Influence of heterogeneous crosslink density on the thermomechanical and hygrothermal properties of an unsaturated polyester resin: 2. Hygrothermal studies

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The effect of equilibrium moisture content (M_∞) on the glass transition region of a cured unsaturated polyester resin has been studied. Variation of the accelerator content has been shown to result in different values of M_∞. The moisture sensitivity has been studied by comparing the rate of change of the glass transition temperature with equilibrium moisture concentration $|dT_g/dM_\infty|$ over a range of accelerator concentrations. Following the arguments in Part 1[1], it is demonstrated that variations in moisture sensitivity arise from differences in average crosslink density. The moisture dependence of the expansion coefficient can also be interpreted on the basis of a heterogeneous crosslink density, which results from the statistics of the addition copolymerization responsible for cure.

(Keywords: crosslink density; moisture absorption; polyester; resin)

INTRODUCTION

The increasing use of polymer matrix composites in structural applications inevitably results in them being exposed to a wide range of environments. How such materials behave under a variety of hygrothermal conditions has been a subject of interest for a number of years. The influence of the hygrothermal environment on polymer matrix composites can be considered in three ways:

(i) the physics of moisture and thermal diffusion in an anisotropic, heterogeneous medium;
(ii) the changes in thermomechanical properties of a composite and, in particular, the matrix; and
(iii) the deformation and residual stresses which result from thermal and swelling strains in the laminate.

In this study it is the changes in the thermomechanical properties of a cured unsaturated polyester resin on exposure to a number of humid environments which have been examined.

Jones *et al.*[2,3] noted that unusually high residual thermal strains occurred in glass fibre reinforced polyester crossply laminates, and these were shown to be attributable to an unexpected moisture effect, in which the thermal expansion coefficient of the matrix resin was enhanced in a non-linear manner. Since the thermal expansion coefficients of the longitudinal plies are relatively insensitive to this effect, the restrained shrinkage, transverse to the fibres, on cooling from the cure temperature, results in an increase in thermal strain. The effect of small quantities of absorbed moisture on the thermomechanical response was consistent with the previously reported hypothesis that the free radical cure of an unsaturated polyester resin resulted in a heterogeneous microstructure.

A model which describes the diffusion of moisture into a two-phase resin system[4] was found to describe the moisture absorption behaviour exhibited by the unsaturated isophthalic polyester resin considered above. These studies provided further indirect evidence for the presence of regions of high crosslink density surrounded by areas of lower crosslink density[5], as proposed by Funke[6] and Bergmann and Demmler[7].

It is generally recognized that the absorption of moisture into a resin results in:

(i) a reduction of the glass transition temperature;
(ii) a reduction of the modulus and strength coupled with an increase in strain to failure;
(iii) a small increase in the thermal expansion coefficient below the glass transition temperature; and
(iv) dilation (swelling).

The magnitudes of these effects are sensitive to both the quantity of moisture absorbed and its distribution within the resin.

In Part 1[1], we described a study of the effect of microstructural variation as a result of differences in accelerator concentration, on the glass transition temperature and modulus of the resin. In this paper, the anomalous thermal expansion behaviour of unsaturated polyester resins previously reported elsewhere[2] has been

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confirmed, and the effect of varying the heterogeneous structure on the glass transition temperature and thermomechanical properties of the resin under various hygrothermal conditions is discussed.

EXPERIMENTAL

Materials

The resin selected for this study was the propylene glycol/diethylene glycol/isophthalic acid/maleic anhydride copolyester dissolved in styrene, Crystic 272 (Scott Bader Co Ltd) used in Part 1 of this study[1]. In all cases the resin was cured using 2 phr (parts per hundred resin) of Catalyst M (50% methyl ethyl ketone peroxide solution) and between 0 and 1.0 phr Accelerator E (0.4% cobalt octoate solution). Reproducible void-free resin castings were machined into specimens suitable for both thermomechanical analysis (t.m.a.) and dynamic mechanical thermal analysis (d.m.t.a.) and were prepared as described elsewhere[1]. They were polished to a better than 1 μm finish prior to post-curing in an air circulating oven at 130°C for 1.5 h. A fully cured structure, with mechanical properties and glass transition temperature (T_g) unaffected by further cure, is achieved[8].

Hygrothermal conditioning

After post-curing the specimens were placed in a vacuum oven at 50°C and dried to constant weight prior to exposure to a selected hygrothermal environment. The specimens were hygrothermally conditioned either by immersion in distilled water or by exposure to a specific relative humidity, while others were retained in the dry state. All conditioning took place at 50°C as this increases the rate of moisture uptake over that at room temperature, but is below the glass transition region of the resin, which is between 70 and 150°C depending on moisture content.

Specific relative humidities were created by means of saturated salt solutions. Several lists of relative humidities over saturated salt solutions have been compiled[9-12]. From these data, salts whose equilibrium relative humidities have a low temperature dependence and a linear variation with temperature can be selected. From the relative humidity diagrams of Young[9], and other data from the literature, three saturated salt solutions, corresponding to three different relative humidities, were selected for use at the conditioning temperature of 50°C (*Table 1*).

Specimens to be conditioned by humidity were suspended over the saturated salt solutions on glass racks, inside insulated glass tanks with sealed lids. Specimens to be conditioned by immersion were placed in glass screw-lid jars filled with distilled water. To maintain the temperature at 50°C both the humidity tanks and the jars were placed in an air circulating oven. Each specimen was exposed to a specific environment for a predetermined length of time prior to testing.

Table 1 Relative humidities over saturated salt solutions at 50°C

Saturated salt solution	Relative humidity (%)
$Mg(NO_3)_2 \cdot 6H_2O$	46
NaCl	75
K_2SO_4	96

Thermomechanical analysis

The thermal expansion behaviour of the resin, both in the dry state and after hygrothermal conditioning, was examined using a Stanton Redcroft 691 Thermomechanical Analyser (TMA). This provides plots of probe displacement and temperature *versus* time. A heating rate of 4 K min^{-1}, which is low enough to avoid any heating rate effect, was used for all the t.m.a. experiments. The specimens used were approximately 2.5 mm thick, and were cut from resin castings in the manner described above. The specimens were polished and post-cured at 130°C for 1.5 h before being dried in a vacuum oven at 50°C prior to testing. A number of specimens were immersed in distilled water for a period of time sufficient for them to reach their equilibrium moisture content. The thermal expansion behaviour of the wet resin was then determined.

Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis was used to investigate the effect of heterogeneous crosslink density on the thermomechanical properties of the resin systems after hygrothermal conditioning. A Polymer Laboratories DMTA (Dynamic Mechanical Thermal Analyser) was used and all the specimens, both dry and at various equilibrium moisture contents, were tested in dual cantilever bending. All the specimens were of the same dimensions (i.e. $2 \times 10 \times 30$ mm) in an attempt to minimize geometric factors. Prior to testing, the conditioned specimens were wiped with absorbant paper to remove excess water or surface contamination and weighed to determine their moisture contents.

Specimens were clamped into the clamping frame of the DMTA using a torque-driver to tighten the clamp bar nuts to a torque of 27 cN m. A free (unclamped) specimen length of 10 mm, a frequency of 1 Hz and a strain of $\times 1$ were selected. A heating rate of 4 K min^{-1} was selected and the temperature was scanned from 30 to 150°C. This heating rate is sufficiently high as to prevent excessive drying out of the conditioned specimens during testing but not so high as to produce any heating rate effect, and this enabled accurate and reproducible results to be obtained. All the values of T_g are the average of 2–6 specimens and the reproducibility was ± 1 K. To prevent bias from casting variations the samples were randomized.

RESULTS

Thermomechanical analysis

Thermomechanical analysis (t.m.a.) allowed thermograms of the change in specimen length (ΔL) with temperature (T) to be constructed for both the dry and hygrothermally conditioned resin. Typical $\Delta L/T$ thermograms for both dry and hygrothermally conditioned specimens of Crystic 272 are shown in *Figure 1*. As has previously been reported[2], the $\Delta L/T$ thermograms for the resin were found to be non-linear, as a result of a temperature dependent expansion coefficient (α).

The value of the thermal expansion coefficient at any temperature ($\alpha(T)$) can then be expressed as:

$$\alpha(T) = (1/L_T)(\delta L/\delta T)_T$$

where L_T is the specimen length at temperature T, and $(\delta L/\delta T)_T$ is the gradient of the thermogram at $L(T)$.

In practice, it is difficult to draw accurately a tangent to the $\Delta L/T$ thermogram, to obtain the gradient ($\delta L/T$), chords were constructed on the curve between ($T+2.5$°C) and ($T-2.5$°C). At these increments this method gives close approximations to ($\delta L/\delta T$). The variation in thermal expansion coefficient with temperature can be seen from a plot of α against temperature (*Figure 2*).

Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis (d.m.t.a.) was used for a more detailed examination of the change in thermomechanical properties of the various accelerator concentration resin formulations after exposure to specific hygrothermal environments. The T_g was taken as the temperature at which $\tan\delta$ reached a maximum. It was found that for each formulation the equilibrium moisture content (M_∞) of the resin increased with increasing relative humidity. The increase in moisture content of the resin resulted in a decrease in the glass transition temperature (T_g) of the resin formulations (*Table 2*). Examples of the decrease in T_g with M_∞ are shown in *Figure 3*. The kinetics of the decrease in T_g with moisture absorption is given in *Figure 4*. It is seen that T_g decreased with time as the moisture content increased, reaching an equilibrium value. Under these conditions, previous studies have shown that the equilibrium would have occurred by $\approx$20 days[5].

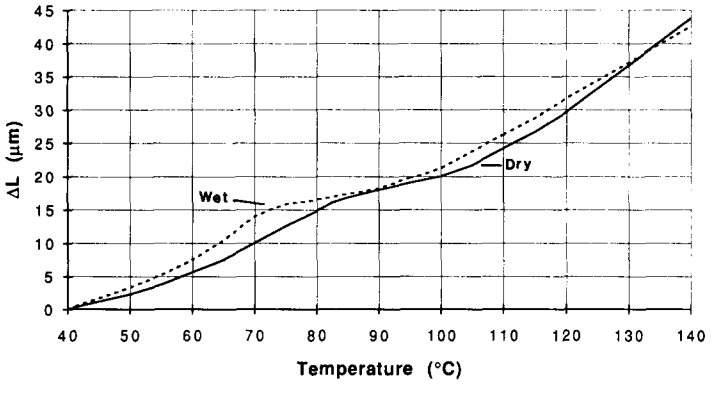

Figure 1 Probe displacement (ΔL) against temperature thermogram for dry (continuous curve) and hygrothermally conditioned (dotted curve) Crystic 272 polyester resin cured with 0.3 phr accelerator and post-cured at 130°C for 1.5 hours

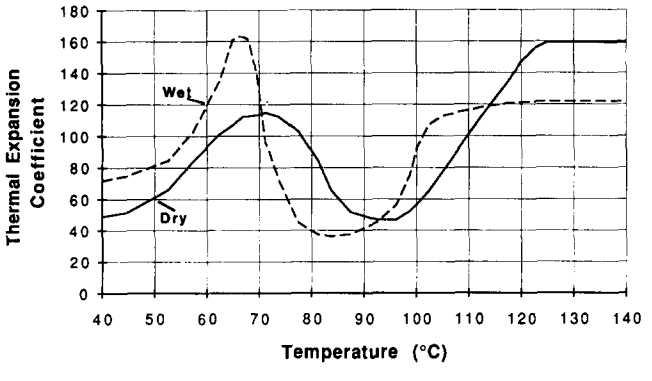

Figure 2 The temperature dependence of the thermal expansion coefficients of wet and dry Crystic 272 polyester resin cured with 0.3 phr accelerator and post-cured at 130°C for 1.5 hours. The wet resin contained 1.5% absorbed moisture

By examining a large number of specimens the basic error in the technique can be examined. Of crucial note is the small spread in the average T_g for the equilibrated wet specimens at saturation despite the fact that these materials require two diffusion constants to describe the moisture absorption kinetics adequately[5]. Furthermore, *Figure 4* demonstrates the accuracy to which small changes in T_g can be estimated and also indicates the reproducibility of our experimental technique. Therefore, the differing degrees of plasticization which occur for differently cured resins reported in *Table 2* need further examination. Such decreases in the glass transition temperature and thermomechanical properties are the expected result of an increase in the presence of moisture within the resin.

The dependence of T_g with M_∞ exhibited different degrees of curvature (*Figure 3*) for the resins cured with the differing accelerator concentrations. In order to examine the sensitivity of these resins to moisture we compared the rate of depression of T_g at low and high moisture contents, especially since we had previously demonstrated significant degrees of clustering above a moisture content of 0.39%, see ref. 13. Thus, values of dT_g/dM_∞ were obtained from the slopes of these curves above and below 0.4–0.5% moisture content. Therefore, $|dT_g/dM_\infty|^i$ is the magnitude of the initial gradient and $|dT_g/dM_\infty|^a$ is the gradient representing the average change in T_g with M_∞ over the range of moisture concentrations. The results of this analysis are given in *Figures 5a* and *5b* where it is seen, as expected from a detailed study of moisture diffusion[5,13], that the initial decrease in T_g is dependent on the accelerator concentration. The error bars represent the maximum and minimum slopes obtained from the curves given in *Figure 3*. It should be emphasized that moisture equilibration has occurred prior to dynamic mechanical thermal analysis. Therefore, the maximum sensitivity to moisture absorption, which occurs at low values of M_∞, is considered to be significant. Since water can be accommodated in the polymer structure either as hydrogen bonded molecules or in the free volume, the lower sensitivity at higher values of M_∞ when clustering

Table 2 Glass transition temperatures (T_g), at equilibrium moisture content (M_∞) for Crystic 272 polyester resin formulations exposed to various hygrothermal environments

	0.1 phr		0.3 phr		0.45 phr		0.6 phr		0.9 phr	
RH (%)	M_∞	T_g (°C)	M_∞	T_g (°C)	M_∞	T_g (°C)	M_∞	T_g (°C)	M_∞	T_g (°C)
0	0	115	0	114	0	114.5	0	113	0	112±0.5
46	0.57±0.02	111±0.5	0.41±0.01	109±0.5	0.46±0.05	110±0.5	0.53	109	0.55±0.03	109±0.5
75	1.06±0.01	108±0.5	0.93±0.02	107	0.91±0.02	107±0.5	0.97±0.06	105.5±0.5	1.05±0.01	107
96	1.61	105±0.5	1.42±0.02	104±0.5	1.33	104±0.5	1.52±0.02	104±0.5	1.42±0.02	104.5±0.5
100	1.77±0.01	105	1.49±0.02	103	1.59±0.01	103±0.5	1.58±0.01	102±0.5	1.55±0.01	104±0.5

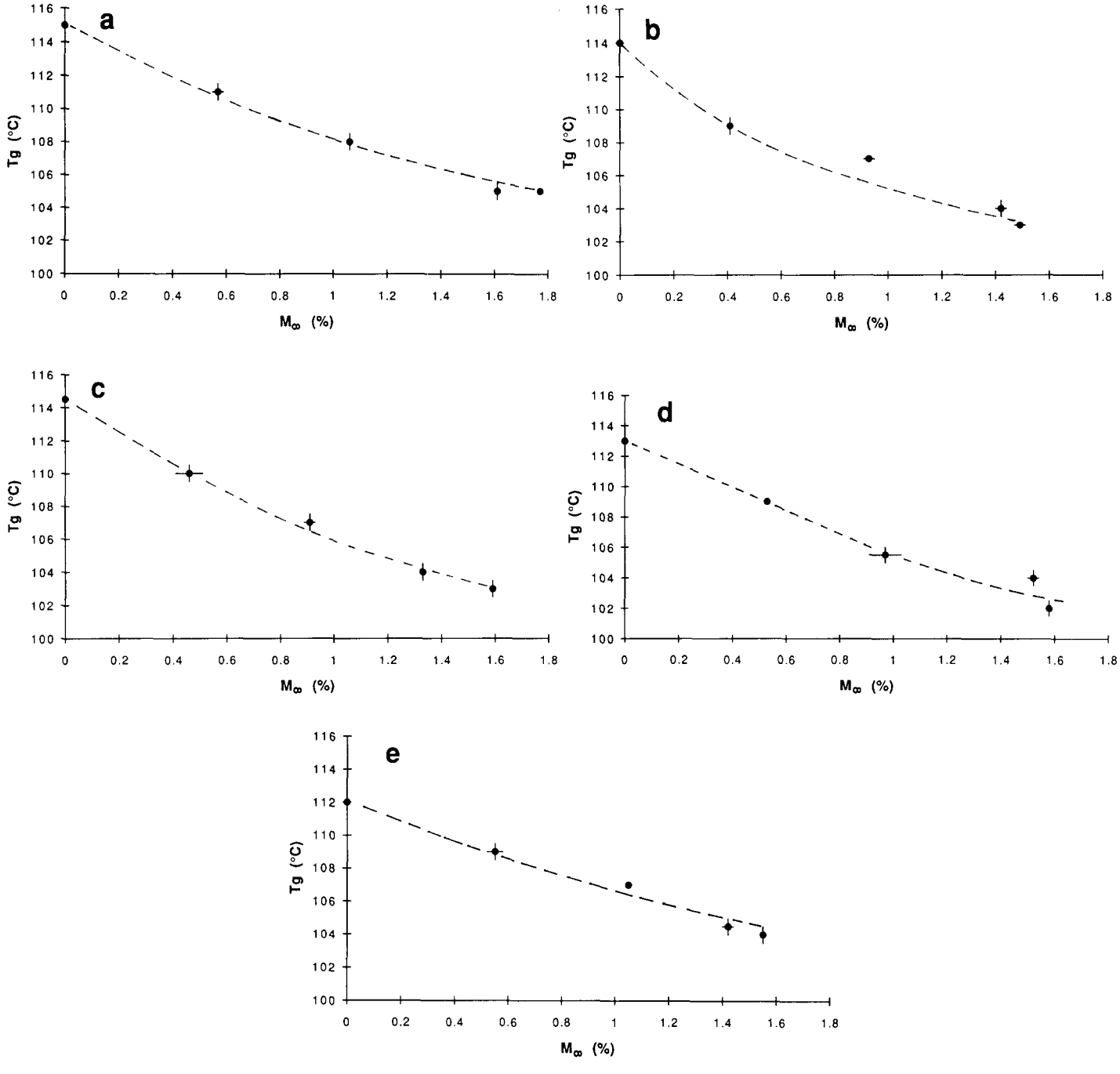

Figure 3 Plots of glass transition temperature (T_g) against equilibrium moisture content (M_∞) for Crystic 272 polyester resin cured with (a) 0.1 phr; (b) 0.3; (c) 0.45; (d) 0.6 and (e) 0.9 phr Accelerator E and post-cured at 130°C for 1.5 hours

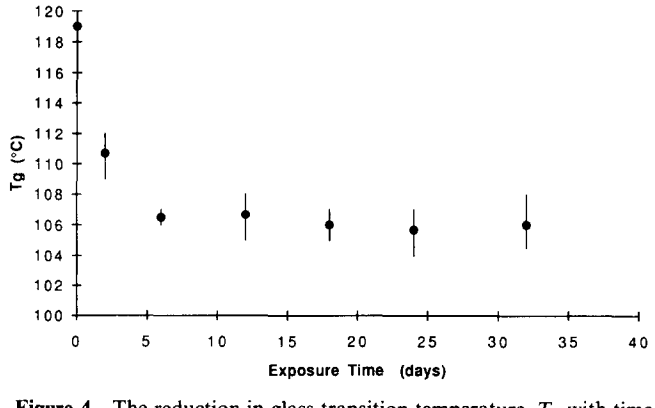

Figure 4 The reduction in glass transition temperature, T_g, with time after conditioning in a humid environment of 96% RH. The resin was fully cured with 0.3 phr Accelerator E and 2 phr Catalyst M

is known to occur, is not unexpected when plasticization involves the former mechanism.

DISCUSSION

The anomaly in the thermal expansion coefficient which occurs when a polyester resin absorbs moisture, described previously by Jones *et al.*[2], has been confirmed by thermomechanical analysis, as shown in *Figure 1*. The presence, and the enhancement, of a relaxation peak below T_g is indicative of a non-homogeneously crosslinked matrix. This phenomenon has been attributed to the heterogeneous microstructure which develops during the free radical cure of the resin. This aspect of the cure of a polyester resin is discussed in detail in Part 1[1]. As a result, modification of the heterogeneous

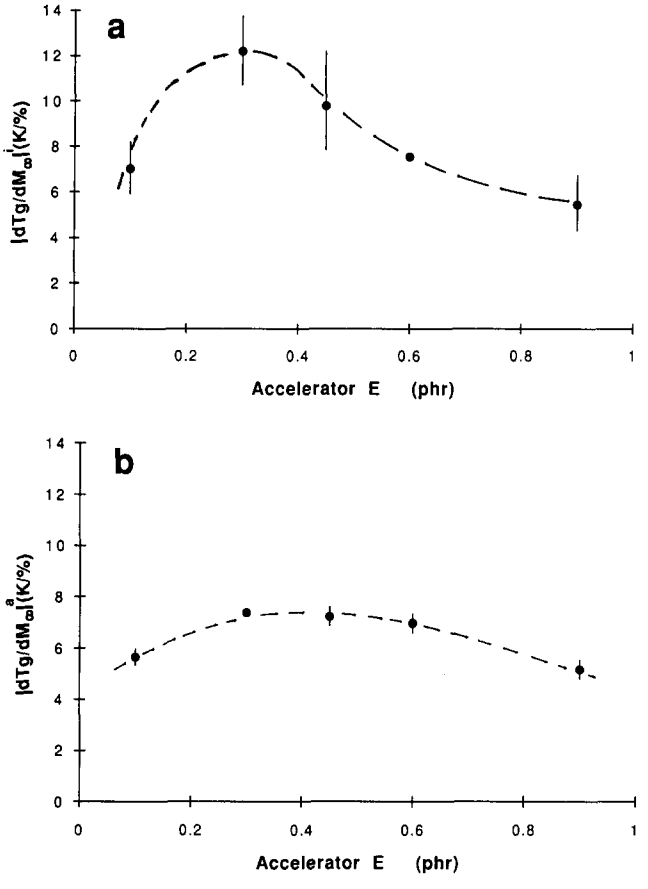

Figure 5 Plot of magnitude of glass transition temperature against equilibrium moisture content (M_∞) against accelerator concentration for Crystic 272 polyester resin post-cured at 130°C for 1.5 hours. (a) Initial slopes $(|dT_g/dM_\infty|)^i$ of *Figure 3* at M_∞ <0.4–0.5%; and (b) the average sensitivity obtained from the maximum depression of T_g, $(|dT_g/dM_\infty)^a$. Accelerator E is a 0.4% cobalt octoate solution

microstructure is expected to result in a change in the thermomechanical response of the wet resin after equilibration in hygrothermal environments of varying humidity.

In Part 1[1], we demonstrated that the nature of the heterogeneity of an unsaturated polyester resin can be modified by altering the accelerator concentration used in the resin formulation. This resulted in a systematic variation in the thermomechanical properties. In this study, we have examined the effect of this on the moisture sensitivity on the castings by exposing the post-cured specimens to a number of different hygrothermal environments.

Specimens prepared from various accelerator concentrations were exposed to different hygrothermal environments for a predetermined length of time to ensure equilibrium moisture content had been reached, prior to testing by d.m.t.a. The moisture content of the specimens increased with increasing relative humidity in the conditioning environment, which resulted in a decrease in both the T_g of the resin (*Table 2*) and the storage modulus (E'). This is to be expected, as the absorption of moisture results in the plasticization of the resin. On examination of this data it was noticed that the moisture sensitivities of the various resin castings (from differing accelerator concentrations) were not identical, in that the rate of change of T_g with moisture (M_∞) differed.

One way of assessing this observation would be to fit a theoretical model for the plasticization of the resin by water, such as that of Kelly–Bueche[14]. This model assumes, (i) that the polymer is homogeneous; (ii) that no interaction between the matrix and diluent occurs; (iii) that the T_g is a fixed point and not a region; and (iv) a fixed value for the T_g of the diluent. A consequence is that it is unable to account for the broadening of tan δ that occurs. The equation is also an approximation which may be insufficiently sensitive to describe the small variations discussed here. Furthermore, there is still doubt about the true value of the glass transition of the diluent (i.e. water). In addition, the variable heterogeneous microstructure which is present in these resins[1] and the tendency of the water to cluster at high humidities[13] makes application of this and similar models difficult.

Since clustering was shown to occur above 0.39% we examined the slopes of the T_g/M_∞ curves above and below 0.4–0.5%, to study the apparent differences in moisture sensitivity with accelerator concentration. This result is presented graphically in *Figures 5a* and *5b* where the change in $|dT_g/M_\infty|$ with accelerator concentration is given. When the water is absorbed as molecular species, its effectiveness as a plasticizer (*Figure 5a*) is strongly dependent on the initial accelerator concentration, whereas at higher moisture concentrations the plasticizing efficiency (*Figure 5b*) is largely unaffected. Since varying the accelerator concentration leads to a change in the distribution and extent of crosslinking of phases of differing density[1], these results are consistent with the simultaneous variation in the distribution of the water throughout the resin. Since the initial slope of the T_g/M_∞ curves represents the effect of plasticization by individual water molecules, whereas at higher moisture contents clustering of the water molecules occurs with a smaller effect on T_g, it follows that the phenomenon highlighted in *Figure 5a* can be attributed to differing proportions of the dense and less dense phases. This is, therefore, further confirmation that changes in microstructure occur with accelerator concentration and that the microstructures produced with 0.3–0.5 phr of accelerator are the most sensitive to moisture.

In Part 1[1], we demonstrated that the dynamic storage moduli (E') above and below T_g tended to a minimum over a similar range of accelerator concentration. The value of T_g for the dry castings also varied in an analogous manner although the minimum appeared to occur at slightly higher levels (0.5–0.8 phr) of accelerator. The moisture sensitivity of these resins is entirely consistent with variations in the distribution of crosslink density but those formulations which exhibit lower average crosslink density are the most sensitive to the plasticizing effect of the absorbed moisture, in the glassy state. This can be understood by the tendency of the more polar components of the polyester chain (i.e. the acidic and hydroxyl end-groups) to be segregated in the least crosslinked areas. There will also be a greater free volume in this phase which enables the absorbed moisture to be more readily accommodated. This argument is fully consistent with the differing moisture diffusion constants[5] and previous studies[1,6,7] where the statistical nature of curing chemistry was highlighted. The high plasticization efficiency of water at the low concentrations, before clustering occurs, indicates that direct interaction with the polyester chain is more important than the additional free volume created when the clustering of the water molecules occurs.

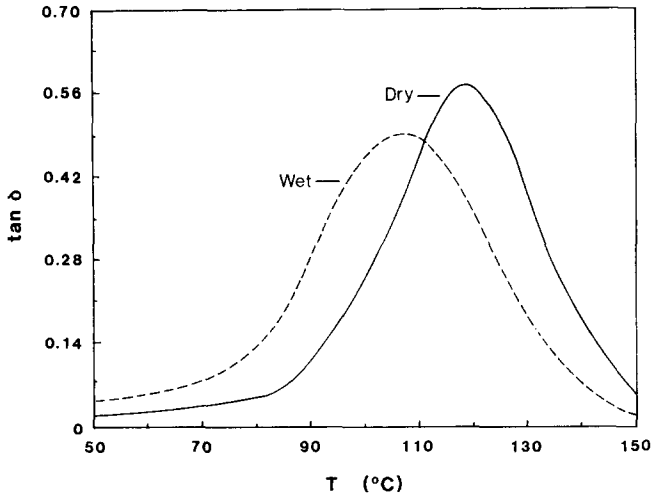

Figure 6 D.m.t.a. traces of tan δ against temperature for dry (continuous curve) and hygrothermally conditioned (dotted curve) Crystic 272 polyester resin cured with 0.3 phr accelerator and post-cured at 130°C for 1.5 hours. $M_\infty = 1.5\%$

For a polymer with well defined phases of differing composition, water absorption results in differing shifts in the values of T_g for the individual components. However, for this cured resin a similar phenomenon can also occur, but since a better description of the material would be one of a dense dispersed phase surrounded by a matrix of graded crosslink density, it follows that moisture absorption will tend to broaden the glass transition range, since these changes in storage and relaxation moduli are insufficiently resolved. As shown in *Figure 6*, water absorption does, in fact, broaden the range of temperature over which the glass transition occurs.

On the other hand, the temperature dependence of $\alpha_m(T)$, given in *Figure 2*, does show the presence of a secondary relaxation peak in addition to the main glass transition. Slight differences in the magnitude of this peak compared with the previous report[2] must arise from variations in the commercial resin, which we understand is now manufactured from different initial materials, differing catalyst/accelerator concentrations and a higher absorbed water concentration. However, the curve follows the general form of that previously presented. In comparison with the tan δ traces in *Figure 6*, it is clear that the d.m.t.a. is insufficiently sensitive to resolve the different components, but the general broadening of the glass transition region in the presence of water is still observed.

This comparison implies that the mechanisms responsible for the expansion coefficient of the cured resin are not simply derived from simple molecular relaxation processes. For the expansion coefficient to fall as it goes through the first transition region, a contraction on the molecular scale is inferred. This would appear to be analogous to the entropic contraction which occurs in a stressed rubber. For an analogous effect to occur as the temperature approaches the first transition for the polyester resin, the softer 'phase' must be under a tensile stress.

Considering the heterogeneous model discussed elsewhere[1,6,7] these internal stresses can arise as a result of the constraint offered by the more densely crosslinked regions, on cooling through the glass transition. A complex stress state in unidirectional glass fibre composites prepared from this resin was previously reported in which the through-thickness and in-plane transverse expansion coefficients were observed to differ, and equilibrate partially during moisture conditioning[2]. This observation is a further indication that the temperature dependence of the expansion coefficients of this cured resin is controlled by an additional mechanism which can be interpreted as the extreme heterogeneity to the crosslink density, which itself is a function of the accelerator concentration. The moisture absorption of these resins, and its effect on the T_g and glassy modulus, follows the trend in average crosslink density. The thermal expansion coefficient, however, is shown to be much more sensitive to the microstructural heterogeneity because of the presence of additional relaxation events. As a consequence the residual stress state and hence performance of composites based on these resins can also be expected to be similarly affected[3].

CONCLUSIONS

The cured isophthalic unsaturated polyester resin Crystic 272 has been found to exhibit a heterogeneous structure of the type described by Bergmann and Demmler[7] and others[1,5,6]. This structure comprises regions of high crosslink density surrounded by areas of lower crosslink density, and arises as a result of the free radical cure of the resin.

Hygrothermal studies on the effect of varying accelerator concentration on the thermomechanical properties of Crystic 272 polyester resin are consistent with such a microstructure. Those formulations which exhibit the lowest average crosslink density are the most sensitive to plasticization by moisture in the glassy state. This can be attributed to the less highly crosslinked component of the cured resin structure being more efficiently plasticized by molecular water. This leads to a greater depression of T_g for a given moisture content.

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