be concluded that the latter adhesives are inadequate for 120°C service. The calculated moisture pick-up indicates that after 30 days of exposure the adhesives reach equilibrium. The other adhesive included in the first group has a higher dry T_g, 127°C, as well as a higher wet T_g, 98°C.

The second class of adhesives represented by Redux 319A, FM-300K and MB-1515 exhibit higher glass transition temperatures in the range of 150 to 175°C, with decreasing transition temperatures to the range of 110 to 135°C after 90 days of conditioning. The relative low T_g of Redux 319A, 150°C, points out that it is marginal for the intended 150°C service temperature.

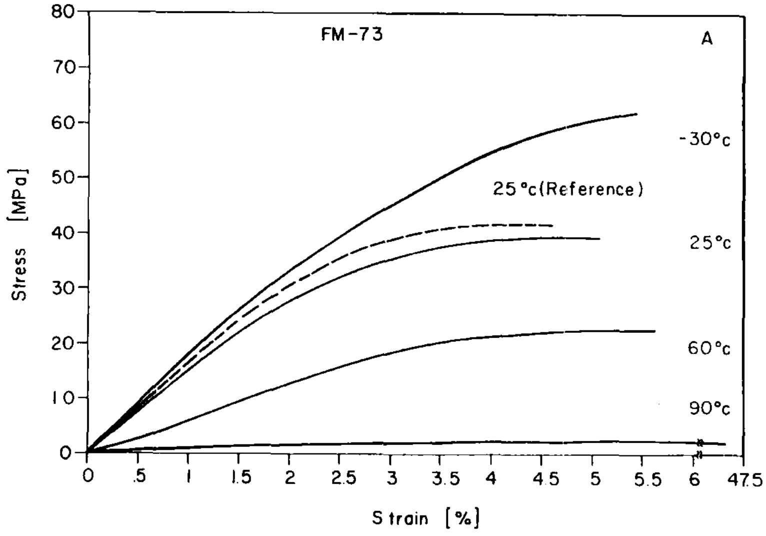
The third category of adhesives, represented by FM-400, has the highest density compared to the other adhesives. This is due to the high loading of aluminum filler—40%.[10] Furthermore, the initial glass transition temperature is the highest obtained, 190°C, and moisture absorption results in a relatively small drop to 165°C.

Figure 1 depicts the stress–strain relationship as a function of testing temperature, following exposure to 90 days at 95% R.H. and 50°C. Three adhesives, namely, FM-73, FM-300K and FM-400, are included in Figure 1, representing the three groups of adhesives investigated. For comparison a reference stress-strain curve (moisture free, tested at 25°C) has been added to each family of curves. As seen in Figure 1, the moisture-containing adhesives at 25°C exhibit lower moduli compared to the moisture-free adhesives. The most pronounced effect occurs in the case of the aluminum-filled adhesive, FM-400. The low moduli are the manifestation of the plasticizing effect of moisture. Due to the relatively high aluminum content of FM-400, its stress–strain curves demonstrate low strain to failure, below 1.5%, which drops below 1% upon moisture absorption. In the case of the filler-free adhesives the strains to failure are higher—above 4.5% in the case of FM-73 and above 3.5% for FM-300K.

Figures 2, 3 and 4 depict the relationship between the tensile modulus and the combination of testing temperatures and moisture content following exposure for 90 days to the hot wet environment, for all three classes of adhesives studied. As can be seen in Figure 2, FM-73 and EA-9628 behave similarly with a large drop of moduli at 90°C. Figure 3 relates the drop in moduli to temperature and moisture content for Redux 319A and MB-1137. The higher densities of these adhesives compared with FM-73 and EA-9628 is manifested in their higher initial moduli. In this case, the effects of humidity are more pronounced, especially at the higher testing temperature of 90°C. Though Redux 319A is designated for 150°C service, it showed unacceptably low modulus and high elongation when tested at 150°C. Consequently, it was evaluated at a maximum temperature of 90°C.

Figure 4 represents the modulus dependence on moisture and temperature, for the second class of adhesives with 150°C maximum service temperature. As can be observed, FM-300K exhibits somewhat different behavior compared with MB-1515, showing an initial increase in modulus from −30°C to room temperature, followed by an expected decline at higher temperatures. Furthermore, while at the low testing temperatures moisture hardly affects the adhesive's stiffness (see Figure 1B), it has a pronounced influence at 150°C. FM-400, the 215°C maximum service temperature adhesive, demonstrates the highest modulus throughout the range of testing temperatures and moisture conditions. The highest initial modulus is affected by moisture pick-up (see Figure 1C) and the adhesive exhibits a respectable stiffness at the highest testing temperature, 200°C.

Comparison of the measured glass transition temperatures, given in Table II,



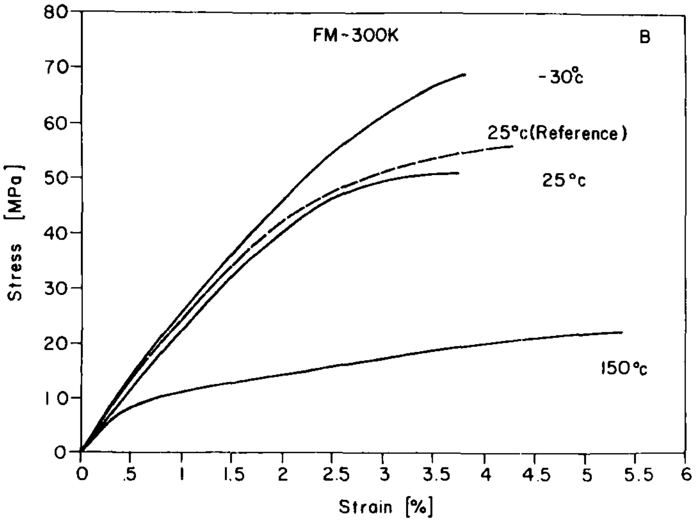


FIGURE 1 The effect of moisture content and testing temperature on the stress–strain curves of various adhesives. (a) FM-73 (b) FM-300K (c) FM-400.

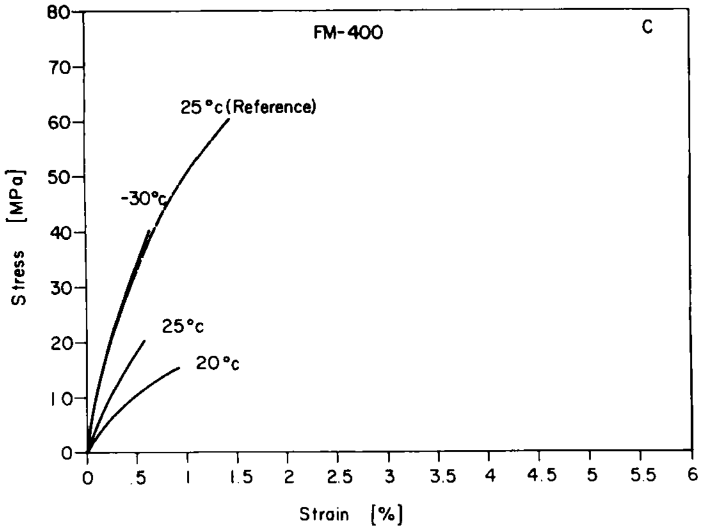


FIGURE 1 (*Continued*)

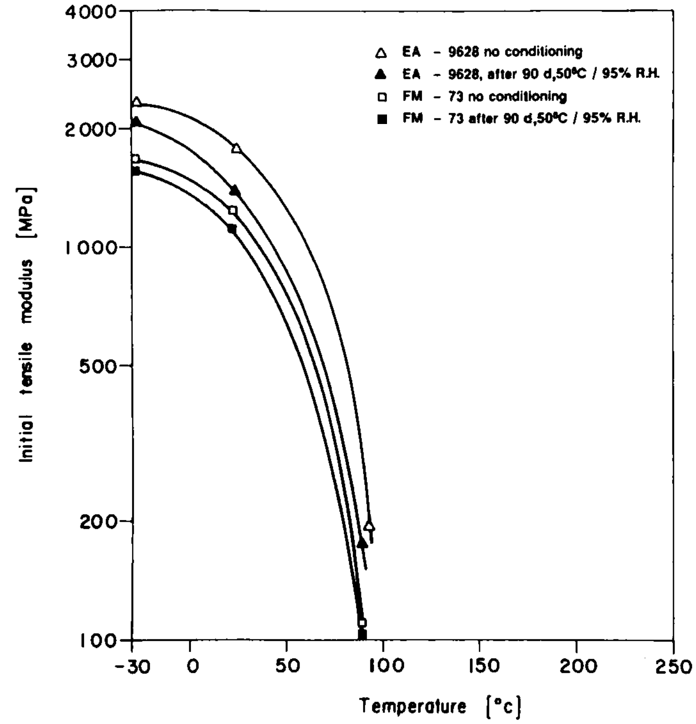


FIGURE 2 The effect of testing temperature and moisture content on the initial tensile modulus of EA-9628 and FM-73.

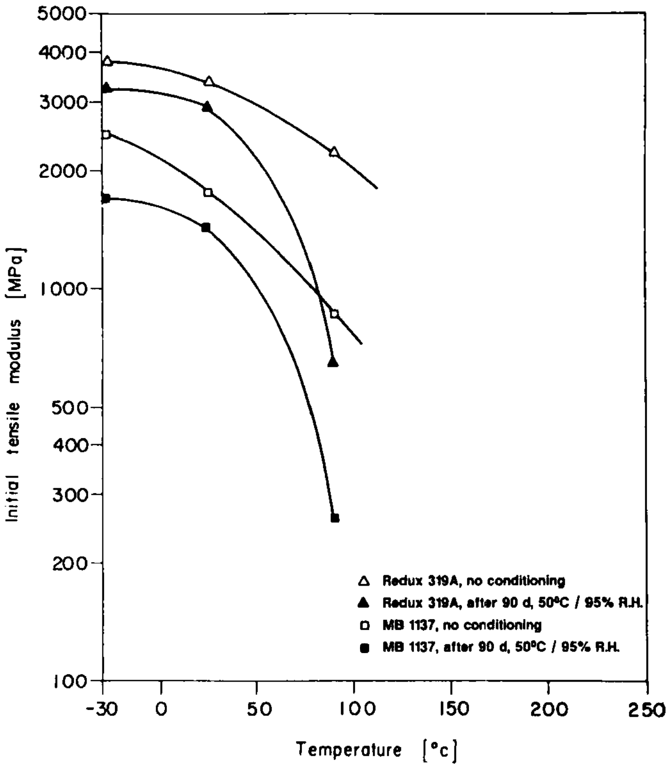


FIGURE 3 The effect of testing temperature and moisture content on the initial tensile modulus of Redux 319A and MB-1137.

and the respective measured values of stiffnesses at various temperatures indicates that, as expected, the modulus depends on the difference between the corresponding glass transition temperature and the testing temperature.

The bulk strengths of all seven adhesives, as related to testing temperatures and moisture pick-up, are given in Figures 5, 6 and 7. Figure 5 depicts the strength reduction with temperature and moisture for FM-73 and EA-9628. In the case of bulk strength compared with bulk modulus, the behavior of FM-73 is different from EA-9628. Strength at low temperatures is higher in the former adhesive but it drops below that of the latter at the 90°C testing temperature. Distinctively, moisture is more influential in the case of EA-9628 compared with FM-73.

The general behavior of Redux 319A and MB-1137 (see Figure 6) in the case of strength is similar to the modulus response for these two adhesives, with an appreciable strength retention of Redux 319A and a pronounced effect of moisture on the strength of the two adhesives.

Figure 7 presents the dependence of tensile strength, of the second and third classes of adhesives, on temperature and moisture. As is evident, FM-300K is the better adhesive with regard to moisture stability, while MB-1515 is highly affected

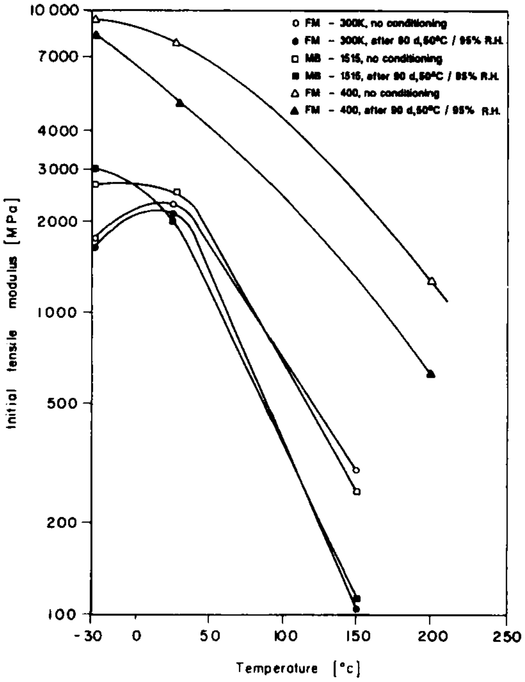


FIGURE 4 The effect of testing temperature and moisture content on the initial tensile modulus of FM-300K, MB-1515 and FM-400.

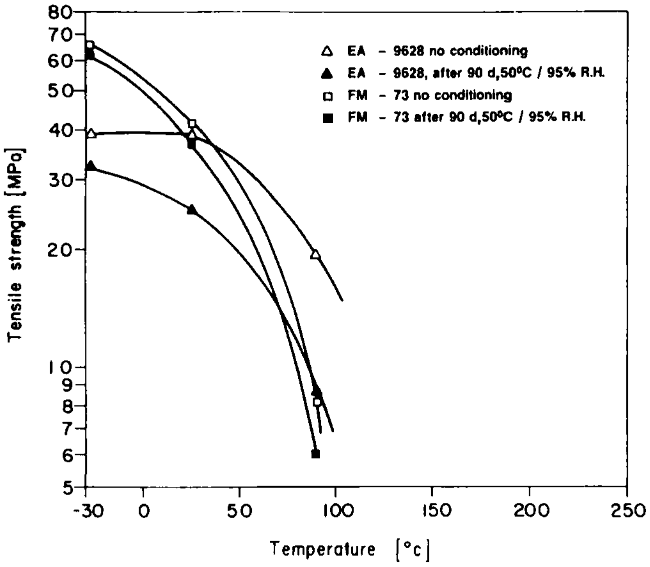


FIGURE 5 The effect of testing temperature and moisture content on the tensile strength of EA-9628 and FM-73.

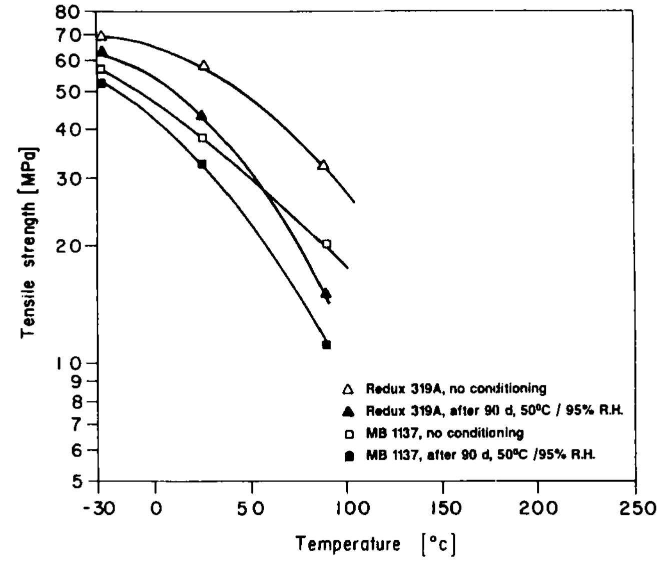


FIGURE 6 The effect of testing temperature and moisture content on the tensile strength of Redux 319A and MB-1137.

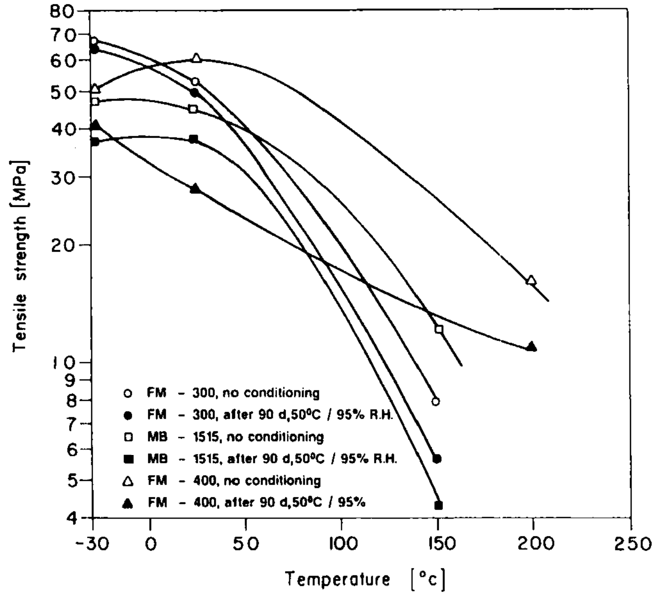


FIGURE 7 The effect of testing temperature and moisture content on the tensile of FM-300K, MB-1515 and FM-400.

by moisture. Moreover, FM-400 is highly influenced by moisture preconditioning. However, it has a respectable level of strength at the 200°C testing temperature.

In general, it seems that the strength dependence on both testing temperature and moisture pick-up could be correlated with the respective glass transition temperatures, as was the case for the modulus relationship.

The resulting general correlation between the experimentally-derived tensile moduli and strengths, and the measured glass transition temperatures, has triggered an attempt to generalize this relationship for all three classes of adhesives. Chamis[9] has shown that the transverse properties of epoxy-based composites, which are matrix dominated, could be correlated with a dimensionless temperature T^* defined by:

$$T^* = \frac{T_{gw} - T}{T_{gd} - T_0} \tag{3}$$

As can be noticed, the dimensionless temperature incorporates both the moisture effect through the wet glass transition temperature, T_{gw}, and the testing temperature, T, in addition to the reference temperature, T_0.

Empirically, Chamis showed[9] that any transverse property could be related to the dimensionless temperature according to the following equation:

$$\frac{P_{tw}}{P_0} = \left(\frac{T_{gw} - T}{T_{gd} - T_0}\right)^{1/2} \tag{4}$$

where P_{tw} is the transverse property as affected by temperature and wetness and P_0 is the corresponding property at reference conditions.

Following Chamis's approach, an attempt to generalize the hygrothermal response of bulk film adhesives was carried out. In the present case the relationship drived was somewhat more general. The dimensionless temperature exponent was determined empirically by using the following equations:

$$\frac{E_{tw}}{E_0} = K_1\left(\frac{T_{gw} - T}{T_{gd} - T_0}\right)^{n_1} \tag{5}$$

and

$$\frac{\sigma_{tw}}{\sigma_0} = K_2\left(\frac{T_{gw} - T}{T_{gd} - T_0}\right)^{n_2} \tag{6}$$

Where E and σ refer to tensile modulus and strength respectively, w and t denote properties at a given moisture and temperature condition, and 0 denotes reference conditions. n_1, n_2 and K_1, K_2 represent the exponents and the pre-exponential constants for the modulus and strength relationships, respectively. To determine n_1 and n_2 the experimental results were plotted according to Eqs (5) and (6) in their full logarithm form. Hence, provided that the tensile properties follow the above relationships, the slope of a full logarithm representation of the results would yield n_1 and n_2 for the modulus and strength respectively, and the intercepts would yield K_1 and K_2. Figures 8 and 9 depict

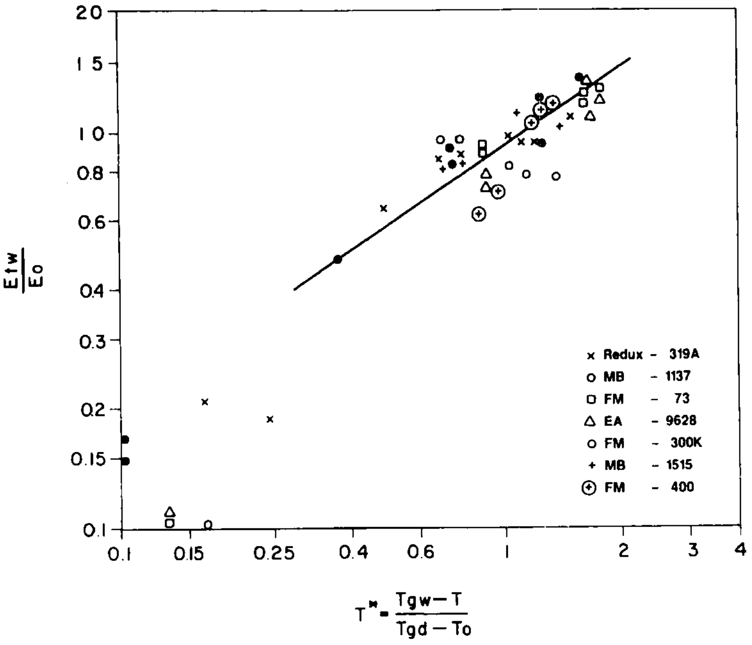


FIGURE 8 Normalized modulus dependence on dimensionless temperature.

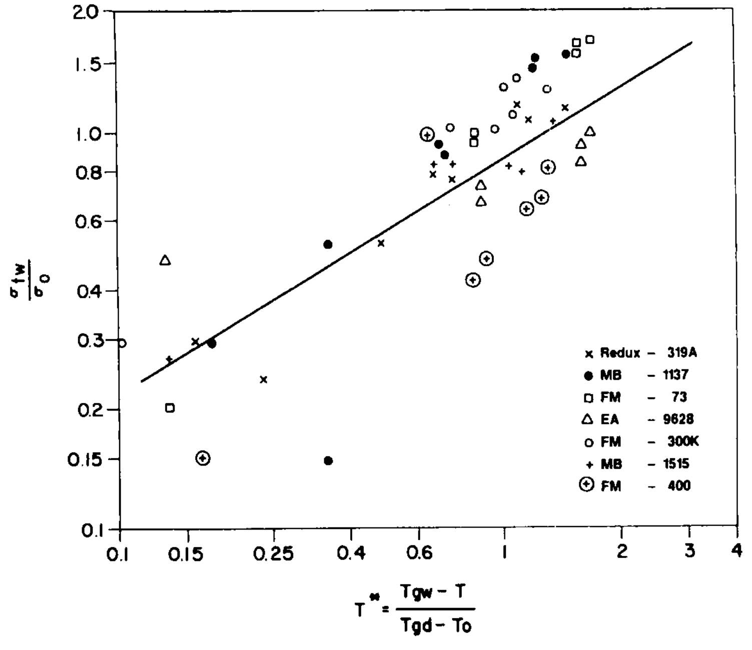


FIGURE 9 Normalized tensile strength dependence on dimensionless temperature.

such representations for the stiffness and strength, respectively. In both cases, reference conditions were selected as 25°C and the moisture-free state.

As can be seen from Figure 8, at temperatures far enough from the dry glass transition temperature (T_{gd}), the experimentally-determined slope n_1 for the modulus relationship of 0.58 and is close to 0.5, as has been found by Chamis[9] for matrix-dominated properties of epoxy composites. K_1 equals 0.95. FM-300K data (designated by open circles) does not coincide with data for all of the other adhesives. This somewhat different response could also be observed in Figure 4. Generally, at temperatures close to the glass transition temperature, i.e. at low values of T^*, the scatter is larger. For the case of tensile strength, Figure 9, the scatter of results is wider than for the modulus relationship. This may be attributed to complicated failure mechanisms. A least squares analysis has indicated that the slope value, n_2, equals 0.59 and the factor K_2 equals 0.87. In

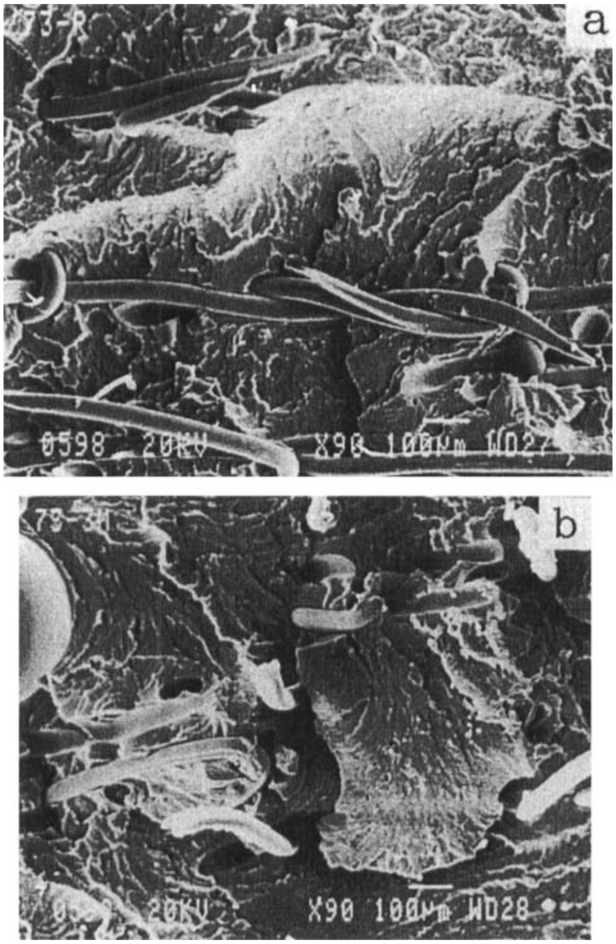


FIGURE 10 Scanning electron micrographs of failure surfaces. (a) FM-73 unexposed (×90). (b) After 90 days at 50°C/95% R.H. (×90).

the two cases the calculated parameters are very close. As in the case of the stiffness, the scatter is greater as the temperatures approach the glass transition temperature.

To complement the study on the hygrothermal response of epoxy film adhesives, the macro-derived strength properties were compared to the microstructure of the fracture surfaces of the adhesives. Figure 10 depicts the scanning electron micrographs of FM-73 specimens following loading at room temperature, at reference as well as after 90 days conditioning. As can be noticed, no major differences appear between the reference and moisturized samples. Both exhibit ductile fracture. This corresponds to the secondary effect of moisture on strength (see Figure 5).

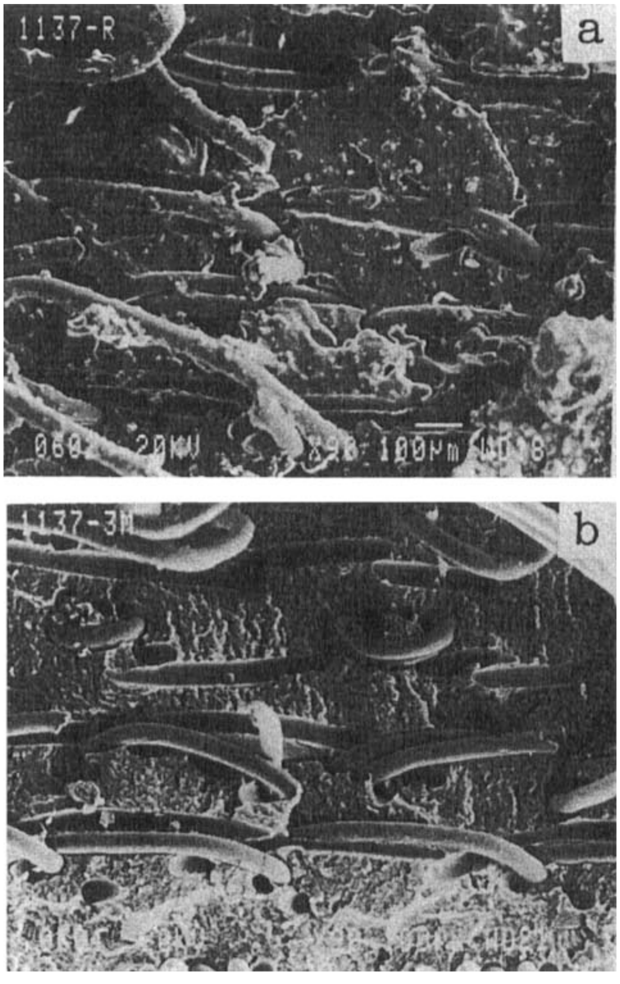


FIGURE 11 Scanning electron micrographs of failure surfaces. (a) MB-1137 unexposed (×90). (b) After 90 days at 50°C/95% R.H. (×90).

MB-1137 demonstrates different appearances of its fracture surfaces when unconditioned and when exposed to humidity and heat. As shown in Figure 11, the unexposed fracture surface is somewhat more ductile, and the epoxy seems to adhere better to the reinforcing thermoplastic carrier, compared with the adhesive after 90 days exposure. As evident from Figure 6, the strength of MB-1137 is more sensitive to moisture compared with FM-73. EA 9628, the third adhesive in the 120°C group, has shown similar fracture topography to MB-1137.

An analysis of the fracture surfaces of FM-300K (Figure 12) reveals that the adhesive, as in the case of FM-73, is hardly affected by moisture, as was the case for the strength level, see Figure 7.

In the case of Redux 319 and MB-1515, moisture was shown to affect their

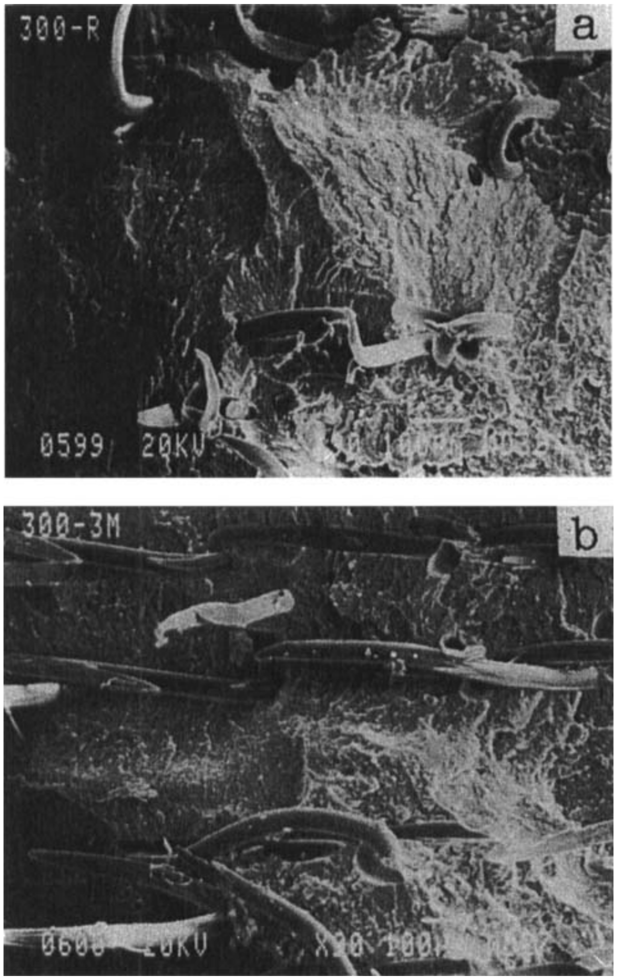


FIGURE 12 Scanning electron micrographs of failure surfaces. (a) FM-300K unexposed (×90). (b) After 90 days at 50°C/95% R.H. (×90).

strength substantially (see Figures 6 and 7). This is also manifested in their fracture surface appearance. For example, Figure 13 depicts the fracture topography of MB-1515 at the reference unconditioned state and following exposure to humidity for 90 days. As can be seen, the 90-day-conditioned specimen reveals large cracks that are absent in the unconditioned adhesives.

FM-400, with its aluminum filler, manifests a completely different fracture appearance compared with the other adhesives (see Figure 14). Furthermore, the moisture-conditioned adhesive shows a completely bare surface of the nylon carrier, with increased number of voids, compared with the moisture-free sample.

The different response of the various adhesives, to humid environment, as

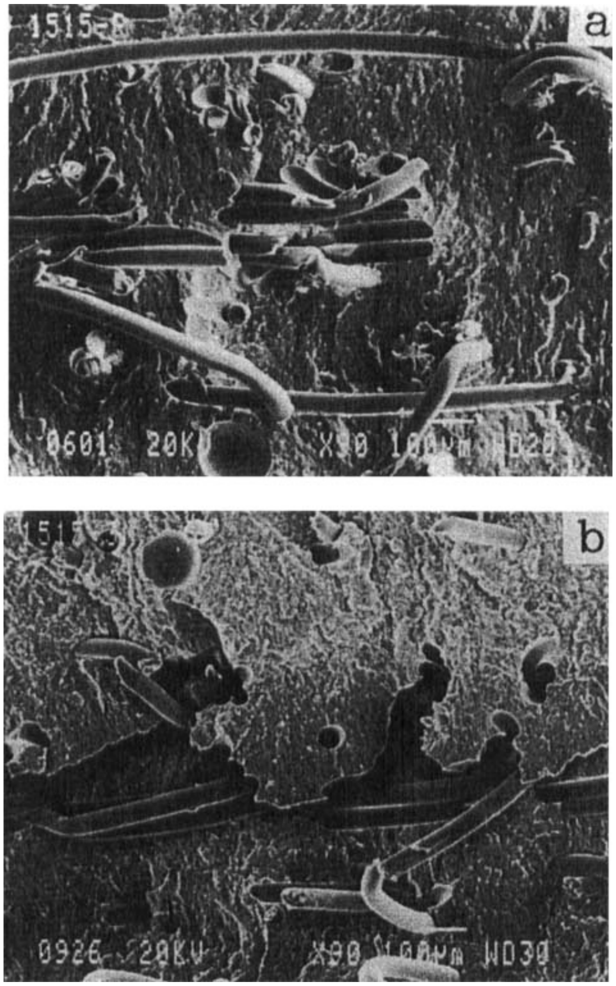


FIGURE 13 Scanning electron micrographs of failure surfaces. (a) MB-1515 unexposed (×90). (b) After 90 days at 50°C/95% R.H. (×90).

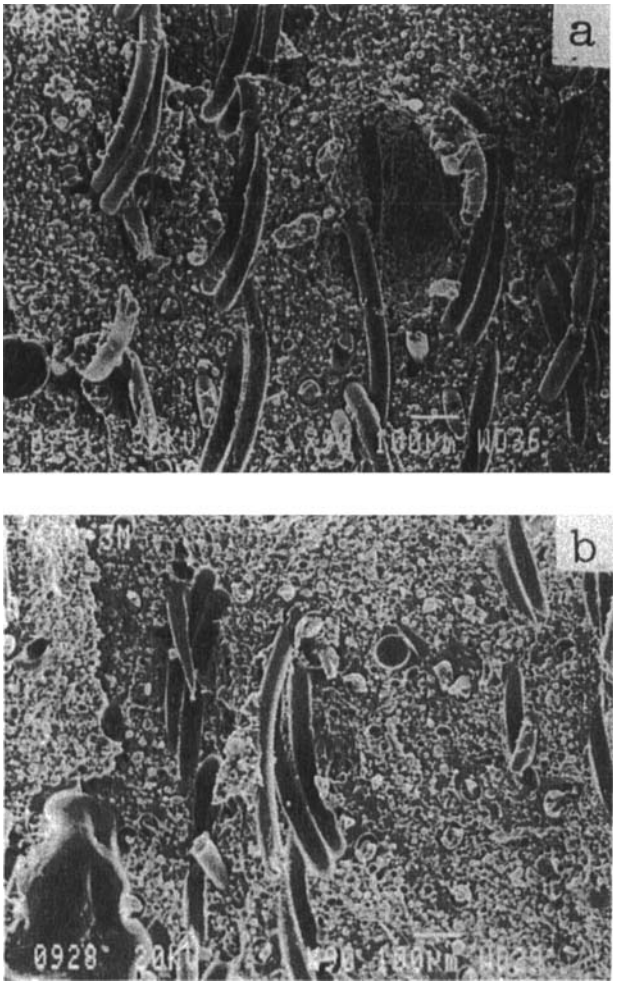


FIGURE 14 Scanning electron micrographs of failure surfaces. (a) FM-400 unexposed (×90). (b) After 90 days at 50°C/95% R.H. (×90).

manifested in the failure surface micrographs, may provide the explanation for the large scatter of results when strength levels were correlated with the dimensionless temperature (Figure 9).

CONCLUSIONS

The effects of moisture content and testing temperatures on the tensile properties of bulk film adhesives could be related to a dimensionless temperature, which includes the wet and dry T_g's in addition to the testing and reference temperatures. The moduli of the adhesives far from their T_g could be related by a single curve, with the exception of FM-300K. However, the strengths of the adhesives exhibited a higher scatter and, consequently, the relationship between strength and the dimensionless temperature was established for each adhesive individually. The effects of moisture on the strength, whether of primary or secondary degree, could be related to the micro-structure of the fracture surfaces of the adhesives. The different failure mechanisms manifested in the electron micrographs may account for the scatter in the relationship between strength and the dimensionless temperature.

The characterization of the effect of moisture and temperature on the bulk tensile properties of adhesives is the first step required for the stress analysis of adhesively bonded joints. As shown earlier,[11] the mechanical properties of adhesives in their bulk state are identical to the ones derived from equivalent bonded specimens. Consequently, the properties presented could be employed in calculating the hygrothermal mechanical response of adhesively bonded joints, provided that the moisture level and temperature in the adhesive layer are known.

Acknowledgements

To Ms S. Uziel and Mr Y. Miller for preparing the adhesive specimens, and to Mr E. Toledo for performing the mechanical testing. To Ms N. Fin and Mr D. Bartal for performing the DMA analysis, and to Mr M. Angelovitz for helpful discussions.

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