The effect of the morphology on the hygroelastic behaviour of polyester and epoxy resins

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(*Received* 2 *December* 1981; *revised* 3 *May* 1982)

The effect of the morphology on the hygroelastic behaviour of polyester and epoxy resins is studied. The morphology is expressed by two factors, namely, the free volume of the polymer and a two-phase formation. The first factor is varied in styrene-crosslinked polyester using different styrene/alkyd proportions, and by using different immersion temperatures. The second is investigated in polyesters by replacing styrene with bromostyrene inducing a two-phase structure, and in epoxies by changing the hardener/epoxy ratio. It is shown that the hygroelastic response is affected markedly by the morphology. In general, both the moisture content and its rate of absorption are higher when the polymer network is more open and when more free volume is available. In some cases, however, the hygroelastic parameters are dominated by a two-phase structure where present.

Keywords Morphology; polyester resin; epoxy resin; hygroelastic behaviour; free volume; two-phase formation; crosslinked polyester

INTRODUCTION

The studies of interactions between polymeric materials and liquid or vapour environments can be classified into three major conceptual approaches. The first is concerned with the penetration mechanisms, where questions related to the transport kinetics and to the diffusion mechanism are emphasized. The second focuses on the interaction between the penetrant and the polymer resulting in chemical degradation, polymer leaching, cracking or crazing and loss of mechanical properties. The third approach gives priority to the dimensional response of the polymer in terms of its swelling or its hygroelasticity which is mostly elastic.

The theme of hygroelasticity has been the subject of our studies for a number of years now. Our previous studies have dealt with some of its aspects starting with the definition of a simple parameter termed the coefficient of hygroelasticity, which reflects quantitatively the dimensional response. Those studies have investigated the analogy between the coefficient of hygroelasticity and that of thermal expansion; they have examined the effects of molecular orientation and of reinforcing the polymer on the anisotropy of the coefficient; and they have looked into its implications in the context of predicting the polymer lifetime under given swelling conditions[1-4].

The polymer morphology

Molecular orientation is just one factor of those which together set a morphological state. Orientation is related to mechanical treatments such as drawing involving flow, and is unaffected by the chemical reactions which take place during the polymerization stage. However, a morphological state, although related to the physical structure of the polymer, may be highly affected by the polymerization reaction. In particular, it may be affected by the crosslinking reaction and by a possible formation of a two-phase structure.

The type and form of the crosslinking reaction determine either or both the crosslink density, reflected in the average molecular weight between crosslink points, M_c, and the length of the crosslinks between the skeletal chains. The formation of a two-phase structure results from a non-uniform creation of crosslink points during the early stages of the crosslink reaction, resulting in a non-uniform development of gelation throughout the polymer[5]. This process yields a two-phase structure, whereby a highly crosslinked continuum encapsulates a softer material or *vice versa*.

The present study deals with some effects of the morphological factors listed above on the hygroelastic behaviour of epoxy and polyester resins. The specific modes employed for obtaining morphological variations are described below.

Hygroelasticity and morphology

One of the important variables which affect the dimensional response of a polymer under a given swelling situation is the free volume which is linked directly to the morphological factors reviewed above. Changing the free volume is possible by a number of ways of which the variation of the stoichiometric ratio between the polymer chain (e.g. alkyld or epoxy) to the crosslinking monomer (hardener) is applied here. In the polyester system, where the number of double bonds per repeating unit of the alkyd chain is constant, changing that ratio results theoretically in altering the calculated average length of the crosslinking chain. In practice, however, the changing of that stoichiometric ratio has a combined effect on both the crosslink density and the crosslink length. When the

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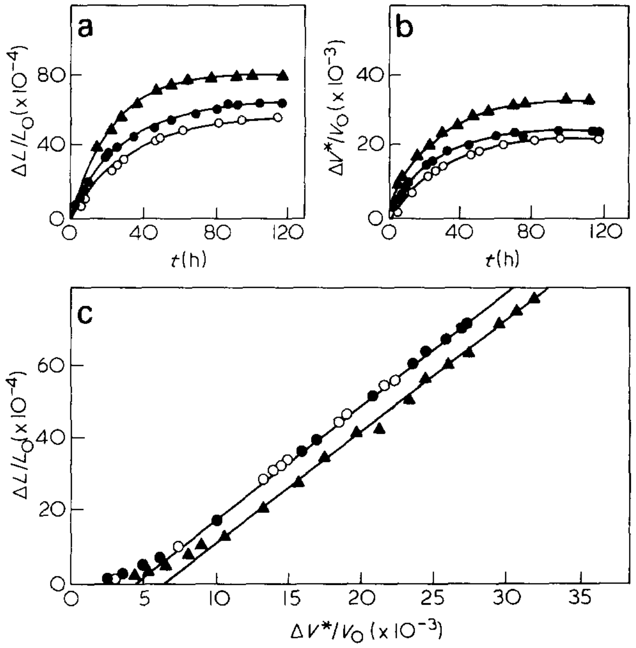

Figure 1 Hygroelastic data for styrene-crosslinked polyesters in water at 60°C: (a) the strain; (b) the relative moisture absorption; (c) plots of the strain vs. the moisture absorption. Curves are (▲) 0.36 moles, (●) 0.48 moles, and (○) 0.60 moles of styrene per 100 g alkyd

relative quantity of the crosslinking monomer is small, the alkyd double bonds cannot react exhaustively, due to high viscosity. This results in a lower crosslink density compared with the upper bound set by the concentration of the alkyd unsaturation. When more monomer is added the upper bound for the crosslink density will gradually be reached; thereafter, the effect of further additions of crosslinking monomer will be to increase the crosslink lengths between the skeletal chains[6]. In the epoxy resin the consequences of changing the ratio between the epoxy and the hardener are reflected in the crosslink density and in the chain molecular weight between adjacent crosslinks, M_c. The number of available amino hydrogens of the hardener determines M_c by forming either a crosslink or a junction point during the crosslinking reaction[7].

The changing of the free volume as described above is characterized by being a concomitant effect to the modification of the network structure of the polymer. For a given network, however, it is still possible to increase the free volume by raising the temperature. Correspondingly, this study also deals with the effect of temperature on the hygroelasticity.

Changing the free volume of the polyester resin is obtained here by yet another technique, involving a modification aimed at increasing the bulkiness of the crosslinking monomer. Specifically, styrene is replaced by bromostyrene, in the assumption that this replacement may not alter the original polymer network except that it becomes more open due to the presence of the bulky bromine atoms.

Finally, the effect of the free volume on the hygroelastic behaviour of the polymer may sometimes act indirectly. This, for example, may occur when changing the stoichiometry of the crosslinking reaction induces morphological changes in the polymer structure, e.g. the creation of two phases. Hence, this study also examines the effect of the creation of a two-phase structure on the hygroelastic behaviour.

In the next sections the experimental results are presented and discussed in conjunction with the questions raised above.

EXPERIMENTAL

The resin systems

The alkyd chains of the polyesters were constructed of fumaric and terephthalic acids and of propylene glycol in the proportions 1:1:2, respectively. These alkyd chains were crosslinked by various proportions of styrene to form the polyester resin. In some formulations bromostyrene replaced the styrene.

The polyester resin was prepared by melting the alkyd at about 100°C and adding the crosslinking monomer together with 1 ppm of 1% benzene solution of copper naphthanate as inhibitor. The mixture was stirred for 1 h to obtain a homogeneous solution, which was thereafter cooled to room temperature. Curing was carried out with 2% methylethyl ketone peroxide, and the curing cycle consisted of 24 h at room temperature, 24 h at 80°C and 2 h at 110°C.

The epoxy resin comprised diglycidyl ether of bisphenol A (DGEBA) cured by methylene dianiline (MDA). Here also a number of compositions were prepared with varied ratio of MDA to DGEBA.

The epoxy resin was prepared by mixing the molten MDA (90°C) with the DGEBA. Curing was carried out for 20 h at room temperature, 2 h at 80°C and 1 h at 180°C.

Hygroelasticity measurements

Hygroelastic data and the coefficient of hygroelasticity were obtained by simultaneously measuring weight gain and expansion with two identical specimens immersed in water. Either a dial gauge or an l.v.d.t. attached to a recorder were used for measuring expansional changes of the order of 0.5 μm.[2] The coefficient of hygroelasticity was calculated as:

$$\mu=\frac{\Delta L/L_0}{\Delta V^*/V_0}$$

where $\Delta L/L_0$ is the strain, V^* is the volume occupied by the penetrant outside the polymer and V_0 is the initial volume of the polymer.

RESULTS AND DISCUSSION

Styrene-crosslinked polyesters

Figure 1 presents the hygroelastic behaviour during water immersion at 60°C for 120 h of three polyesters, whose compositions are presented in *Table 1*, where

Table 1 The effect of the concentration of the crosslinking monomer on the hygroelastic behaviour of the polyesters[a]

No.	Monomer per 100 g alkyd (mol)	$(\Delta V^*/V_0)_\infty$ $(\mathrm{x}10^{-3})$	μ	$\Delta V^*/V_0 = kt^n$ n	k (h^{-n})
I	0.36	33.4	0.305	0.516	0.0046
II	0.48	24.7	0.297	0.509	0.0037
III	0.60	21.8	0.297	0.519	0.0027

[a] Experimental conditions: immersion in water at 60°C for 120 h; specimen dimensions: 10.0 x 2.0 x 0.2 cm³

Table 2 The effect of the MDA concentration on the hygroelastic behaviour of the epoxies[a]

No.	MDA per 100 g DGEBA (g)	μ	$t = 5$ h $\Delta L/L_0$ ($\times 10^{-4}$)	$t = 5$ h $\Delta V^*/V_0$ ($\times 10^{-3}$)	$t = 30$ h $\Delta L/L_0$ ($\times 10^{-4}$)	$t = 30$ h $\Delta V^*/V_0$ ($\times 10^{-3}$)
IV	18	0.266	23.6	12.8	51.6	25.3
V	27	0.321	24.0	8.9	61.3	20.7
VI	36	0.148	3.5	5.8	18.6	14.3

[a] Experimental conditions: immersion in water at 98°C for 30 h; specimen dimensions: 5.0 x 3.0 x 0.35 cm^3

Table 3 The effect of the MDA concentration on M_c and on the probabilities for amino hydrogen reaction with epoxides

MDA per 100 g DGEBA (g)	M_c	$p(0)$ (%)	$p(1)$ (%)	$p(2)$ (%)	$p(3)$ (%)	$p(4)$ (%)
27	580	1.5×10^{-4}	1.6×10^{-2}	0.68	12.58	86.72
36	689	0.58	6.10	23.96	41.90	27.40

additional hygroelastic data are also listed. The kinetics of the absorption process were checked by calculating the constants k and n of the general function $\Delta V^*/V_0 = kt^n$ in the range $0 \leqslant \Delta V^*/V_0 \leqslant 0.4(\Delta V^*/V_0)_\infty$. (The correlation coefficient was $r^2 = 0.998$.)

It is seen that increasing the styrene/alkyd ratio in the examined range does not affect the diffusion mechanism, which for $n \sim 0.50$ is Fickian. However, the rate of absorption reflected in k, and the equilibrium moisture absorption $(\Delta V^*/V_0)_\infty$, decrease significantly with increasing that ratio. The results indicate that as the styrene/alkyd ratio is increased, more fumarate double bonds become accessible, and their reaction with styrene to increase the crosslink density is promoted rather than homopolymerization of the styrene to increase the length of the crosslinking chain[6]. Consequently, the free volume decreases followed by the observed reduction in the rate of absorption and in the equilibrium absorption capacity.

Contrary to the sensitivity of the styrene/alkyd ratio exhibited by the rate and by the equilibrium parameters, the coefficient of hygroelasticity is independent of this ratio. To understand this point the Young's moduli of the three polyesters were determined in bending. The three resins gave identical average values of 3.45 GPa. The fact that the Young's moduli are equal means that in these materials equal stresses produce equal strains. Thus, if the stress is a linear function of $\Delta V^*/V_0$, μ will be independent of the composition as long as the modulus is.

It is concluded that although increasing the styrene/alkyd ratio in the examined range decreases the rate of absorption and the equilibrium capacity, the coefficient of hygroelasticity remains unaffected as long as the elastic properties of the resin are unaffected.

Methylene dianiline-cured epoxies

The changing of the hardener/epoxy ratio in epoxy resins discussed above is expected to affect the hygroelastic behaviour through M_c. The specific compositions and the hygroelastic results of 30 h immersion experiments at 98°C are presented in *Table 2*. (The weight ratio of 27/100 of MDA/DGEBA is the stoichiometric ratio.) The results show that resin IV exhibits the highest rate of absorption, resin V exhibits the highest coefficient of hygroelasticity, and resin VI exhibits the lowest rate and the lowest coefficient. Evidently, the hygroelastic response as a function of the composition is entirely different from that of the polyesters.

The key to understanding the effect of the hardener/epoxy ratio on the hygroelasticity is to know how the structure and the morphology of the resin relate to this ratio. When the epoxy is in excess compared with the hardener (resin IV), the curing reaction results in a fraction of the epoxy chains bonded to the three-dimensional network through one of their epoxide groups only[8]. The probabilities that some epoxy chains do not react at all, or that alternative curing reactions occur, are small[9]. Hence, the resulting structure is one of some three-dimensional regions to which dangling chains are attached. Such a structure is expected to be fairly open, and to exhibit a relatively high moisture absorption capacity. The smaller μ compared with that of the stoichiometric resin might be explained by a higher free volume by which water molecules may be contained without generating strains.

When the hardener/epoxy ratio is equal to or higher than the stoichiometric one, M_c is determined by the probabilities that one, two, three or all four MDA amino hydrogens react with epoxides. *Table 3* presents these probabilities and the calculated M_c values for epoxies V and VI, as calculated by the method presented in detail in ref. 8. The results show that for the stoichiometric composition $p(3) + p(4) = 99.3\%$, being the proportion of the MDA molecules which result in crosslink points, while only 69.3% do so in resin VI, where $p(3) + p(4) = 69.3\%$. Correspondingly, the chain molecular weights are 580 and 689.

If the molecular weight between adjacent crosslinks is the crucial structural factor for determining the hygroelastic behaviour of the polymers, it will be expected that the rate of absorption and the maximum uptake of resin VI will be greater than those of resin V. However, a number of recent studies show that the morphological changes which occur with changing M_c are in fact dominant[5,10]. In particular, a recent study on epoxies cured by *m*-phenylene diamine/aniline mixtures shows that as the proportion of aniline increases, resulting in higher M_c values (448, 605 and 874), both the rate of absorption and the maximum uptake decrease[7]. It is shown that the formation of a two-phase structure consisting of softer, less crosslinked resin domains encapsulated by highly crosslinked shells is facilitated by higher M_c values. Etching experiments similar to those reported in ref. 7 indeed revealed the existence of a two-phase structure which was more prominent in resin VI. Thus, the experimental observations might be explained by considering that the highly crosslinked phase slows down markedly or even prevents moisture penetration into the encapsulated less crosslinked epoxy. This is expected to reduce the rate of moisture absorption. In addition, the maximum moisture uptake is also expected to reduce, since less water can accumulate within the highly crosslinked resin, while the less crosslinked resin is inaccessible.

In conclusion it is seen that in the epoxy resins the ratio of hardener/epoxy affects the hygroelastic behaviour differently than does the monomer/alkyd in the polyesters. The coefficient of hygroelasticity of the epoxies is dominated by the composition-induced morphology.

Bromostyrene-crosslinked polyesters

The new evidence on the effect of the resin morphology on the hygroelastic response has driven us to re-examine the very interesting system of bromostyrene-crosslinked polyester. This resin was reported to be crack-proof under severe humidity conditions and a number of hypotheses were proposed to explain this unique characteristic[11].

Figure 2 presents the hygroelastic behaviour during water immersion at 60°C for 250 h of styrene- and bromostyrene-crosslinked polyesters. *Table 4* contains additional hygroelastic and physical data. The most striking difference between the bromostyrene- and styrene-crosslinked resins is their humidity resistance. This is demonstrated by *Figure 3* which shows the surfaces of the two polyesters after exposing them to water at 98°C for 70 h. This treatment resulted in major cracking of the styrene-crosslinked resin, while only minor cracking occurred in the bromostyrene polyester. Another difference between the two resins is their n values, indicating that the diffusion mechanism in the bromostyrene polyester deviates slightly from Fickian with $n = 0.594$.

The initial experimental data suggest that the effect of the bromostyrene on the hygroelastic behaviour of the resin is a morphological effect. The assumption that the presence of the bulky bromine atoms opens up the polymer network is not relevant here, since the results show significantly lower take-up values of the bromostyrene-crosslinked resins. Thus the lower values of $(\Delta V^*/V_0)_\infty$ and of k may be explained by the presence of an inaccessible phase. This assumption is supported by the fact that bromostyrene is less volatile than styrene, and it is more active and tends to homopolymerize, which may result in less crosslinked regions in the resin. It is therefore feasible that during the initial polymerization stage

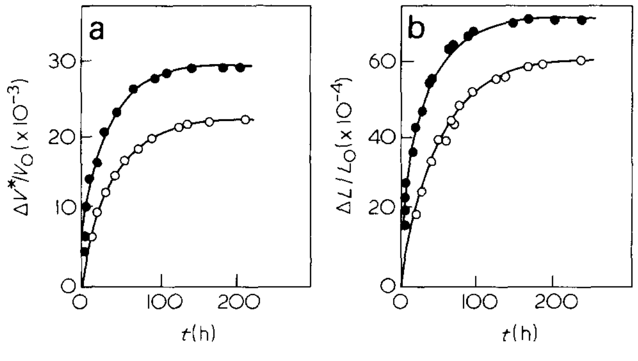

Figure 2 Hygroelasticity data for styrene- and bromostyrene-crosslinked polyesters in water at 60°C (0.48 moles of monomer per 100 g alkyd): (a) the relative moisture absorption; (b) the strain. Points: (●) Styrene, (○) bromostyrene

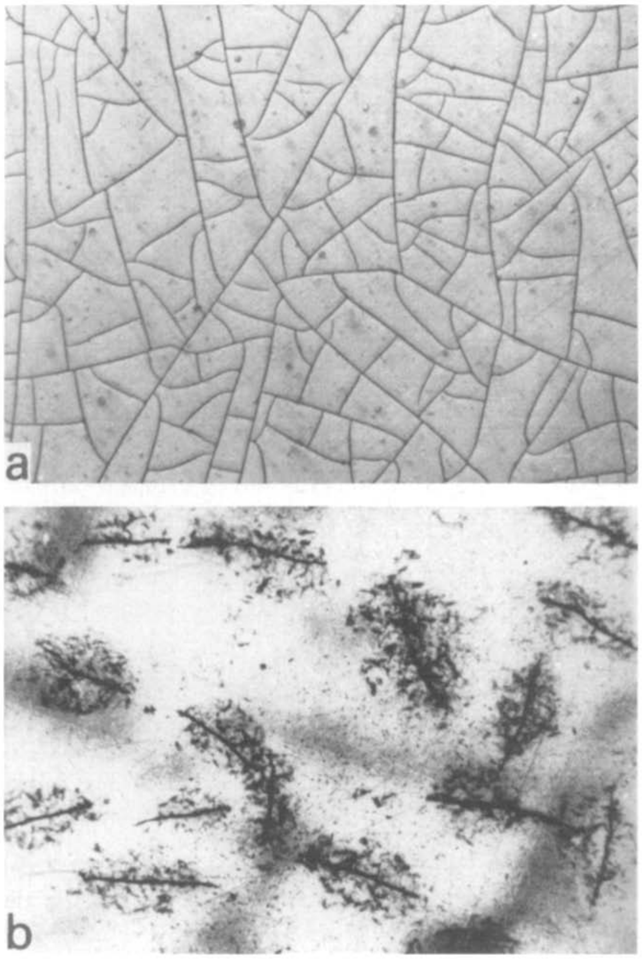

Figure 3 The surfaces of styrene- and bromostyrene-crosslinked polyester specimens after 70 h in water at 98°C: (a) styrene; (b) bromostyrene

Table 4 Hygroelastic data for styrene- and bromostyrene-crosslinked polyesters[a]

Monomer	$(\Delta V^*/V_0)_\infty$ ($\times 10^{-3}$)	$(\Delta L/L_0)_\infty$ ($\times 10^{-4}$)	μ	$\Delta V^*/V_0 = kt^n$ n	$\Delta V^*/V_0 = kt^n$ k (h^{-n})	ρ (g cm^{-3})	E at 60°C (GPa)
Styrene	29.3	71.7	0.298	0.507	0.0037	1.191	1.80
Bromostyrene	22.5	60.8	0.314	0.594	0.0018	1.418	1.35

[a] Water immersion at 60°C for 250 h; specimen dimensions 10.0 x 2.0 x 0.2 cm^3

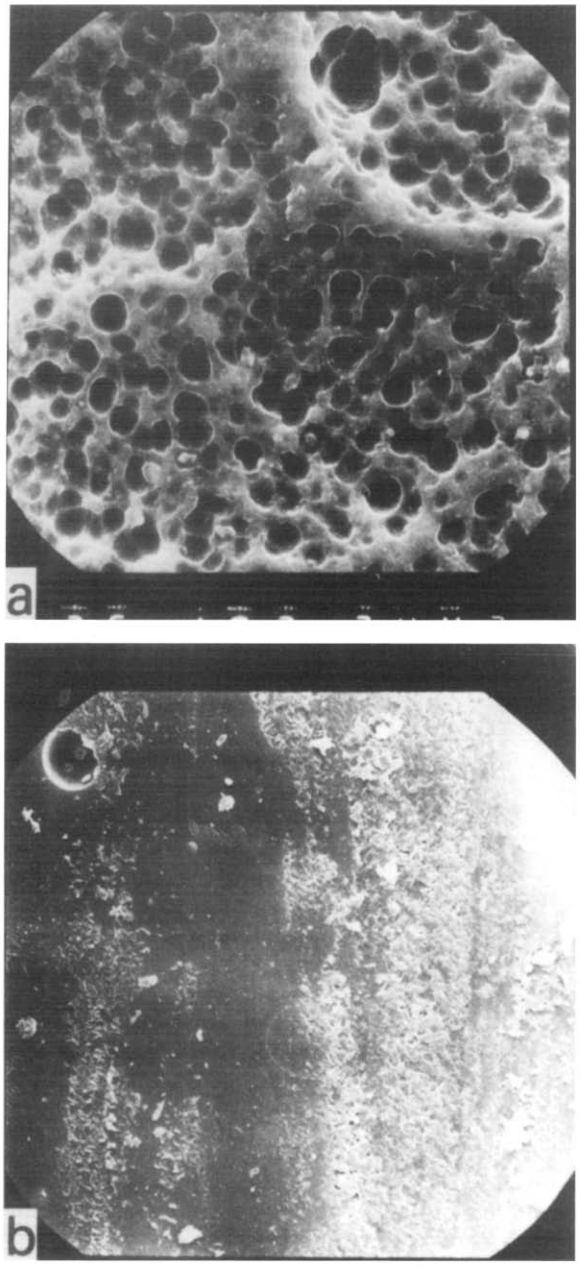

Figure 4 H_2SO_4/CrO_3 etched surfaces of styrene- and bromostyrene-crosslinked polyester specimens previously immersed in water at 98°C for 120 h: (a) styrene, (b) bromostyrene (x1500)

relatively long chains of homopolybromostyrene are formed, while later, due to the relative increase in the concentration of the fumarate double bonds, they polymerize to form wide regions of high crosslink density.

Etching experiments supply further evidence for the two-phase model. *Figure 4* shows the surfaces of styrene- and bromostyrene-crosslinked polyesters exposed to boiling water for 120 h, and thereafter etched at 80°C by a CrO_3/H_2SO_4 solution. Whereas the styrene resin does not exhibit any indications of a two-phase structure, the etched bromostyrene resin exhibits a porous structure indicative of a soft discontinuous phase embedded in a highly crosslinked shell.

This picture of a two-phase structure correlates very well with the high cracking resistance of the resin. The resin is no longer brittle throughout, but contains pockets of tough material comprising less crosslinked resin. The cracks which form in the brittle regions due to the swelling stresses are blunted and stopped when they interact with such a pocket, which is consistent with the observation in *Figure 3*.

Finally, the coefficient of hygroelasticity of the bromostyrene-crosslinked resin is slightly higher than that of the styrene one. This may be a result of the lower modulus at 60°C of the first (*Table 4*), since equal stresses for equal $\Delta V^*/V_0$ values result in a higher strain for a lower modulus.

In conclusion it is maintained that whereas varying the styrene/alkyd ratio does not affect the morphology, the replacement of styrene with bromostyrene does. The existence of the two-phase structure affects the hygroelastic response and, most of all, it is responsible for the exceptionally high cracking resistance.

The temperature effect

The temperature effect on the hygroelastic behaviour is expected to be complex, being a superposition of at least three contributions. These are the increase in the free volume, the increase in the diffusion rate and the decrease in the modulus.

The temperature effect was investigated with styrene-crosslinked polyesters immersed in water at 40°, 60° and 80°C for up to 320 h in the lowest temperature. *Figure 5* presents the hygroelastic behaviour as a function of the immersion period, and *Table 5* gives the complementary information. It is seen that increasing the temperature accelerates the absorption and increases its maximum level. The diffusion process, however, remains Fickian regardless of the temperature, as indicated by $n \sim 0.5$.

The plot of the strain *versus* the moisture uptake has two important features. The first, corresponding to the initial stage of the absorption process, is characterized by a lower $(\Delta L/L_0)/(\Delta V^*/V_0)$ ratio, which reduces with

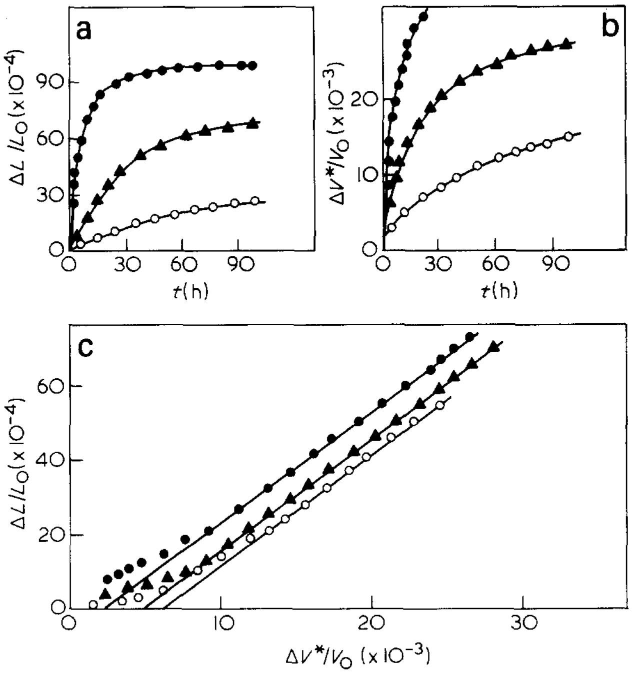

Figure 5 The effect of temperature on the hygroelastic behaviour of styrene-crosslinked polyesters: (a) the strain; (b) the relative moisture absorption; (c) plots of the strain vs. the moisture absorption. Points: (●) 80°, (▲) 60°, (○) 40°C

Table 5 The effect of the immersion temperature on the hygroelastic behaviour of polyesters[a]

T (°C)	$\Delta V^*/V_0 = kt^n$		$(\Delta V^*/V_0)_\infty$	$(\Delta L/L_0)_\infty$		
	n	k (h^{-n})	($\times 10^{-3}$)	($\times 10^{-4}$)	μ	E (GPa)
40	0.495	0.0017	23.1	47.7	0.298	2.56
60	0.504	0.0037	27.4	71.7	0.298	1.81
80	0.548	0.0077	35.3	98.2	0.297	0.32

[a] Specimen dimensions 10.0 x 2.0 x 0.2 cm^3

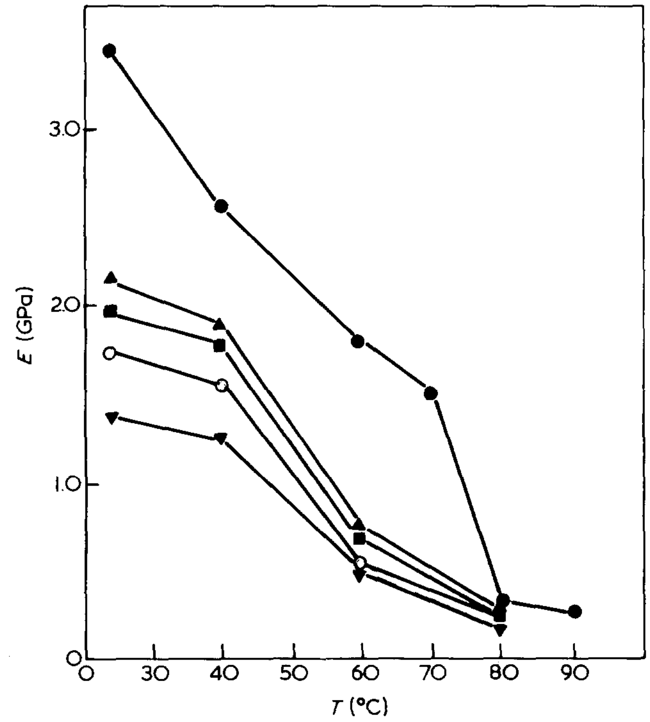

Figure 6 The effect of temperature on the flexural Young's modulus of styrene-crosslinked polyesters with different moisture contents: (●) 0, (▲) 8.5, (■) 11.5, (○) 15.5, (▲) 19.0 ($\times 10^{-3}$)

reducing temperature. The second is characterized by a linear behaviour beginning at about $\Delta V^*/V_0 = 0.01$, and exhibiting an equal slope of $\mu = 0.30$ for the three temperatures. These observations can be understood by realizing the complementary action of the moisture content and of the temperature in reducing the glass transition temperature of the polyester. The effect of the temperature on the flexural Young's modulus of polyesters with various moisture contents is shown in *Figure 6*. It is obvious that the modulus of the resin in the rubbery state is not influenced by the moisture content. Hence, for a given temperature, once a particular moisture content is achieved, the resin is in the rubbery state, where its modulus and therefore μ are independent of $\Delta V^*/V_0$.

In summary, the hygroelastic response of the polyesters exhibits two stages, corresponding to the initial and to the linear portions of the $\Delta L/L_0$ *versus* $\Delta V^*/V_0$ plots. During the initial stage the resin with the highest modulus (lower testing temperature) exhibits smaller strains (and a smaller μ). Later, when the combination of moisture concentration and temperature brings the resin to its rubbery state, the hygroelastic response becomes insensitive to the temperature.

CONCLUSIONS

The hygroelastic response of polyester and epoxy resins is affected markedly by their morphologies. In general, both the moisture content and its absorption rate are higher when the polymer network is more open, and when more free volume is available. However, in some cases such as the epoxy resins and the bromostyrene-crosslinked polyester, the hygroelastic parameters are dominated by a two-phase structure. The coefficients of hygroelasticity reflect the changes in the rigidity of the resins as a function of their composition.

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