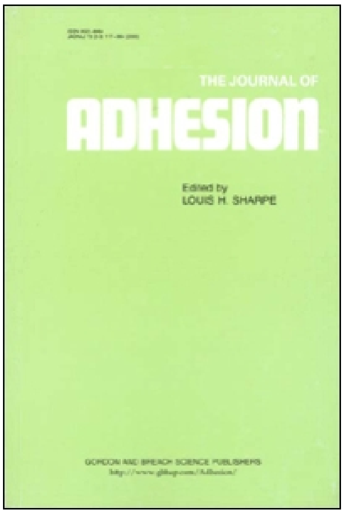

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B. Van Mele[a]; E. Verdonck[a]
[a] Department of Physical Chemistry and Polymer Science, Free University of Brussels VUB, Brussels, Belgium

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Physico-Chemical Characterisation of the Influence of Moisture on the Fibre/Matrix Interaction in Epoxy/Anhydride Composites*

B. VAN MELE and E. VERDONCK**

Department of Physical Chemistry and Polymer Science, Free University of Brussels (VUB), Pleinlaan 2, 1050 Brussels, Belgium

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The effect of moisture on the fibre/matrix interaction in epoxy/anhydride composites is investigated and explained through the characterisation of the matrix cure in the interphase. The fibre/matrix interaction is inferred from ILSS measurements on the composite, which are compared with a recently-introduced DSC interaction parameter. The matrix cure in the bulk as well as in the interphase is characterised through FT-IR microspectroscopy. Complementary information is gained by measuring the overall T_g value. Moisture is shown to lower the fibre/matrix interaction if the prepreg (= composite precursor) is stored at room temperature or lower prior to final cure. This is due to the reduced crosslink density of the matrix. For PE prepreg stored in ordinary atmospheric conditions, moisture from the surroundings lowers the fibre/matrix interaction sharply. If the prepreg is stored in a dry environment, nearly no effect of the storage is detected on the fibre/matrix interaction in PE (polyethylene) fibre composites, while for PVAL (polyvinylalcohol) fibre composites a strong decrease is still found, caused by water adsorbed at the more hydrophilic fibre surface.

KEY WORDS: polyethylene fibre; polyvinylalcohol fibre; epoxy/anhydride composite; DSC; micro-FT-IR; cure; moisture; fibre/matrix interaction

1 INTRODUCTION

The adhesion between the reinforcing phase and the matrix in a composite can be influenced to a large extent by the presence of an interlayer.[1] In an anhydride cured epoxy matrix an interphase develops, *e.g.* by the adsorption of the catalyst (tertiary amine or imidazole) at the filler surface[2-4] or by the effect of water adsorbed at the fibre surface.[2, 5-6] Material suppliers warn about the detrimental effect of moisture on the adhesion in the composite when using anhydride curing agents.[5]

The aim of this paper is a more systematic investigation of the effect of moisture on the adhesion and related properties of the epoxy/anhydride composites. The adhesion

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[*] One of a Collection of papers honoring Jacques Schultz, the recipient in February 1995 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M.*

[**] Corresponding author.

will be characterised by means of an interlaminar shear strength (ILSS) test. The effect of moisture on the cure of the matrix, and the possible development of an interphasial region, will be investigated *via* Fourier transform infrared (FT-IR) microspectroscopy.[7-9] Moreover, the glass transition temperature of the composites will be determined with Differential Scanning Calorimetry (DSC) to support the IR results. In this way, variations in the ILSS value will be correlated with differences in composition and properties of the matrix. Two types of composites will be investigated: one type is based on the hydrophobic polyethylene fibre and the other on the more hydrophilic polyvinylalcohol fibre.

A physico-chemical approach to study the fibre/matrix interaction in composites based on these thermoplastic fibres was recently developed in our laboratory.[9-10] It is based on the study by DSC of the fibre melting in the composite: the higher the thermo-mechanical constraints from the matrix during fibre melting, the higher the melting temperature of a particular fibre. This effect was quantified by defining a DSC interaction parameter. *Via* the DSC characterisation procedure the influence of varying matrix properties, as well as different fibre parameters (*e.g.* surface treatment, diameter), was investigated.[9-10] In this paper the DSC interaction parameter will be compared with ILSS values and the compositional changes in the composites.

2 EXPERIMENTAL

2.1 Materials

The matrix was composed of three components (from Ciba-Geigy): LY556 (DGEBA-based resin), HY917 (hardener based on methyl tetrahydrophthalic anhydride), and DY070 (accelerator, containing 1-methyl imidazole). They were mixed in a ratio of 100/90/1 parts by weight, respectively.

PVAL fibres from Kuraray were employed (as-received or after drying in a desiccator), as well as untreated PE fibres (Dyneema SK60) from DSM High Performance Fibers.

2.2 Sample Preparation

The composites were prepared *via* an intermediate stage of prepreg (= fibres pre-impregnated with fluid matrix mixture). A more detailed description of the prepreg production method is given elsewhere.[10] The prepreg was used for composite production either immediately after its preparation ("fresh"), or after a certain storage time ("aged") at room temperature (= 23°C). The prepreg was stored either in a sealed DSC pan ("closed" storage), or in ordinary atmospheric conditions and covered on both sides by a release foil ("open" storage). Subsequently, the final cure to produce the composite was performed.

Curing of the PE prepreg was done at 120°C; the standard cure time was 60 min. The PVAL prepreg was cured during heating up to 280 °C at 10 °C/min.

For the ILSS test, 24 prepreg layers were stacked and cured in an autoclave. Samples of 18 mm (length) × 4 mm (thickness) × 3 mm (width) were cut with a waterjet saw.

T_g and the DSC interaction parameter were determined on a composite sample of 2–3 mg, which was made up from one prepreg layer, cured *in situ* in the DSC furnace. Unreinforced ("pure") matrix, thermally treated in the same way as the composite (and its prepreg precursor), was measured as a reference.

For the IR measurements, a fibre filament was pulled out of the cured composites and the matrix that adhered to this filament was analysed ("first set up"). By squeezing the sample between KBr crystals after the cure, it is not certain that only that part of the matrix nearest to the filament was investigated. Therefore, another experimental set up was also used in which bulk matrix and matrix in the interphasial region were defined more unambiguously. For this purpose a monofilament was deposited in a droplet of uncured matrix on a KBr window ("second set up"). This impregnated fibre was squeezed between two KBr crystals, and the sample was then aged at room temperature for a certain time prior to investigation. By squeezing the uncured matrix, the proximity of a certain matrix part to the fibre during storage was ensured. No final cure was performed on these samples. More details about the sample preparation are given elsewhere.[8-10]

2.3 Techniques

The composition of the matrix was deduced from IR analysis with a 2000 FT-IR spectrometer (Perkin-Elmer), equipped with an IR-Plan microscope (Spectra-Tech) and a 2" × 5" motorised micropositioning stage (Spectra-Tech). A resolution of 4 cm^{-1} was used. 100 scans were averaged for each spectrum. The sample was put between two KBr crystals which were subsequently squeezed in a sample compression cell (μ-Sample Plan, Spectra-Tech). The region of interest for the IR transmission analysis was restricted by redundant aperturing.[7] An analysis region of about 20 to 40 μm (perpendicular to the fibre axis) × 80 to 150 μm (parallel to the fibre axis) was chosen. Bulk matrix (see second IR set up in 2.2) was investigated in a position at least 200 μm away from the fibre; a schematic representation of the sampling positions is given in Figure 1. The background spectrum was taken at a position on the KBr crystals where no sample was present.

T_g of the composites was measured with a DSC-7 (Perkin-Elmer) at a heating rate of 10°C/min. The DSC interaction parameter was obtained from the same experiment by calculation of the partial peak area of the endothermic fibre signal above a reference temperature (chosen as 150.0°C for PE composites and 255.0°C for PVAL composites). Normalisation of the DSC interaction parameter was performed by dividing by the maximum DSC interaction parameter for the particular type of composite. An example for a PVAL composite is depicted in Figure 2.

The ILSS measurements were performed on an Instron 1195 test bench, and according to ASTM D-2344.

The amount of moisture at the fibre surface was determined with a TGA-7 (Perkin-Elmer) during heating at 10 °C/min to 115 °C and subsequent isothermal operation for 30 min.

More details about the techniques are given elsewhere.[8-10]

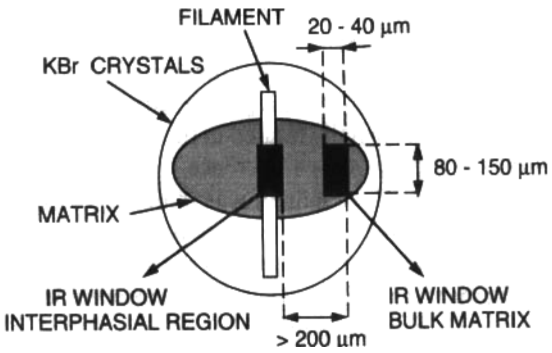
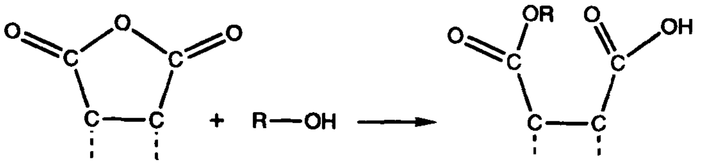


FIGURE 1 IR set up for the comparison of the cure reaction of the matrix in bulk and near a fibre filament.

3 RESULTS AND DISCUSSION

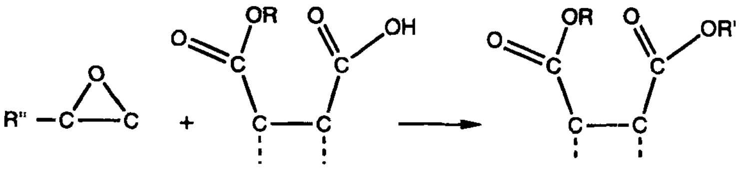
3.1 Development of an Interphase as a Result of Moisture on the Fibre Surface

The influence of moisture from the fibre surface on the cure reaction of the epoxy-anhydride matrix was studied with IR microspectroscopy by "impregnating" one fibre filament with excess of matrix (second set up, see also Fig. 1). The reaction proceeding at room temperature is illustrated in Figure 3 (a and b) and is most obvious from the difference spectrum (b–a). The anhydride ring (absorptions at 1858 cm^{-1} and 1780 cm^{-1}) is opened by a proton donor (*e.g.* a hydroxyl group from the epoxy resin), and an ester linkage (absorption at 1740 cm^{-1}) and a carboxyl group (absorption at 1708 cm^{-1}) are formed:[11-13]



(I)

Subsequently, the carboxyl group is converted into an ester by reaction with the epoxide ring:



(II)

A polyester network is built by further reaction of the reactive groups in *R* and *R′*. The consumption of the epoxy ring will not be considered since its IR absorptions are

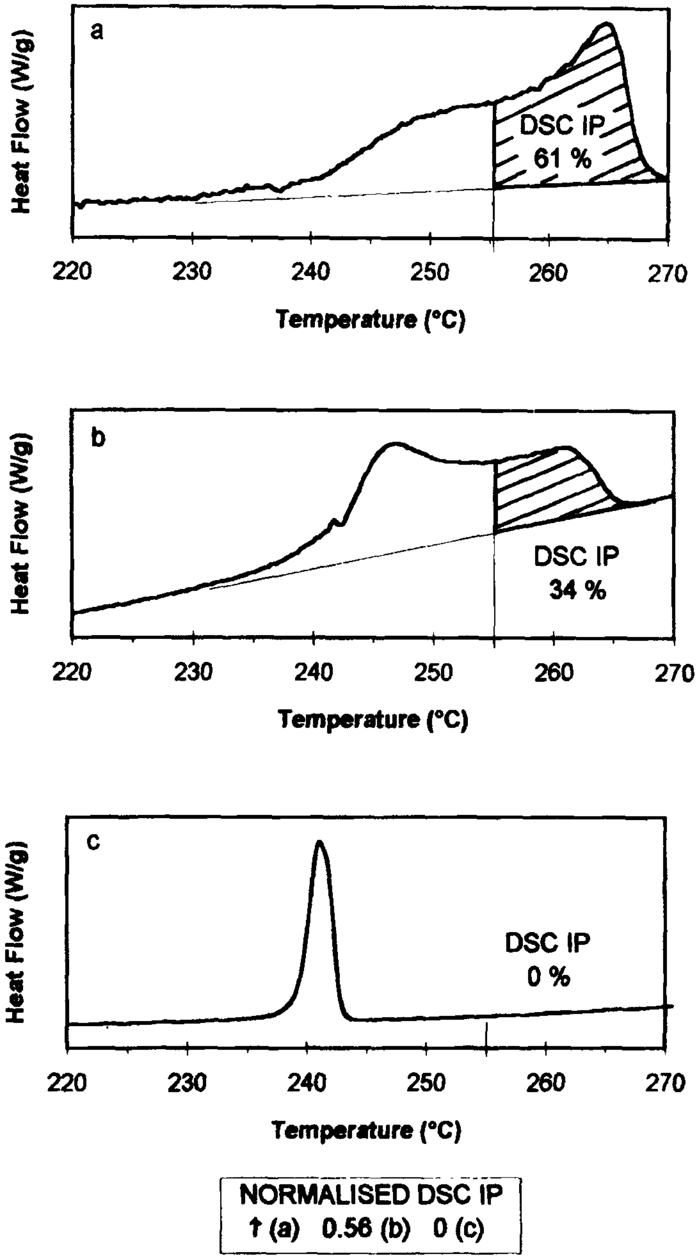


FIGURE 2 Determination of the DSC interaction parameter (IP) for PVAL fibre composites; situation corresponding to: (a) maximum interaction; (b) intermediate level of interaction; (c) zero interaction: the fibre melts at a temperature as low as if there was no matrix surrounding it. Normalisation of the DSC IP is performed by dividing by the DSC IP of (a).

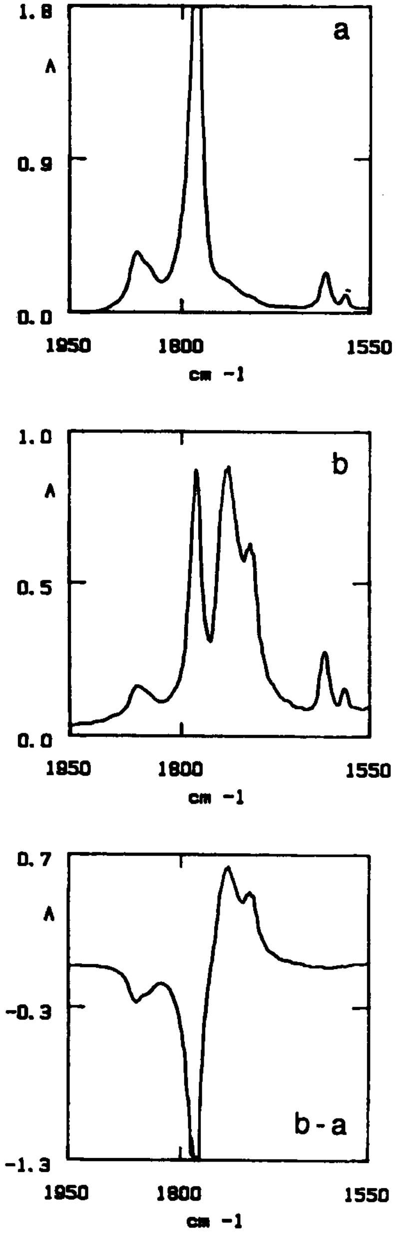
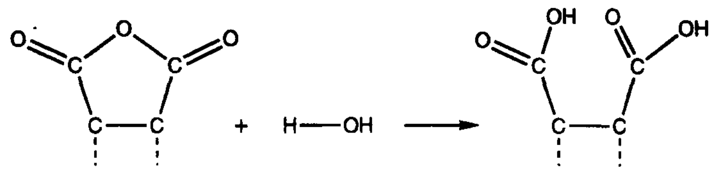


FIGURE 3 IR spectra of the epoxy/anhydride matrix: (a) immediately after mixing; (b) after reaction at room temperature for 100 hours; difference spectrum (b–a).

either too weak or overlapped by peaks of the anhydride hardener. The absorption of the phenylene units of the epoxy resin (at 1608 cm^{-1}) is used for spectral normalisation. Since for the PE and PVAL filament there is no overlap between fibre absorptions and the interesting matrix vibrations,[8] the cure reaction of the matrix can be studied in the immediate vicinity of these fibres. For purposes of comparison between the matrix in bulk and in the interphasial region, the difference spectra are used.

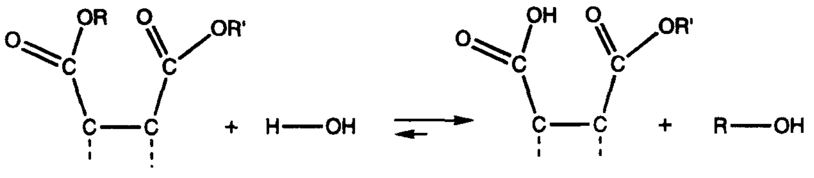
The influence on the epoxy/anhydride cure reaction of hydrophobic PE fibres as well as more hydrophilic PVAL fibres was studied. The amount of moisture on the fibres was determined in a TGA heating experiment: while the PVAL fibres contain about 1.4 mass% water, the PE fibres possess only about 0.1 mass% water.

As is illustrated in Figure 4, the epoxy/anhydride cure reaction (at room temperature) proceeds in a different way "close" (μm scale) to the fibre filaments. Compared with the bulk matrix (Fig. 4a), the anhydride consumption is higher in the presence of a PE fibre (Fig. 4b and b–a), and this effect is even more pronounced for a PVAL filament (Fig. 4c, c–a and c–b). The ester formation, however, is higher in the bulk matrix than close to a filament. The carboxyl production, on the contrary, is highest near the PVAL filament. Similar observations are described by Garton and co-workers[5, 6] for an epoxy/anhydride matrix in the presence of humid polyamide or polyacrylonitrile surfaces. In the presence of moisture the anhydride consumption described by reaction equation (I) is accelerated by:[5, 6]



(III)

In this way the faster diminution of anhydride near the fibre filaments (especially PVAL) can be understood. The reduced ester yield and the enhanced acid production in the vicinity of the fibres is explained by the shift of the equilibrium of the reversible condensation-esterification towards the acid formation in the presence of water:[5, 6]



(IV)

Besides moisture, the hydroxyl groups from the PVAL fibre surface could also influence the cure reaction. This effect, however, is expected to be of minor importance since the amount of hydroxyl groups, available from water adsorbed at the fibre surface, is calculated to be about a hundred times larger.

3.2 Effect of Moisture on Some Composite Properties

In composite production technology the prepreg intermediate is often stored over an extended period of time before its final lay-up and cure. Ordinary conditions involve

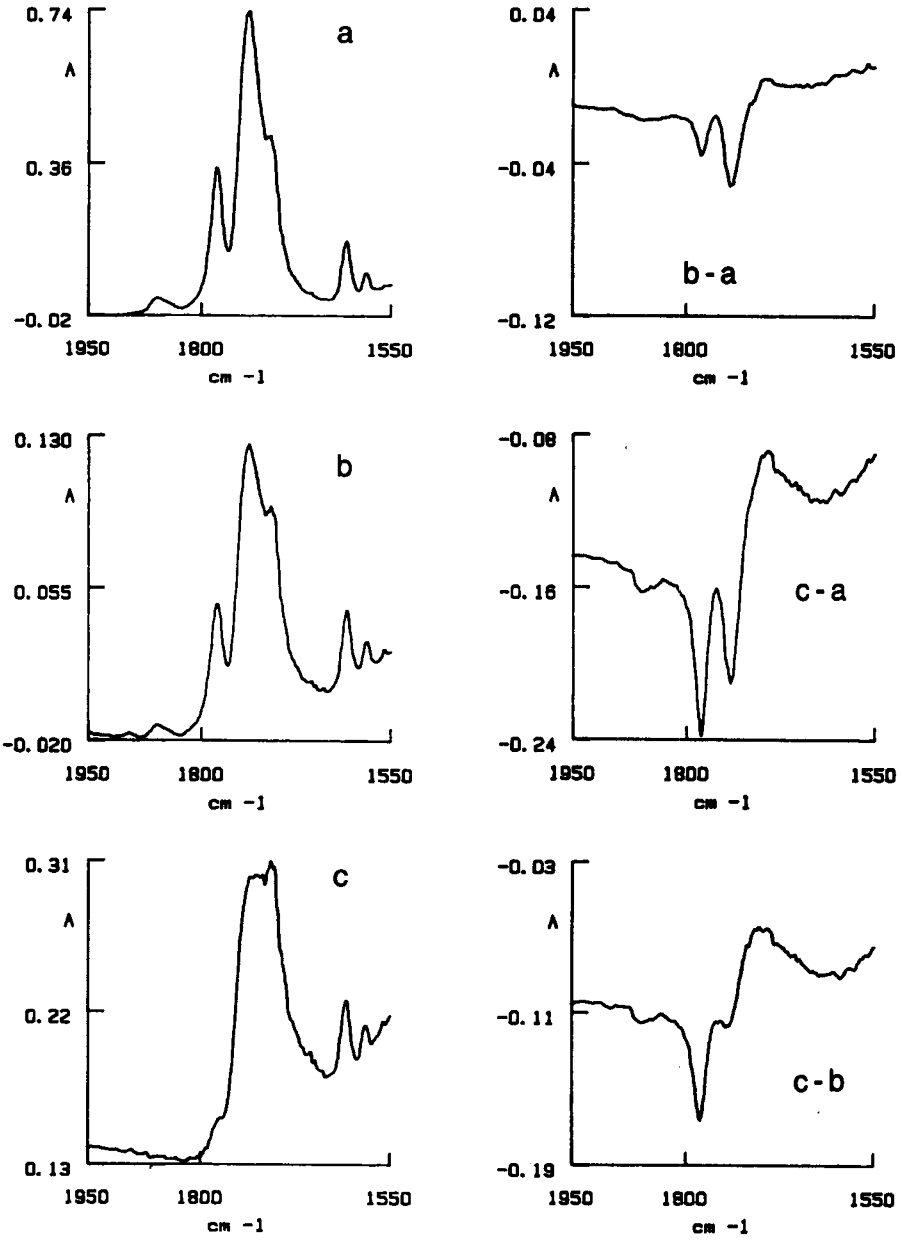


FIGURE 4 IR spectra of the matrix after 260 hours reaction at room temperature: (a) bulk matrix; (b) matrix around a PE fibre; (c) matrix around a PVAL fibre; difference spectra (b–a), (c–a) and (c–b).

storage between release foils in a freezer. In the previous section it was shown that during storage at room temperature an interphase develops because of the effect of moisture from the fibre surface. Similar effects occur during storage in a freezer, but on a much larger time scale.[9] As a result one could expect significant variations in the properties of composites made from "fresh" or "aged" prepreg. In this section the effect of prepreg ageing on the ILSS value, the matrix T_g and the DSC interaction parameter of the composite is investigated. Besides, variations are linked to differences in the matrix composition, detected by IR analysis of the matrix sticking on a filament that is pulled from the composite (see first IR set up in Section 2.2). The prepreg was stored at room temperature instead of in a freezer, to accelerate all chemical reactions and thus reduce the time scale of the investigation. The prepreg was stored in sealed pans (closed storage) or between release foils (open storage) to detect whether there is an additional influence of moisture from the surroundings on the cure reaction of the matrix.

The ILSS value of the PE composites is plotted in Figure 5 as a function of the ageing time of the prepreg in open conditions. After an induction period, a sharp decrease is observed: if the prepreg is stored for 1 day at room temperature the resulting ILSS value of the composite is already less than half the original one.

The differences in matrix composition of the PE composites from fresh and aged prepreg (open storage) are deduced from the IR spectra in Figure 6. All of the anhydride has been consumed (no peaks at 1780 and 1858 cm^{-1}) and is mostly converted into ester groups for the composite from fresh prepreg (curve a), while for the composite from aged prepreg a lot of carboxyl groups are still present (curve b). This can be explained by the reaction mechanism. During storage at room temperature, moisture opens the anhydride ring rather than other proton donors, resulting in the formation of a diacid (reaction equation III) rather than a monoester (reaction equation I). Since the matrix formulation is originally mixed in stoichiometric ratio, *i.e.* one epoxy group per anhydride ring, there is not enough epoxy present to convert all of the acid groups into ester. So by the interference of water *via* reaction equation (III) the network density of the matrix is reduced.

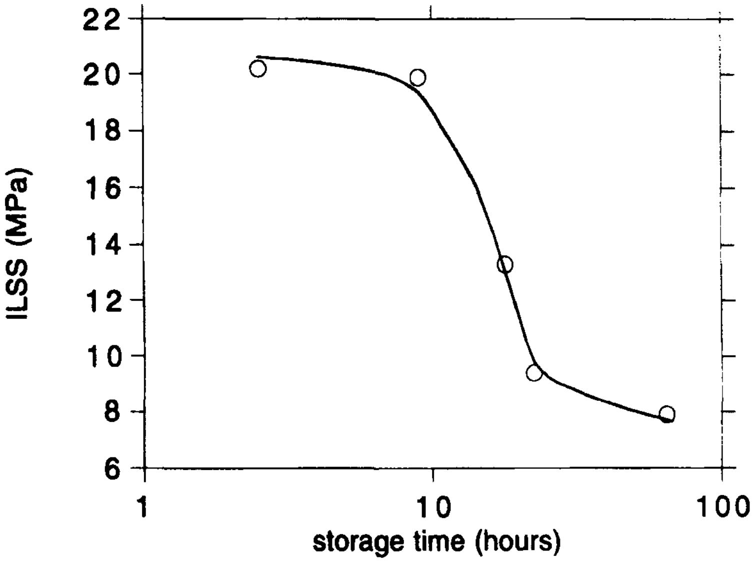


FIGURE 5 ILSS of the PE composite as a function of the storage time at room temperature of the prepreg.

If the prepreg was aged in closed conditions instead of open, the IR spectrum of the matrix in the composite (Fig. 6, curve c) seems to be identical to the spectrum of the matrix in the composite from fresh prepreg (Fig. 6, curve a), even for a storage time as long as 170 hours. From the difference spectrum (c–a), however, analogous but less pronounced phenomena seem to be involved as for the ageing in open conditions (compare c–a with b–a). If the prepreg is stored in open conditions the effect of moisture from the surroundings obviously overrules the effect of moisture from the PE fibres. It should be noted that in Section 3.1 the effect of moisture from the fibres is more obvious, since in that case probably a larger fraction of the interphasial region is investigated.

The ILSS value seems to be correlated with the ratio of ester to carboxyl groups, which in turn determines the crosslink density of the matrix. According to the IR results the crosslink density of the matrix is lower for composites from more aged prepreg, and probably the matrix modulus is thus lower also. This can explain the decreased ILSS value for these composites, since there is some evidence that the interfacial shear strength in a composite is proportional to the modulus of the matrix.[14-15]

Additional evidence for the decreased crosslink density of the matrix in the presence of moisture is obtained from the evolution of its glass transition temperature. T_g of the cured composites and the cured "pure" matrix is depicted in Figure 7 as a function of the storage time before cure. Open as well as closed storage conditions were tested to

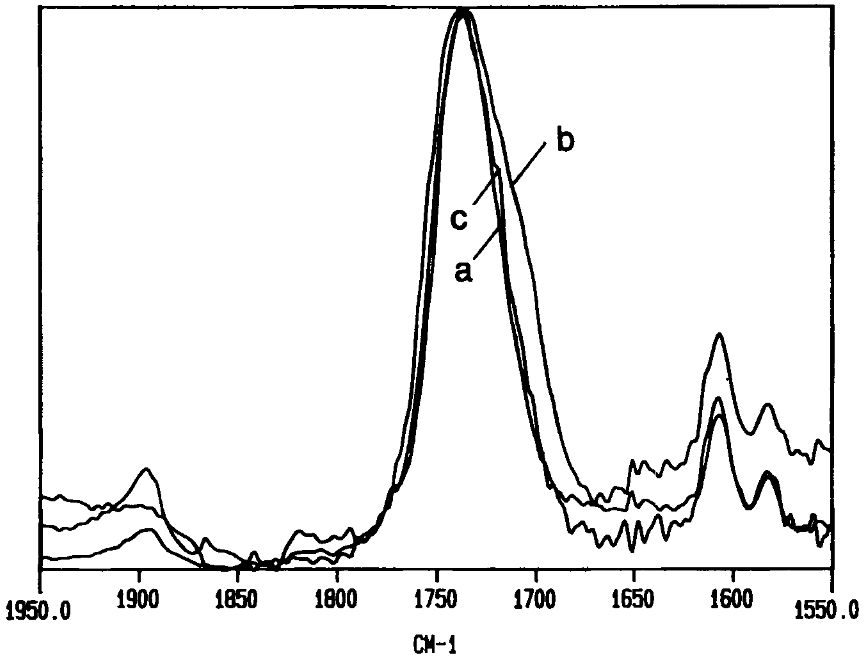


FIGURE 6 IR spectra of the matrix in the PE composite: (a) made from fresh prepreg; (b) the prepreg precursor has been stored in open conditions for 20 hours; (c) the prepreg precursor has been stored in closed conditions for 170 hours; difference spectra (b–a) and (c–a).

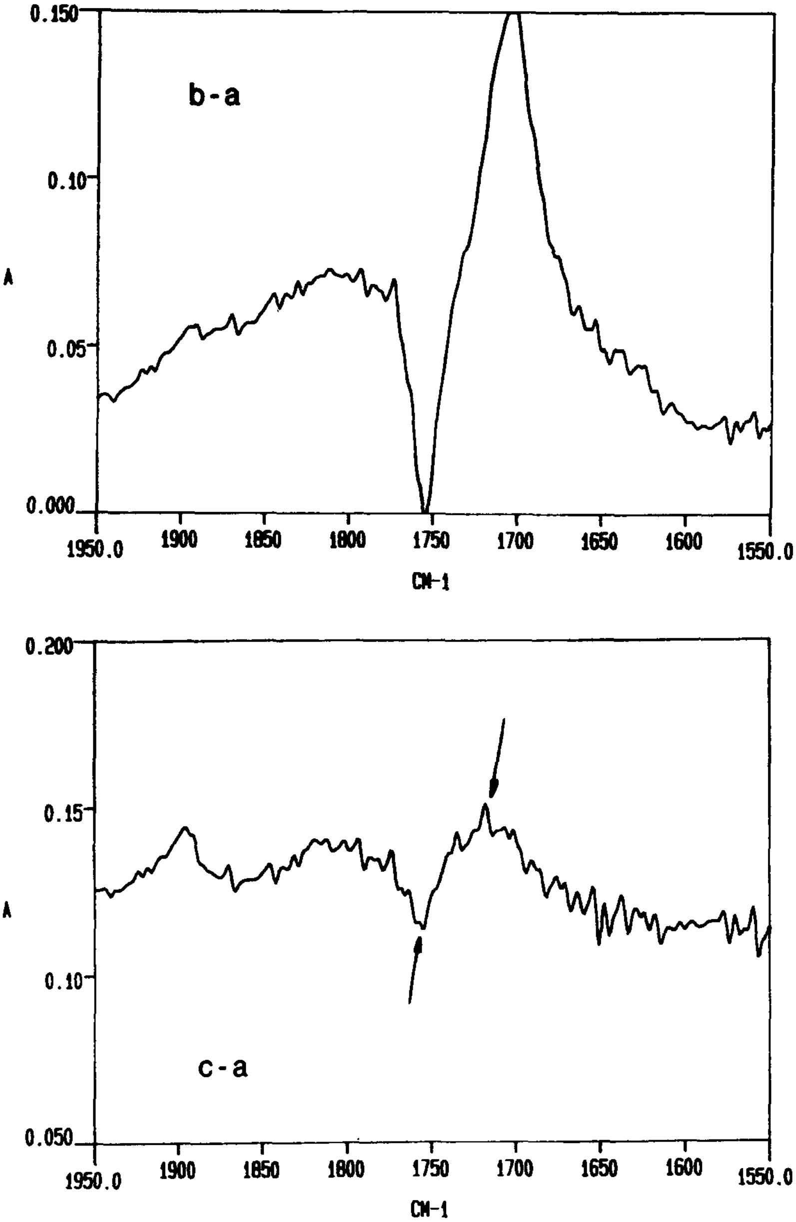


FIGURE 6 *(Continued).*

detect the effect of, respectively, moisture from the surroundings and moisture from the fibre surface. PVAL fibres, dried PVAL fibres and PE fibres were studied, to look at the influence of a varying moisture level of the fibre surface (the fibres contain, respectively, 1.4, 0.9 and 0.1 mass% water). After an induction period, a strong decrease of T_g is found for PE prepreg aged in open conditions (compare with the shape of the curve in Fig. 5). This is a consequence of the reduced crosslink density of the matrix due to the influence of water. Since T_g of the unreinforced matrix behaves exactly the same as T_g of the PE composite, it is obvious once again that moisture from the surroundings overrules any fibre effect when the material is stored in open conditions. For closed storage conditions, the T_g value of the PE composite decreases slightly as a function of the storage time of the prepreg, and again closely resembles the evolution for the "pure" matrix. So no effect of moisture from the PE fibres is detected on the T_g value of the composite. Note that the measured T_g is an overall value (bulk and interphase), and so the moisture content on the PE fibres is too low to detect any influence on the overall matrix T_g. For the more humid PVAL fibres, however, the effect of moisture from the fibre surface is clearly identifiable for prepreg stored in closed conditions (and so for which the effect of moisture from the surroundings is excluded); the strong T_g decrease is slowed down if the PVAL fibres are dried prior to impregnation. In contradiction to the case where moisture from the surroundings is involved, no significant induction period is detected here. In the case that the fibre surface is the main moisture source, a larger matrix fraction is initially influenced by water (and so has a lower T_g) than if moisture starts to diffuse from outside of the prepreg. Consequently, the initial decrease of the overall matrix T_g is much steeper for PVAL composites than for PE composites made from prepreg stored in open conditions.

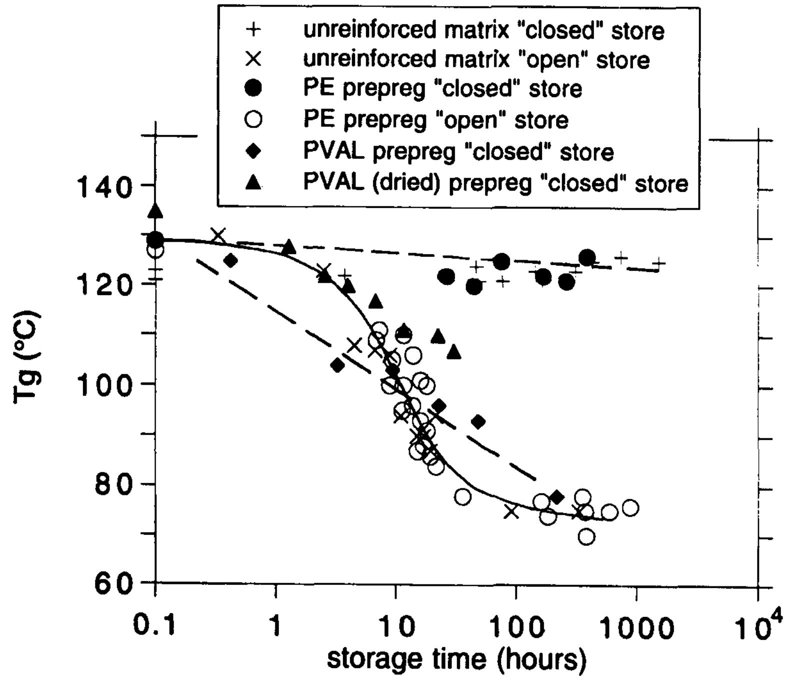


FIGURE 7 T_g of the composites and the unreinforced matrix as a function of the storage time at room temperature of their precursor; either open or closed storage conditions are involved.

Recently, a DSC procedure to study the influence of varying matrix properties on the fibre/matrix interaction in the composite has been developed in our laboratory.[9-10] The principle is based on the fibre melting in the composite: the higher the thermo-mechanical constraints from the matrix during fibre melting, the higher the melting temperature of a particular fibre. Quantification of this effect results in a DSC interaction parameter.[8-10] Since the reference temperature for the determination of the DSC interaction parameter is chosen more or less arbitrarily, the absolute values of this parameter cannot be compared for PE and PVAL composites, and the evolution is studied using relative (normalised) values (see also 2.3). A larger (normalised) DSC interaction parameter for a particular type of fibre correlates with higher thermo-mechanical constraints from the surrounding matrix during fibre melting. A higher crosslink density of the matrix is related to higher thermo-mechanical constraints of the matrix.

The evolution of the normalised DSC interaction parameter in PE and PVAL composites as a function of the storage conditions of the prepreg is depicted in Figure 8. The DSC interaction parameter shows an equivalent behaviour to the T_g value of the composites (see Fig. 7): a slight decrease is observed for PE composites stored in closed conditions, while a large decrease is found for PVAL composites and for PE composites stored in open conditions. Again, the initial decrease is faster for the PVAL composites. In this case, the crosslink density of the matrix starts to decrease first in the interphasial region due to the effect of moisture on the fibre itself. In the case of PE prepreg stored in open conditions only the matrix at the outer prepreg surface is influenced by moisture initially, so the crosslink density around a large part of the fibres is not yet decreased. Since the thermo-mechanical constraints on the fibre during melting are caused by the matrix in immediate contact with the fibre (the interphasial zone), it is obvious that the DSC interaction parameter will initially decrease more steeply if the moisture source is in the vicinity of the fibre.

The crosslink density of the matrix cannot only be varied by the effect of moisture at room temperature, but also through partial cure from prepreg to composite. To illustrate this effect, PE composites were prepared from fresh prepreg, but instead of using the standard 60 min cure time (see 2.2) shorter cure times were employed. Note that T_g and the DSC interaction parameter reach their maximum values after a cure time of 60 min at 120 °C, for composites made from fresh prepreg as well as aged prepreg. As a result of the shorter cure times the glass transition temperature of the matrix is decreased, and since conditions are chosen in which gelation has already occurred this is related to a diminished crosslink density. In Figure 9 the DSC interaction parameter is plotted as a function of the T_g of the matrix, for partially-cured composites made from fresh prepreg as well as for the fully-cured composites made from aged prepreg (the latter results are a combination of Figures 7 and 8). There seems to be no unique relation between the interaction parameter and T_g. This T_g, however, is an overall value related to the properties of the matrix in bulk as well as in the interphasial region. The DSC interaction parameter, on the other hand, is mostly influenced by the properties of the matrix in the immediate vicinity of the fibre (interphasial region). In the case of (partial) cure at 120 °C of fresh prepreg, no effect of water on the cure reaction of the matrix could be detected with the IR technique and probably the interphase is too thin to influence the fibre melting. The DSC interaction

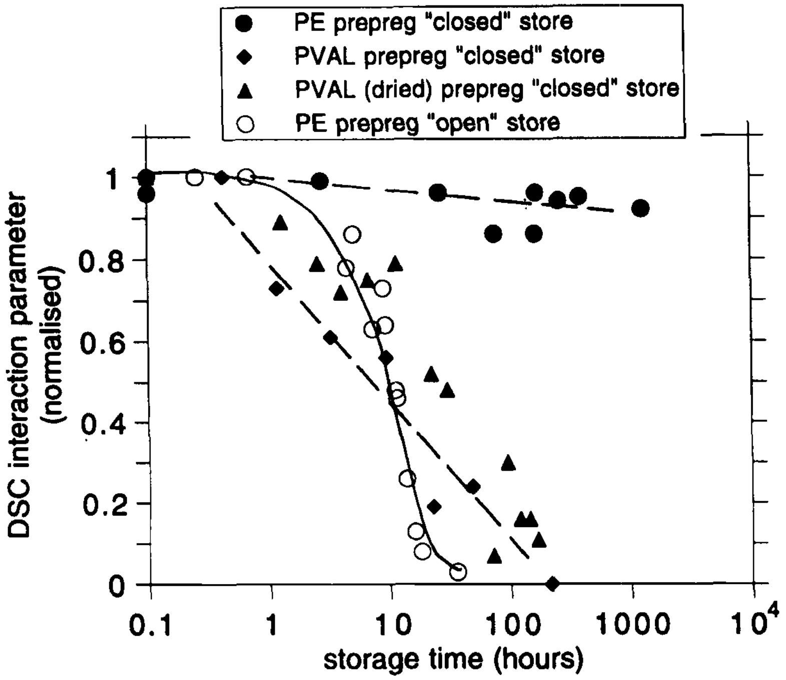


FIGURE 8 Normalised DSC interaction parameter as a function of the storage time at room temperature of the prepreg.

parameter is then related to the properties of the bulk matrix. In the case of full cure of aged prepreg, however, a more extensive interphasial zone with lower crosslink density than the bulk matrix is created (see IR results). The overall (measured) T_g value is then probably higher than the real T_g of this interphase. In this way, the non-unique relation between T_g and the DSC interaction parameter can be understood. One could think about using the curves of Figure 9 in an inverse way: T_g of the interphase in a composite from aged prepreg could be deduced by measuring its DSC interaction parameter and by using the curve for partially-cured composites made from fresh prepreg at the same DSC interaction value. Before drawing any definite conclusion, however, this statement needs further investigation especially concerning the relation of the size of the interphase, its crosslink density and the DSC interaction parameter.

Note that for the partially-cured composites the DSC interaction parameter becomes zero when T_g of the matrix is about $-10°C$. This T_g value corresponds to gelation of the matrix.[16] In this case, the matrix is not yet crosslinked and fibre melting occurs without thermo-mechanical constraints (as if there was no matrix present).

The reason that water is able to participate in the cure reaction during storage (= partial cure) at room temperature, rather than during (partial) cure at 120 °C, is probably due to a different competition of diffusion effects and chemical reaction at these particular temperatures. During cure at lower temperatures, the chemical

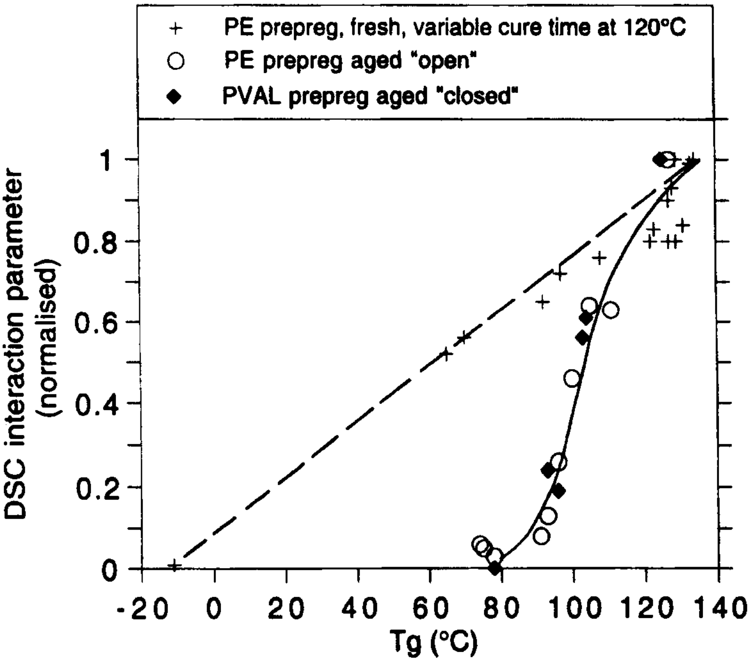


FIGURE 9 Normalised DSC interaction parameter as a function of the glass transition temperature of the composite.

reactions are probably slow enough to allow the interference of water *via* reaction equations (III) and (IV), while during cure at higher temperature the diffusion of water in the matrix or interphase will be avoided because of the rapid network formation.

4 CONCLUSIONS

During storage of prepreg at room temperature moisture influences the cure reaction of the epoxy/anhydride matrix, so that the network density in the fully-cured composite is decreased. As a result, the ILSS value and the DSC interaction parameter of the composite are reduced. For prepreg stored under ordinary conditions, moisture from the surroundings overrules any effect of the PE fibres. If the prepreg is stored in a dry environment, however, moisture adsorbed at the fibre surface mainly influences the network formation. This can be detected from the investigation of the interphasial region by IR microspectroscopy. While in PE fibre composites a minor effect is noticed, in PVAL fibre composites the moisture from the fibre obviously affects the curing. Although the evolution of the ILSS value and the DSC interaction parameter are dictated by the crosslink density of the matrix, no unique relation between T_g and the DSC interaction parameter is found for composites produced in different conditions. A different relation is found whether or not moisture is allowed to interfere with the ordinary cure reaction of the matrix. This is due to the fact that the DSC interaction parameter is a probe for the crosslink density of the matrix in the immediate vicinity of the fibres, while T_g is an overall value for matrix in the bulk as well as in the interphasial area.

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