Effect of moisture on the static and viscoelastic shear properties of epoxy adhesives

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The effects of moisture on the structural properties of two commercially available adhesives, FM73M and FM300M, are investigated. The experimental study consists of static and viscoelastic shear measurements made from bonded joint specimens soon after they were cured and after lengthy exposure in 63% and 95% relative humidity environments. Static shear modulus and shear creep compliance data for each adhesive at each moisture level throughout a wide range of temperatures are illustrated. Also shown are the effects of temperature and moisture on the ultimate shear strength behaviour, and the temperature and moisture viscoelastic shift functions. It is concluded that the effect of moisture as an external plasticizer on the shear properties of these adhesives is equivalent to raising the environmental temperature.

1. Introduction

The role of adhesive joints has increased substantially in recent years due to the improved structural capabilities of adhesives. This mode of joining provides a lightweight durable bond where in many cases no other mode of joining is feasible. Adhesives are even more integral in joining polymer resin composites, since conventional metal-forming techniques are not possible.

This introduces the problem of characterizing, among other things, the environmental response of the adhesives. Polymeric materials, including adhesives, relax under sustained loadings and, depending on the temperature, significant viscoelastic deformation may occur. Also, it has been observed that polymers absorb moisture which causes adverse effects in the adhesive's structural properties.

In this study the influence of absorbed moisture on the thermal properties of two commercial structural adhesives, American Cyanamid's FM73M and FM300M, are investigated. Both are elastomer-modified epoxy film adhesives supported by a polyester random-mat carrier. The respective cure temperatures are 121° C (250° F) for FM73M and 177° C (350° F) for FM300M. The adhesives are tested in bonded form to most accurately determine the properties in the state in which the adhesives are used.

The test programme consists of several series of static and creep compliance tests. Each is performed between room temperature and temperatures above the glass transition T_g . To determine the effects of moisture, each adhesive is tested in its dry state and after exposure to 63% and 95% relative humidity environments. Observations on the ultimate strength, static shear modulus, and the shear creep compliance are made. In addition, the effects of moisture on the glass transition temperature and the temperature and moisture viscoelastic shift functions are reported.

2. Specimen design

There are many types of adhesive joints which are suitable for use as test specimens, so a



Figure 1 Shear and normal stress distributions across an adhesive joint at various overlap lengths with h = 0.653 cm.

criterion must be established in order to choose the optimal bonded specimen configuration. First, due to the large number of specimens to be tested, demand must be placed on a design which is economical, easy to fabricate and easily tested. Secondly, the magnitude and the uniformity of the stress state in the adhesive layer should be known. Next, there must exist a method of measuring the adhesive deformation in order to determine its stiffness properties. Lastly, the bond areas should be sufficiently large to minimize the effects of localized imperfections such as voids and disbonds at the bond interface.

Primarily from a cost standpoint, an aluminium symmetric single-lap shear specimen, described in Section 3, has been selected to determine bonded adhesive shear properties [1]. In addition, several deflection measuring devices are available with this type of specimen. Unfortunately, the dimensions of this specimen are not standardized and frequently vary within the literature. The relative specimen dimensions govern, most importantly, the stress uniformity of the adhesive.

As will be shown, these dimensions have a

pronounced effect on the state of stress within the adhesive. The critical dimensions are the adherend thickness h and the joint overlap length L. The cured adhesive thickness, η , is generally predetermined by the manufacturer. Renton [2] derived a stress analysis based on plate theory which yields a closed form solution for the shear stress (τ) and normal stress (σ) distributions across the adhesive layer of a single lap shear joint. What was sought from the analysis were the dimensions of a single lap joint specimen which resulted in the most uniform shear stress distribution and the smallest normal stresses. This was accomplished with a parametric study of L and h.

Setting h = 0.635 cm (0.25 in.), the effect of overlap length was investigated. In each case, the load P was applied such that $\tau = P/A =$ 6.9 MPa (1000 psi), where A is the bond area per unit width. The results are shown in Fig. 1. The shear and normal stresses for various overlap lengths have been plotted against x/L, where x is the distance across the overlap. The figure shows that shorter overlap lengths have more uniform stress distributions. Even though a thick adherend specimen has been used, the peak shear and normal stresses in longer overlap cases are well beyond any acceptable limit.

The excessive peel stresses in Fig. 1 can be controlled somewhat by increasing the bending stiffness of the adherend. This was done by increasing the adherend thickness. Fixing h = 0.953 cm. (0.375 in.), the overlap length is varied in small increments. It was found that L = 0.953 cm produced the most uniform shear stress distribution, as shown in Fig. 2.



Figure 2 Shear (τ) and normal (σ) stress distributions across and adhesive joint with $L \doteq h = 0.953$ cm (0.375 in.).



Figure 3 Mechanical drawing of symmetric single-lap shear joint. Dimensions given in cm (in.).

A mechanical drawing of the specimen is shown in Fig. 3.

It is interesting to note that both L = h = 0.635 cm and L = h = 0.953 cm have nearidentical stress distributions. Given a choice, L = 0.953 cm has the advantage of greater bond area, being less sensitive to local bonding imperfections.

3. Experimental procedure

The testing programme was designed to determine the shear modulus and the time-dependent shear creep compliance throughout a wide range of temperatures. This was done for both adhesives under dry conditions and after exposure to 63% and 95% relative humidity (RH) environments. To accomplish this, 450 specimens were prepared of which approximately half resulted in acceptable test data. The remaining specimens were used in sampling or were discarded because of improper fabrication or incorrect instrumentation during testing. The method in which the specimens were prepared along with a description of the shear deflection measuring device are presented below.

The aluminium adherend material was delivered precut into $24.1 \times 30.5 \times 0.953$ cm $(9.5 \times 12.0 \times 0.375 \text{ in.})$ plates. Following the manufacturer's recommendations, the aluminium plates were degreased, deoxidized in acid etch solution, and then primed on one side with American Cyanamid's BR-127 primer. A layer of adhesive was stacked between two plates and then the plates were bonded together in an autoclave, using a vacuum bag, at the respective curing temperatures of 121°C (250°F) for FM73M and 177° C (350° F) for FM300M. The plates were held at cure temperature under 0.28.MPa (40 psi) for one hour. The cured adhesive thicknesses were 0.25 and 0.33 mm (0.010 and 0.013 in.), respectively. After the plates were bonded together they were machined as shown in Fig. 3.

The specimens were divided into three groups, each group to be tested after exposure to a particular level of moisture. The three humidity levels were dry (i.e. no humidity), 63% and 95%. RH. Little attention was required for the dry group of specimens; they were tested as cured. The second group of specimens was placed in a sealed aluminium cabinet inserted in an oven. An aqueous solution of NaNO₃ was used to maintain a constant relative humidity of 63% at a temperature of 54° C. The last group, 95% RH, was placed into three Blue M Magni Whirl constant temperature water baths. The bath temperatures were maintained between 56 and 59° C.

An expression is given for the in-plane moisture diffusion in a rectangular adhesive joint. The equation is an approximation of Fick's second law expanded in two dimensions [3, 4]:

$$\frac{M}{M_{\rm m}} = 1 - \exp\left[-7.3\left(\frac{1}{u^2} + \frac{1}{v^2}\right)^{0.75}(Dt)^{0.75}\right]$$
(1)

This relates the amount of absorbed moisture M with the amount of exposure time. The joint dimensions are u and v, and D and M_m are the moisture diffusivity and the maximum moisture content determined for FM73M and FM300M presented in Table I [3].

Using Equation 1, a moisture content of $M/M_{\rm m} = 0.67$ was achieved after 90 days of exposure for FM73M and 120 days of exposure for FM300M in each humidity environment. Moisture diffusion can be accelerated by increasing the temperature; however, some epoxies have exhibited non-Fickean moisture diffusion caused by microcracking during prolonged

TABLE I Properties of adhesives at 95% RH

Adhesive	Т (°С)	$\frac{D}{(\mathrm{cm}^2\mathrm{sec}^{-1})}\times10^9$	M _m (%)
FM73M	38	6.2	1.55
	49	8.0	2.05
	60	8.7	2.20
	71	9.8	2.30
FM300M	38	3.9	2.10
	49	5.4	2.40
	60	6.7	2.60
	71	8.2	2.60



Figure 4 Sketch of KGR-1 instrument used in measuring adhesive deflection in symmetric single-lap shear joints.

humidity exposures at temperaturtes above 70° C [5, 6]. This was undesirable in this case since only the plasticizing effect of the moisture is sought.

Several existing measurement devices are capable of measuring the adhesive shear deformation of a symmetric single-lap shear joint [1]. Included in the list is the KGR-1, designed and later patented for use with this joint. The designer Raymond Kreiger [7] graciously loaned the device for use in this testing programme.

An illustration of the KGR-1 device is given in Fig. 4. It consists of two linear voltage differential transformers (LVDT) mounted on each side of the joint. The KGR-1 is secured by two flat blade springs (not shown) and it rests on three hardened steel points on each side of the joint. Focusing on the glueline region, the steel points are located approximately 1.3 mm (0.05 in.) away from the adhesive centerline. Sinse the KGR-1 makes no other contact with the specimen, it is free to rotate with the glueline as it is loaded. Also, the shear deformation of the aluminium between mounting points and the glueline, which would be included in the LVDT reading, is limited to a small amount. This amount can be measured and deducted from the LVDT reading, resulting in the adhesive deflection.

The KGR-1 device is used with a supporting module which controls the a.c. signals to and from the LVDTs, converts the a.c. output from the LVDTs to d.c., and then amplifies the d.c. signal so it can be recorded on a standard X-Y

chart. Resoluton of the KGR-1 was of the order of 10^{-4} mm and the output remained linear up to a deflection of 0.43 mm.

4. Results

Tests for shear modulus and ultimate shear strength were performed with an Instron mechanical testing mechine at a constant crosshead speed of 0.02 cm min⁻¹. An oven was mounted in the Instron surrounding the specimen and loading fixtures. The temperature was monitored by a thermocouple mounted on the specimen surface. The adhesive was tested no sooner than 15 min after the tempeature at the outer surface of the specimen had stabilized. This allowed the temperature throughout the joint to become uniform and the KGR-1 to become thermally stable as well. No effort was made to control the humidity in the test environment. Due to the low moisture diffusivity of the adhesive and the small surface area from which moisture could escape, the amount of moisture lost during the tests was negligible. The specimens were selected at random within each moisture group. In addition, no specimen was tested more than once because of the timedependent nature of the adhesive.

Four representative load-deflection curves are shown in Fig. 5. The curves demonstrate the behaviour of dry FM37M at temperatures ranging from room temperature to temperatures above T_g ($T_g = 99^\circ$ C). The load-deflection curves for other moisture levels of FM73M and for FM300M are similar to those in Fig. 5 with respect to the value of T_g . The effect of the



Figure 5 Sample load-deflection curves of dry FM73M at various temperatures.



Figure 6 Experimental values of shear modulus against temperature at each moisture level for FM73M: \triangle dry, \bigcirc 63% RH, \Box 95% RH.

elastomer in the epoxy adhesive is shown by the large amount of strain to failure, particularly at low temperatures.

Plots of the shear modulus G against temperature for FM73M and FM300M are given in Figs. 6 and 7. Each graph contains three curves representing each of the three moisture levels. All six curves demonstrate the general response expected of cross-linked polymers. There is a glassy region where the modulus is fairly temperature-independent, followed by a transition region where the modulus decreases substantially. At higher temperatures the modulus of cross-linked polymers levels off to a rubbery value. Unfortunately there are not many data in the rubbery region due to the subjectivity in defining the linear tangent in the load-deflection data.



Figure 7 Experimental values of shear modulus against temperature at each moisture level for FM300M: \triangle dry, \bigcirc 63% RH, \square 95% RH.



Figure 8 Experimental values of ultimate shear strength against temperature at each moisture level for FM73M: \triangle dry, \bigcirc 63% RH, \square 95% RH.

Plots of ultimate shear strength τ_u against temperature for FM73M and FM300M are given in Figs. 8 and 9. As can be seen, there is no clear relationship; there is only a decreasing trend in strength as temperature increases. Part of the reason for the large fluctuations in strength is the mode in which the adhesive joint fails.

Failure of an adhesive joint may occur in one of two ways, excluding failure of the adherend. Failure can occur within the adhesive layer, termed *cohesive failure*, or at the adhesive– adherend interface, termed *adhesive failure*. The trend in these experiments is that the degree of adhesive failure increased as the temperature increased. At temperatures near and above T_g



Figure 9 Experimental values of ultimate shear strength against temperature at each moisture level for FM300M: \triangle dry, \bigcirc 63% RH, \square 95% RH.

almost all of the failures were predominantly adhesive. Concluding from the data, failure surfaces with a large percentage of adhesive failure resulted in lower ultimate strength values. In addition, the amount of moisture in the adhesive had only limited effect on the failure behaviour. In general, the 95% RH group experienced slightly greater degrees of adhesive failure than the other two groups. These observations agree with previously obtained data for similar materials [8, 9].

The effect that moisture has on the stiffness properties of these adhesives is evident. In the glassy region, where G is relatively temperatureinsensitive, there is minimal distinction between the data at the various humidity levels. As the temperature increases, each curve enters a transition region. As anticipated, with increasing moisture content the temperature associated with the glass transition decreases. Finally, the modulus value in the rubbery region is expected to be reasonably moisture-independent, as it is in the glassy region. The significant difference in the modulus curves are the values of the glass otherwise. transition temperatures; the appearance of each modulus curve is nearly identical.

Although T_g is associated with mechanical glass-transition behaviour, it is not correct to derive its value from the shear modulus diagrams. It cannot be assumed that a particular temperature near the modulus transition region is equivalent to T_g as defined more commonly by volumetric expansion or by calorimetry. For this reason, an *apparent* glass transition temperature is defined from the shear modulus data which is known to correspond to a particular value of G in the transition region. This interpretation corresponds to a consistent value of T_g most associated with the mechanical deformation behaviour of the two adhesives.

The values of the apparent T_g were defined as the temperature at which G = 69.MPa for FM73M, and G = 71.MPa for FM300M. This corresponds to the approximate median value of G between the glassy and rubbery regions [10]. The values are listed in Table II.

The viscoelastic response of the adhesives was determined following the method of reduced variables procedure described by Ferry [11]. The major benefit of this method, which is based on time-temperature equivalence, is that a wide

TABLE II Values of T_g determined from static tests

Atmosphere	$T_{\rm g}$ (° C)	<i>T</i> _g (° C)	
	FM73M	FM300M	
Dry	99	155	
63% RH	91	146	
95% RH	80	128	

range of viscoelastic behaviour can be determined by short time tests at varying temperatures. The short-time results are then shifted horizontally along the time axis to generate a continuous master curve.

Creep compliance tests were performed using the structural frame of the Instron. The dead weights rested on top of the crosshead when the specimen was unloaded. To load the specimen, the crosshead and the weights were lowered until all of the weights were supported by the specimen. This provided a quick and smooth load transfer in a period of 1 to 2 sec. The same oven, thermal warm-up, and specimen selection procedures used in the static tests were used in the creep tests as well.

The amount of weight used in the creep tests varied between 85 and 105 kg. This resulted in a shear stress of 3.45 to 4.14 MPa, which is approximately 10% of the room temperature ultimate strength. The deflection as a function of time was measured with an X-Y recorder having a time movement feature. Measurements began at 5 sec when the dynamic effects settled out. The creep experiment ran continuously and was stopped after 1000 sec. At ten points corresponding to 5, 10, 20, 40, 65, 100, 200, 400, 650, 1000 sec the creep compliance J(t) was evaluated using the equation

$$J(t) = \frac{U_{adh}(t)/\eta}{P/A}$$
(2)

 $U_{adh}(t)$ is the time-dependent creep deflection, η is the adhesive thickness, and P/A is the deadweight load divided by the bond area. The reduced compliance in terms of a reference temperature T_0 is given by

$$J_{\rm red}(t, T_0) = \frac{\varrho T}{\varrho_0 T_0} J_{\rm red}(t, T)$$
(3)

where ϱ refers to the density of the material. As in most cases, the density ratio is small and was neglected in these calculations.

Following the method of reduced variables



Figure 10 Plot of the reduced creep compliance against time for dry FM73M.

procedure, logarithmic plots of the reduced compliance against time were made for the adhesives at their respective moisture levels. There is a total of six such sets of data, as shown in Figs. 10 to 15. In each case $T_o = T_g$, using the values of T_g found in Table II.

The next step was to horizontally shift the various pieces of data until they aligned and formed a continuous master curve, where the position along the time axis is associated with the particular value of T_0 . The distance the individual pieces of data must be shifted is defined as the viscoelastic shift function due to temperature, $\log a_T$. The six master curves



Figure 12 Plot of the reduced creep compliance against time for FM73M at 95% RH.

generated from the data in Figs. 10 to 15 are shown in Figs. 16 and 17.

It is seen that the viscoelastic response of the adhesives resembles the response observed in the static tests. The glassy creep behaviour is best observed in Figs. 10 to 15. There were some uncertainties in shifting this data, and consequently the glassy region does not appear completely in the master compliance curves. The data in the transition region appear to be quite well defined after examining the shape and uniformity of the overlapping curves. At large compliances the curves begin to level off at a rubbery plateau. In many cases specimens



Figure 11 Plot of the reduced creep compliance against time for FM73M at 63% RH.



Figure 13 Plot of the reduced creep compliance against time for dry FM300M.



Figure 14 Plot of the reduced creep compliance against time for FM300M at 63% RH.

failed prematurely due to creep rupture at the adhesive-adherend interface. As a result, a rubbery plateau was only partially established.

Plots of $\log a_T$ against reciprocal temperature are shown in Figs. 18 and 19. Usually $\log a_T$ against *T* is presented; however, plotting $\log a_T$ against 1/T demonstrates more clearly the interrelationship between the three moisture conditions. Several compliance curves have been omitted from Figs. 10 to 15 for graphical clarity but their values of $\log a_T$ appear in Figs. 18 and 19.

Two basic semi-empirical models exist which relate the horizontal shift distance, $\log a_T$, and temperature. In the glassy region, transition state theory is used to derive an Arrhenius-type relation, and in the transition and rubbery



Figure 15 Plot of the reduced creep compliance against time for FM300M at 95% RH.

regions, free volume theory is used to derive the Williams, Landel, Ferry (WLF) relationship.

In the glassy region, material deformation is governed by small, localized molecular motion. This behaviour can be described by transition state theory, which states that two molecules must pass through a transition state, or activated complex, before they may react [12]. Assuming that molecular relaxation involved in time-dependent behaviour is related to the above transition state model with constant activation energy ΔH , then a_T and temperature are related by

$$\log a_T = \frac{\Delta H}{2.303R} \left(\frac{1}{T} - \frac{1}{T_0} \right)$$
 (4)

where R is the universal gas constant.



Figure 16 Master curves at each of the three moisture conditions for FM73M at a reference temperature of 80° C.



In the glass transition and rubbery regions, large-scale molecular motions occur and the modulus becomes highly temperaturedependent. Based on the assumption that the free volume is constant below T_g and grows linearly with temperature above T_g , the WLF relation describes the time-temperature relationship at temperatures greater than T [11]:

$$\log a_T = \frac{-C_1(T - T_0)}{C_2 + T - T_0}$$
(5)

If only limited $\log a_T$ against temperature data are available, the constants may be estimated by averaged values compiled from large numbers of polymers at the glass transition temperature:

$$\log a_T = \frac{-17.44(T - T_g)}{51.6 + T - T_g}$$
(6)



Figure 18 Plots of $\log a_T$ against reciprocal temperature at each of the three moisture conditions for FM73M: \triangle dry, \bigcirc 63% RH, \square 95% RH.

Figure 17 Master curves at each of the three moisture conditons for FM300M at a reference temperature of 128° C.

As shown in the plots of $\log a_T$ against 1/T, the WLF equation shows good agreement with these experimentally determined values of $\log a_T$, although the data are somewhat sparse. At T_g a gradual change in the shift function relationship occurs. It is physically associated with the changing deformation mechanisms which take place above and below T_g .

At temperatures below T_g an Arrhenius relation with constant activation energy is applicable. The purpose of presenting the $\log a_T$ data against reciprocal temperature was to illustrate the linear region where the activation energy is constant. It is important to notice that the activation energy appears to have the same value for each of the moisture levels for each



Figure 19 Plots of $\log a_T$ against reciprocal temperature at each of the three moisture conditions for FM300M: \triangle dry, \bigcirc 63% RH, \square 95% RH.

adhesive. The values of ΔH are 146 and 101 kcal mol⁻¹ for FM73M and FM300M, respectively. These are greater than other values reported for epoxy resins [10].

Typically the time-temperature equivalence property of a polymer is established as a result of the method of reduced variables technique. If it can be demonstrated that the horizontally shifted segments of data closely overlap and that the relationship between $\log a_T$ and temperature is consistent with previous observations, then a polymer can be considered time-temperature equivalent, also termed thermorheologically simple. It is clearly evident in the six master curves that the shifted data overlap nicely and that there is agreement between the experimental shift function data and the two semiempirical relations. As a result, both of the adhesives may be considered thermorheologically simple materials at each moisture level, and thus deserve the analytical and experimental simplifying assumptions related to timetemperature equivalence.

The damage caused by increasing moisture can be assessed in terms of the lowering of T_g and any associated temperature-dependent properties. Considering viscoelastic properties, the effect that externally absorbed moisture has on the time-dependence of a material is the same as increasing the temperature. Accordingly, a horizontal shift factor due to moisture, a_M , can be defined which is analogous to a_T . It follows that viscoelastic properties at different temperatures and different moisture contents may be superimposed by a horizontal shift in time scale [13].

The effect moisture has on the shear creep compliance is shown by the positions of the master compliance curves in Figs. 16 and 17. These three curves are plotted with respect to the same reference temperature T_g of each adhesive at 95% RH. The horizontal distance between the curves, $\log a_M$, is due solely to moisture levels contained in the adhesives. This corresponds to a reduction in time of $10^{1.35}$ at 63% RH and $10^{3.65}$ at 95% RH for FM73M, and $10^{1.20}$ at 63% RH and $10^{3.50}$ at 95% RH for FM300M.

Overlapping the three master curves for each adhesive demonstrates the close matching of shapes between the three moisture levels. This leads to the most important conclusion that increasing the moisture content has the same effect on the creep compliance behaviour is increasing the temperature. This was suspected to be true and has now been verified in the range of time and temperatures used in this study.

Caution should be used when interpreting viscoelastic data shifted to time decades beyond the actual experimental time range. Long-term thermal and moisture degradation of polymer may occur, causing unexpected deformations and behaviour changes [14]. Beyond the typical plasticizing effects, the moisture leads to microcracking in the polymer network and subsequent chemical decomposition. In the event that this occurs, the values of a_T and a_M , and the time, temperature and moisture interrelations become invalid.

5.Summary and conclusions

At present there is limited information regarding the mechanical testing and behaviour of adhesively bonded joints. This includes the lack of a standardized bonded joint test specimen and a lack of empirical thermal and moisture data.

It was first necessary to develop an acceptable bonded joint specimen. In selecting a specimen design there were several factors considered; the most important were economics and ease of testing. This led to the commonly used symmetric single-lap shear joint. The specific dimensions of the test section were determined as a result of a computer-aided parametric study which sought the most uniform shear stress and the minimum normal stress distribution.

Mechanical testing indicated that the thermal response of the two adhesives was typical of general cross-linked polymer behaviour. In addition, it was discovered that both adhesives can be treated as thermorheologically simple materials, even when they are moisture-influenced. The amount of moisture diffusion into the adhesives, reflected by the relative humidity of the conditioning environment, had definite adverse effects on the mechanical properties. It was shown that the presence of moisture has the same effect as raising the environmental temperature, or equivalently lowering T_g , on the static and viscoelastic shear properties of the two adhesives.

It is interesting to compare the data profiles of the two adhesives. Both are classified as modified epoxy film adhesives, except that FM73M has a 121° C (250° F) cure temperature and FM300M is cured at 177° C (350° F). Other than the temperatures at which the glass transitions occur, the two adhesives show notable similar mechanical response.

Depending on the service temperature, and hence the horizontal position of the creep compliance curves, the shift in time due to moisture may represent several seconds or several years. In either case, it is evident that the effects of moisture must be accounted for in predicting the creep life expectancy of a bonded component.

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