Water absorption by an epoxy resin and its effect on the mechanical properties and infra-red spectra

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A filled epoxy resin used as a structural adhesive and based on the diglycidyl ether of bisphenol A cured with dicyandiamide has been subjected, in its bulk form, to ageing at 40, 55 and 70°C and ca. 100% relative humidity. Gravimetric, viscoelastometric and *FT*i.r. studies have been effected after various times of exposure. Water absorption in the polymer is essentially Fickian, although closer inspection reveals the finer behaviour to be sigmoidal. The activation energy for diffusion is of the order of 80 kJ mol^{-1}, but there appears to be no clear relationship between equilibrium absorption values and temperature. Viscoelastometry has shown that T_g diminishes from ca. 115°C before ageing to ca. 90°C at saturation, 1% of water uptake corresponding to ca. 8°C reduction in T_g. Reductions in Young's modulus were observed both in the glassy and rubbery states after ageing and the latter is associated with molecular chain scission. *FT*i.r. analysis has shown several modifications occurring due to water absorption, the main one being an increase in intensity of the band at 1740 cm^{-1}. It is concluded that water absorption leads both to plasticization effects and chemical modification of the epoxy resin.

(Keywords: epoxy resin; chemical modification; water absorption)

INTRODUCTION

Epoxy resins are widely used as structural adhesives in both the aerospace and automotive industries. The advantages of adhesive bonding over mechanical methods of assembly, such as riveting and bolting, are several. Amongst the more important of these are the reduction of stress concentrations necessarily incurred near holes used for mechanical fastening, reduction in weight and the ability to join thin and/or dissimilar materials. However, there are some disadvantages associated with structural adhesive bonding of which probably the most major is the shortening of service life following exposure to humidity at elevated temperatures. Various modes of degradation of a bonded joint may occur under these conditions, namely deterioration of the polymeric adhesive itself or, perhaps less commonly, of the substrates due to water ingress, and modification of the interfacial zone separating adhesive and adherend[1,2]. Although interfacial phenomena are often of paramount importance in the overall behaviour of bonded joints, characterization of changes occurring to the adhesive itself following water uptake is clearly a necessary step in understanding the ageing process. The present study, constituting part of a more general project aimed at better understanding the deterioration of bonded joints in adverse conditions of humidity and temperature, was undertaken with this in mind.

An industrial (rather than a model) adhesive based on an epoxy resin cured with dicyandiamide has been studied in its bulk form. Water ingress has been monitored using gravimetric measurements whilst changes in mechanical properties have been followed using viscoelastometry. In order to link variations in mechanical behaviour with chemical modifications occurring in the polymer, *FT*i.r. spectroscopy has been employed.

EXPERIMENTAL

The epoxy resin studied was based on the diglycidyl ether of bisphenol A (DGEBA), crosslinked with dicyandiamide (DDA), and contained fillers (Ciba-Geigy XB3131). Crosslinking was effected at 150°C over 1 h after heating at a rate of 8°C min^{-1}. Samples were moulded as sheets of dimensions 190 × 70 × 4 mm and machined.

Gravimetric measurements of sorption and desorption were performed on sheets of dimensions 90 × 70 × 2 mm using an analytical balance. Sorption was effected by exposing the samples to an atmosphere of ca. 100% relative humidity (*RH*) at 40, 55 and 70°C whilst desorption was followed at the same temperatures in dry ovens. Samples were periodically removed, blotted, weighed and replaced in the ovens.

Viscoelastometric studies were effected using a Metravib Viscoanalyseur. The samples, of dimensions 12 × 6 × 4 mm, were tested in compression–compression mode at a frequency of 5 Hz with the temperature

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increased from −130°C to 180°C at a heating rate of 2°C min^{-1}.

*FT*i.r. spectra were recorded from 4000 to 400 cm^{-1} on pellets composed of 1% polymer powder and 99% KBr powder using a Nicolet 20 SXC spectrometer.

RESULTS AND DISCUSSION

Water uptake

Curves of water absorption by the adhesive at the three temperatures studied are shown in *Figures 1* and *2*, results being plotted as weight uptake (%) *versus* $t^{1/2}/e$, where t is the absorption time and e is the sheet thickness. As expected, the diffusion rate is temperature related. The approximate times necessary to reach the equilibrium value W_∞ for sheets of thickness 2 mm are given in *Table 1*. Time to attain W_∞ is temperature dependent but there appears to be no clear relationship between the value of W_∞ and temperature (see *Table 1*). The variation of W_∞ noted at 40°C is due to changing the oven.

Results obtained at 40°C in the first oven showed a plateau at 3.5%, but after transferring the sheets to the second oven the mass increased to 4.5%. Some examples have been aged in the second oven alone and a plateau at 4.5% was obtained directly. In the literature it has been reported for epoxies that W_∞ is an increasing function of temperature for an equivalent value of RH^{3-7}. We therefore infer that the problem is linked with RH.

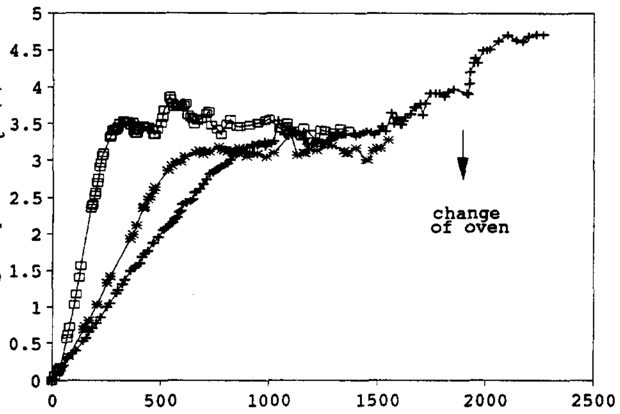


Figure 1 Water absorption curves at three temperatures: (□) 70°C; (*) 55°C; (+) 40°C

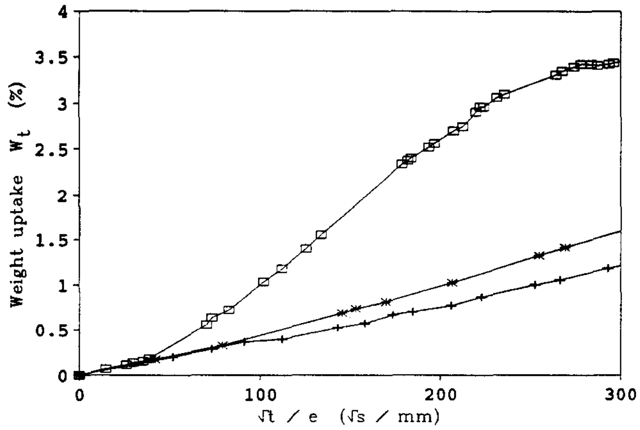


Figure 2 Magnification of the early stages of the water absorption curves of *Figure 1*

Table 1 Results of water uptake experiments

Temperature (°C)	Approximate time to reach W_∞ (h)	W_∞ (%)	10^{-8} D (cm^2 s^{-1})
40	1100 (2100)	3.5 (4.5)	0.26 ± 0.02 (0.15 ± 0.01)
55	480	3.1	0.70 ± 0.09
70	170	3.5	3.6 ± 0.5

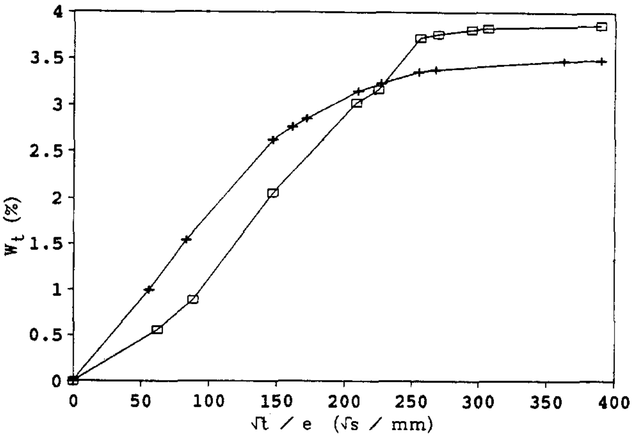


Figure 3 Absorption (□) and desorption (+) of water at 70°C

It has indeed been well established that W_∞ is a function of RH, i.e. $W_\infty = a(RH)^b$, where a and b depend on the polymer in question$^{6-8}$. A value of RH near 100% cannot be accurately measured with hygrometers currently available, thus we cannot be absolutely certain that the atmosphere is saturated. Another possible explanation of why W_∞ at a lower temperature should be greater than the equivalent value at a higher temperature has been given by Carfagna *et al.*[4]. They have shown, studying a triamine-cured DGEBA at 20°C and 70°C in water immersion, that W_∞ is influenced by the ratio of epoxy to hardener.

A lack of hardener or a stoichiometric mixture of resin and hardener leads to W_∞ (20°C) < W_∞ (70°C), whereas a large excess of hardener leads to W_∞ (20°C) > W_∞ (70°C). In our case, there is known to be an excess of hardener (see *FT*i.r. results below), but no definite conclusion may be reached since a different curing agent has been employed.

In *Figure 1*, sorption curves appear to show Fickian behaviour, but magnification of the scale (see *Figure 2*) shows non-linear behaviour at the start of water uptake. This type of curve has been observed experimentally in several systems[9]. The sorption curves are sigmoidal in shape with a single inflection point. The initial rate of desorption exceeds that of sorption, but desorption soon becomes slower and the curves cross. We observed this phenomenon after ageing and drying sheets at 70°C (see *Figure 3*). Curves are plotted in the form of fractional uptake W_t *versus* $t^{1/2}/e$, where W_t is the weight uptake at time t. This type of curve is termed sigmoidal and has been explained by Crank[10] using a history-dependent diffusion coefficient. Rising penetrant concentration is assumed to lead to an immediate increase in diffusion coefficient, followed by a slow drift towards an equilibrium value as a result of a relaxation process

Table 2 Values of activation energy for diffusion of water in epoxy systems

Ref.	Epoxy	Hardener	ΔH (kJ mol^{-1})
This study	DGEBA	Dicyandiamide	78 ± 5 (92 ± 5)
3	DGEBA	Triamine	37
4	DGEBA	TETA[b]	55
6	DGEBA	Diamine	47 ± 4
	DGEBA	Dicyandiamide	44 ± 4
7	TGDDM[a]	DDS[c]	34
20	DGEBA	Anhydride	36

[a] Tetraglycidyl-4,4'-diaminodiphenylmethane
[b] Triethylenetetramine
[c] 4,4'-Diaminodiphenyl sulfone

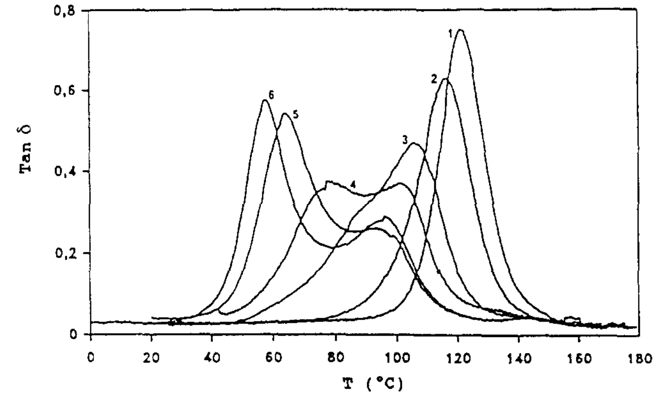


Figure 4 Loss tangent tan δ *versus* temperature T as a function of ageing: (1) 0 h; (2) 9 h; (3) 48 h; (4) 71 h; (5) 168 h; (6) 1195 h

characteristic of the glassy state. This implies that the value of the diffusion coefficient in any element of the system depends on the concentration history of the element.

In most cases reported, epoxy systems show Fickian behaviour[3,5–8,11–14], but anomalous behaviour has been observed[4,15–18]. Carfagna *et al.*[4] and Mikols *et al.*[15] have observed sigmoidal behaviour for two systems.

In both studies, a DGEBA/triamine system was examined and Mikols *et al.* also considered a tetraglycidyl-4,4'-diaminodiphenylmethane/4,4'-diaminodiphenyl sulfone (TGDDM/DDS) system. For both materials apparently Fickian behaviour was observed in the case of a stoichiometric ratio of resin and hardener or a lack of hardener, but sigmoidal behaviour was evident in the case of an excess of hardener.

Notwithstanding the interest presented by this anomalous absorption, our principal objective is the overall characterization of the material to be used as a structural adhesive and, as such, we shall neglect these finer details of the diffusion mechanisms for the following. The treatment will be simplified by approximating the observed behaviour to that described by Fick's equations. Using this simplification, the coefficient of diffusion D is given by

$$\frac{W_t}{W_\infty} = \frac{4}{e}\left(\frac{Dt}{\pi}\right)^{1/2} \beta \qquad (1)$$

where β is a factor correcting for edge effects[19] and is equal to 1.05 for the sheets considered. The results obtained for the three temperatures are given in *Table 1*. We note that the difference between the two values of W_∞ obtained at 40°C leads to a non-negligible difference in the values of D calculated. Values of ln D are plotted against reciprocal temperature $1/T$ in order to apply the Arrhenius relationship

$$D = D_0 \exp\left(-\frac{\Delta H}{RT}\right) \qquad (2)$$

where D_0 is a constant (equal to the extrapolated value of D for $1/T = 0$), ΔH is the activation energy for diffusion, R is the universal gas constant and T is the (absolute) temperature of diffusion.

Using a regression analysis we obtain $\Delta H = 92 \pm 5$ kJ mol^{-1} for $W_\infty = 4.5\%$ at 40°C and $\Delta H = 78 \pm 5$ kJ mol^{-1} for $W_\infty = 3.5\%$.

Typically, rather lower values of the activation energy for diffusion have been reported in the literature for various epoxy/hardener systems, as shown in *Table 2*.

Viscoelastometry

Bulk adhesive samples were aged at the three temperatures 40, 55 and 70°C and ca. 100% *RH* for up to 2500 h.

Results obtained at 70°C are shown in *Figures 4* and *5* plotted as loss tangent tan δ *versus* temperature (*Figure 4*) and as the absolute value of complex modulus $E = (E'^2 + E''^2)^{1/2}$ *versus* temperature for different ageing times[21]. As the ageing time increases, there is a shift of the maximum of the loss tangent to lower temperatures. This represents a decrease of the glass transition temperature T_g. After 48 h of ageing, a split in the peak occurs. This second peak has been observed previously[22,23] and is probably due to absorbed water not chemically linked to the polymer network. After one week of ageing, T_g remains stable. This corresponds to water saturation. At 40°C and 55°C the behaviour is qualitatively similar and T_g does not change after water saturation.

Figure 5 shows that Young's modulus in the glassy state E_G is lowered by ageing but that this phenomenon is (relatively) far more marked for the rubbery plateau (E_R). It is perhaps worth noting from *Figure 5* that once the adhesive is saturated with water, the upper limit to its useful service temperature range drops to ca. 40°C. Gravimetric experiments have also been performed on viscoelastometric samples (12 × 6 × 4 mm) in order to correlate water uptake at the three temperatures directly with the viscoelastometric data. The results are shown in *Figures 6* and *7*. *Figure 6* shows the glass transition

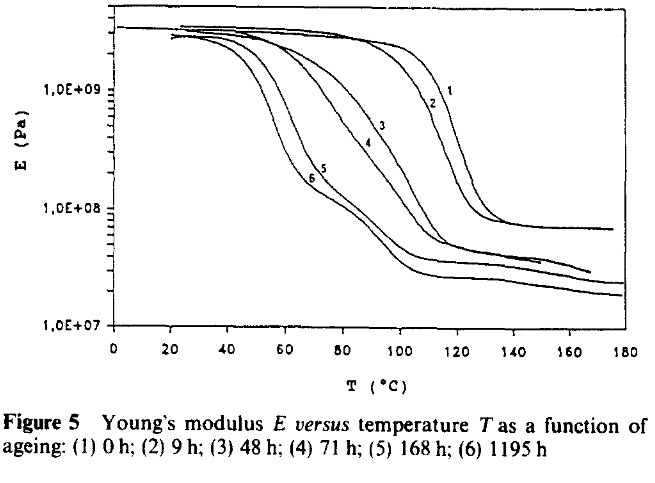


Figure 5 Young's modulus E *versus* temperature T as a function of ageing: (1) 0 h; (2) 9 h; (3) 48 h; (4) 71 h; (5) 168 h; (6) 1195 h

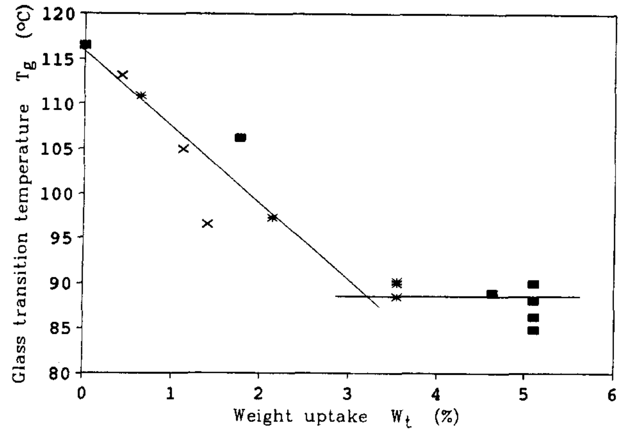


Figure 6 Change of T_g with water uptake at three temperatures: (■) 70°C; (*) 55°C; (×) 40°C

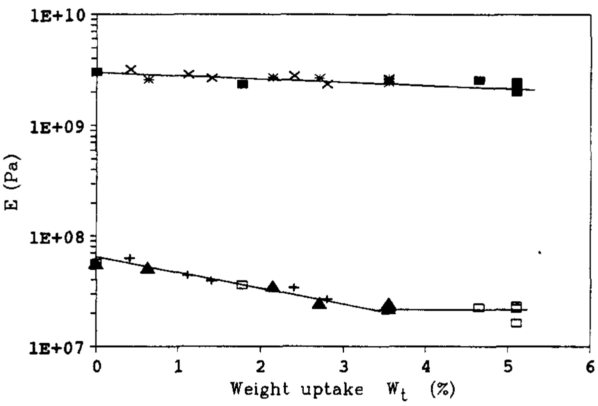


Figure 7 Change of Young's modulus with water uptake: (■) E_G, 70°C; (□) E_R, 70°C; (*) E_G, 55°C; (▲) E_R, 55°C; (×) E_G, 40°C; (+) E_R, 40°C

temperature (corresponding to the loss tangent maximum) *versus* water uptake. The changes in Young's modulus in the glassy state at 30°C and in the rubbery state at 150°C with water uptake are presented in *Figure 7*.

It should, however, be noted that the equilibrium value of water uptake is not the same at the three temperatures and differs from values obtained with larger sheets. With the smaller samples, W_∞ is equal to 4% at 40°C, 3.5% at 55°C and 5% at 70°C. The difference between these values and those obtained with sheets is probably due to condensation of vapour on the smaller samples, which leads to a partial immersion of the samples. Such an effect will be less marked on larger samples. The three figures show the same trend: a decrease of both T_g and elastic modulus as water uptake increases, followed by stability once water uptake has reached equilibrium.

T_g decreases from ca. 115°C to ca. 90°C linearly, 1% absorption of water leading to approximately a 8°C reduction in T_g. Such a phenomenon has been reported in the literature[7,8,16,17] and indicates plasticization of the adhesive. Wright[8] found a decrease of 20°C for each 1% of water absorbed for different epoxy/hardener systems.

As noted above, E_G (in the glassy state) decreases with exposure of the sample to humidity (see *Figure 7*). Before ageing, E_G is equal to 3400 MPa at 30°C, but after water saturation it is reduced to ca. 2200 MPa. The fractional reduction of the modulus in the rubbery state E_R (i.e. at 150°C) is in fact even more significant as it drops from 70 to 25 MPa (and does not recover after drying, suggesting permanent damage).

The Young's modulus of a polymer matrix in the rubbery state E_M is related to its average inter-crosslink molecular weight M_c by the expression[24]

$$E_M(T) = \frac{3RT\rho}{M_c} \tag{3}$$

where R and T are respectively the gas constant and the absolute temperature and ρ is the polymer density. This equation is, however, only valid for a pure polymeric substance. The present epoxy contains ca. 40% of fillers by weight, equivalent to ca. 16% surficial fraction. Assuming a simple rule of mixtures to pertain, equation (3) may be suitably modified.

Considering the adhesive to be a composite material consisting of the polymer of Young's modulus E_M containing a volume fraction V_f of fillers of Young's modulus E_F and assuming the system to be homogeneous and isotropic (on the bulk scale), we may approximate the effective modulus E_R (in the rubbery state) by

$$E_R \approx \frac{E_M E_F}{V_f^{1/3} E_M + (1 - V_f^{1/3}) E_F} \tag{4}$$

Using equation (3) and rearranging, we obtain

$$M_c \approx \frac{3\rho RT(E_F - E_R V_f^{1/3})}{E_R E_F (1 - V_f^{1/3})} \tag{5}$$

Since the fillers are of a mineral origin and are therefore hard, we may take $E_F \gg E_R$ and simplify equation (5) to

$$M_c \approx \frac{3\rho RT}{E_R (1 - V_f^{1/3})} \tag{6}$$

Assuming the fillers to consist of essentially spherical particles, $V_f^{1/3}$ may be estimated from the surficial fraction S_f as obtained from image analysis applied to bulk adhesive cross-sections

$$V_f^{1/3} \approx \left(\frac{4}{3}\right)^{1/3} \frac{S_f^{1/3}}{\pi^{1/6}} \approx 0.91 S_f^{1/2} \tag{7}$$

Bearing in mind that ρ and S_f will be only slightly temperature dependent, we employ their values at 20°C ($\rho = 1.5\,\mathrm{g\,cm^{-3}}$ and $S_f \approx 0.16$) in equations (6) and (7). With a value of 70 MPa for E_R at 150°C before ageing, we obtain a value for M_c of ca. 350 g mol^{-1}. After ageing, with E_R reduced to 25 MPa, the effective value of M_c increases to ca. 1000 g mol^{-1}. Although this calculation uses some simplifications and thus too much importance should not be attached to the absolute values of M_c obtained, the orders of magnitude are reasonable and it is clear that chain scission is occurring within the bulk adhesive as a result of humid ageing. This effect, together with the direct plasticization due to the presence of water and demonstrated by a decrease in T_g, shows how a humid environment may lead to serious degradation of the mechanical properties of the polymer.

In the case of the aged adhesive, as stated above, the value of M_c obtained will be effective rather than real since ageing will presumably lead to scission along a macromolecular chain rather than at a crosslink junction. The resulting aged polymer will probably contain most of its original junctions but the overall integrity of the crosslinked network will be reduced.

The value of M_c of the order of 400 g mol^{-1} obtained for the unaged polymer is of some interest. Although the

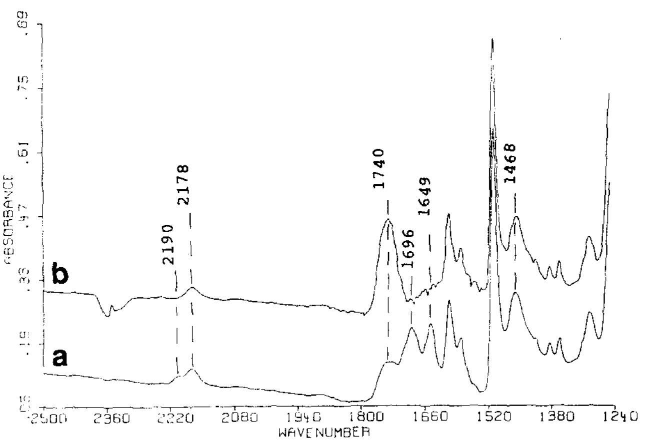


Figure 8 *FT*i.r. spectra of (a) unaged adhesive and (b) adhesive aged for 700 h at 70°C

Table 3 Infra-red absorptions of epoxy and DDA

Wavenumber (cm^{-1})	Type of bond	Origin
3800–3100	νO–H and νN–H	
3039	ν=C–H	DGEBA
2984, 2924, 2870	νC–H	DGEBA
2180–2170	νC≡N	DDA
1740	νC=O	
1696	νC=N	Acyclic DDA $\mathrm{H_2N}\underset{\mathrm{NH}}{\underset{\|}{\mathrm{C}}}\mathrm{NHC{\equiv}N}$
1649	νC=N	Acyclic DDA, α,β unsaturated $\mathrm{(H_2N)_2C{=}NC{\equiv}N}$
1609–1593	νC=C	Aromatic ring of DGEBA
1510–1480		
820	γ-C–H	1,4-Substituted aromatic ring of DGEBA

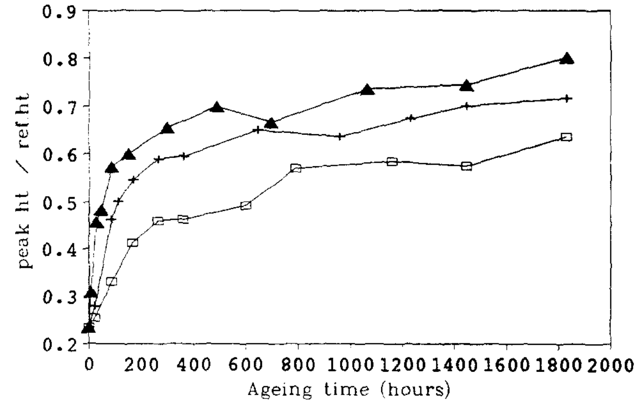


Figure 9 Change of the $1740\,cm^{-1}$ band for the C=O bond of an ester on ageing in water at three temperatures: (▲) 70°C; (+) 55°C; (□) 40°C

overall composition of this adhesive is unknown to us, it is recognized that the basic material is DGEBA. Since the DGEBA unit typically has a molar mass of the order of $300–400\,g\,mol^{-1}$ (depending on the type – unknown in the present case), the above figure for M_c does suggest that the initial degree of crosslinking of this adhesive is high in the state obtained using the curing conditions described earlier.

*FT*i.r. has been used to investigate chemical changes in the adhesive due to ageing.

FT*i.r. analysis*

Infra-red spectra were obtained on the unaged adhesive and on the adhesive aged for different times at the three temperatures of 40, 55 and 70°C.

Figure 8 shows an *FT*i.r. spectrum of the adhesive before ageing and after 700 h at 70°C and ca. 100% *RH*. It corresponds to the sum of epoxy, dicyandiamide and fillers. *Table 3* gives the infra-red frequencies of dicyandiamide and the epoxy[25].

Before ageing, the doublet near $2180\,cm^{-1}$, which is characteristic of dicyandiamide[25], shows an excess of hardener. Changing the curing cycle from 1 h at 150°C to 1 h at 170°C does not affect this presence of an excess of hardener. After ageing, considerable modifications are apparent. The main change is the increase in intensity of the band at $1740\,cm^{-1}$. There is a decrease of the dicyandiamide doublet intensity and the band at $2190\,cm^{-1}$ disappears. Similarly, there is a decrease of the two other bands associated with DDA at 1696 and $1649\,cm^{-1}$ with the disappearance of the $1696\,cm^{-1}$ band. There is an increase of the stretching band at $1468\,cm^{-1}$, corresponding to the epoxy. These modifications have been observed at all three ageing temperatures. The results are plotted in *Figures 9* to *12* in normalized form. The height of the peak in question divided by the height of a reference peak (chosen as the $1510\,cm^{-1}$ band which remains unchanged) is plotted *versus* the ageing time.

Several authors[26–34] have noted that curing DGEBA with DDA leads to the emergence of a peak near

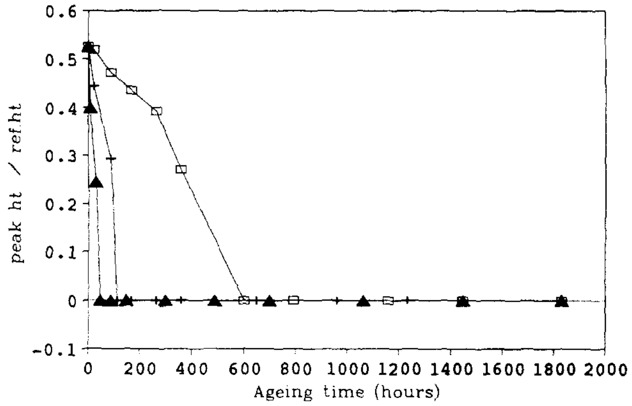


Figure 10 Change of the $1696\,cm^{-1}$ band for the C=N bond of DDA on ageing in water at three temperatures: (▲) 70°C; (+) 55°C; (□) 40°C

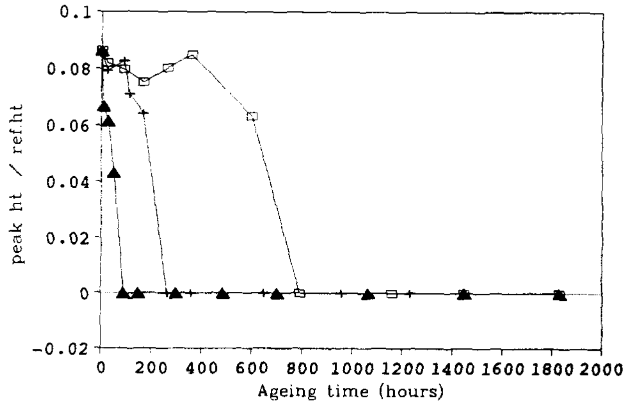
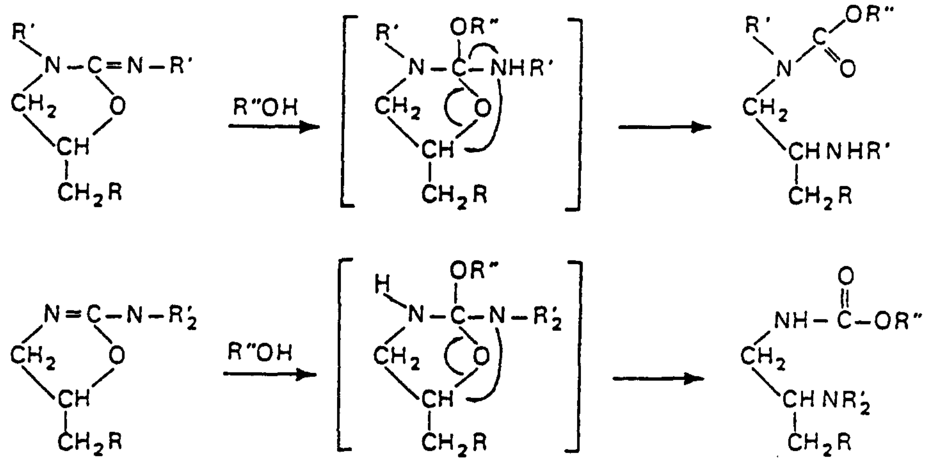


Figure 11 Change of the $2190\,cm^{-1}$ band for the C≡N bond of DDA on ageing in water at three temperatures: (▲) 70°C; (+) 55°C; (□) 40°C

Table 4 Infra-red absorptions in the region of 1740 cm^{-1} reported in the literature and the chemical groups to which they have been attributed

Ref.	Epoxy	Hardener	Wavenumber (cm^{-1})	Chemical groups
26	DGEBA	DDA	1739	Aldehydes, ketones, carboxylic acids, esters
27	DGEBA	DDA	1740	Substituted guanylurea $\underset{\underset{NH}{\|}}{H_2NC}\underset{\underset{O}{\|}}{NHC}NH_2$
28	DGEBA	DDA	1740	Aliphatic carbonyl group
	TGMDA[a]	DDA		
29	DGEBA	DDA	1730	Substituted guanidines
30	DGEBA	Anhydride	1725	Aromatic ester
			1705	Carboxylic acid
31	Phenyl glycidyl ether	Cyanamide	1736	Urethane ester group
32	DGEBA	DDA	1740	Carbonyl groups
33	DGEBA-BDMA[b]	DDA	1740	Carbonylurea groups
34	DGEBA	Substituted urea	1730	Urethane

[a] Tetraglycidylmethylenedianiline
[b] Benzyldimethylamine



Scheme 1 Explanation of the formation of the urethane ester group according to Zahir[31]

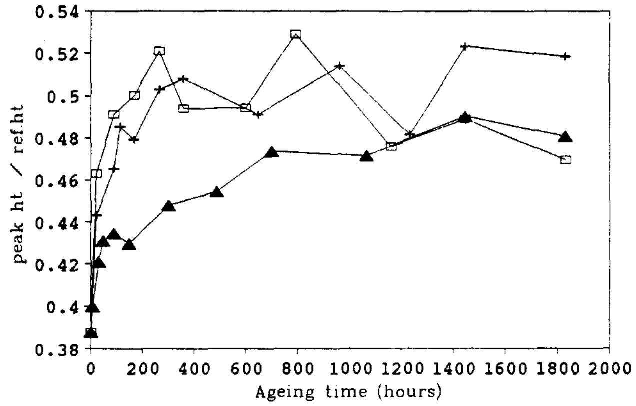


Figure 12 Change of the 1468 cm^{-1} band for the C=C bond of DGEBA on ageing in water at three temperatures: (▲) 70°C; (+) 55°C; (□) 40°C

1740 cm^{-1}. The exact position and the chemical group to which it corresponds are uncertain and there is some disagreement between authors. *Table 4* gives the peak positions obtained and the chemical groups to which they are attributed in different studies[26–34]. Some authors[28,33] have noted an increase of the 1740 cm^{-1} band with the cure temperature. Sprouse *et al.*[28] consider thermal oxidation of the sample as the cause of this increase.

An interesting explanation of the formation of this peak is given by Zahir[31]. He considers the compound DGEBA-DDA as a 2-aminooxazolidine or a 2-iminooxazolidine. A possible route to the formation of an ester functional group from these two compounds is given in *Scheme 1*. The base-catalysed addition of an alcoholic OH group across the imino double bond followed by ring opening can lead to a urethane ester group. In the present case, the 1740 cm^{-1} band increases in the presence of water. It is conceivable that water supplies the OH group required to lead to the ring opening.

CONCLUSIONS

The degradation of an epoxy/dicyandiamide adhesive under the combined effects of elevated temperature and humidity has been studied both in terms of mechanical properties and chemical modifications.

Ageing of the polymer leads to absorption of water which is not strictly Fickian but rather sigmoidal. The absorption of water leads to a decrease in the glass transition temperature, 1% absorption leading to approximately a 8°C reduction in T_g. This indicates plasticization of the polymer. There is also a decrease of the Young's modulus in the glassy and rubbery states. The latter modulus can be related to the average inter-crosslink molecular weight M_c and its decrease shows an important degree of chain scission. The *FT*i.r. results show a degradation of the dicyandiamide (decrease of the doublet) and an increase of a 1740 cm^{-1} band, attributed to an ester.

It is thus concluded that the hygrothermal ageing of this epoxy adhesive leads both to plasticization of the polymer (a physical effect) and chain scission (a chemical effect), accompanied by degradation of the hardener and an increase in quantity of an ester group.

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