

The influence of creep conditions on the macromolecular structure of an epoxy-imide

Nicola Piccirelli, Martin E.R. Shanahan*

Centre National de la Recherche Scientifique, Ecole National Supérieure des Mines de Paris, Centre des Matériaux P.M. Fourt, B.P. 87, 91003 Evry Cédex, France

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Abstract

An epoxy-imide adhesive has been exposed to tensile creep at various elevated temperatures in air. Using viscoelastic techniques, the glass-transition temperature has been monitored both for the polymer having undergone creep and the material simply aged at the same temperature. Defining ΔT_g as the T_g of the loaded material minus that of the aged material, for conditions otherwise equivalent, unusual behaviour has been observed. Initially, ΔT_g increases for short times but later decreases and becomes slightly negative. This behaviour has been attributed to two phenomena, occurring concomitantly: that of macromolecular chain orientation causing a reduction of free volume and a (relative) increase of T_g , and chain scission caused both by chain elongation and thermal degradation, leading to a drop of T_g . A simple model is proposed to explain semi-quantitatively the observed behaviour. © 1998 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The use of thermoset polymers under load at high temperatures requires a knowledge of their creep properties and microstructural evolution. Various phenomenological laws of behaviour have been suggested describing quite accurately the evolution of creep strain as, for example, a function of stress and time [1]. Nevertheless, relatively little work seems to have been reported on the microstructural evolution occurring during the creep of thermoset materials.

The simultaneous effects of stress and high temperature are likely to alter the macromolecular structure and therefore the macroscopic properties. Macromolecular changes often modify the glass transition temperature, T_g . It has been shown that the T_g of a linear or slightly crosslinked amorphous polymer tends to increase with creep strain [2,3] whilst for thermoset materials, T_g is clearly influenced by crosslinking density [3–5].

In the present study, we have considered the creep behaviour of an epoxy-imide and in particular variations in T_g associated with different conditions of temperature and stress. We propose a semi-quantitative explanation of the

experimental observations, relating these to microstructural, or molecular, evolution.

2. Experimental

2.1. Material

The material considered in this study is an epoxy-imide adhesive distributed by CYTEC and known commercially as FM 32. It is supplied as a film of ca. 0.4 mm thickness supported by a glass fibre fabric. The volume fraction of glass fibres is ca. 10%; the fabric is present to facilitate handling of the adhesive.

The cure cycle used was that recommended by CYTEC, corresponding to 4 h at 180°C under a pressure of 3 bar followed by a post-cure for 4 h at 205°C. Temperature increases and decreases at a rate of 3°C/min were used.

This material, once cured and post-cured, is a brittle film (at ambient temperature) with a glass transition temperature of $275 \pm 3^\circ\text{C}$, as determined by viscoelastometry in tension at a frequency of 5 Hz (Metravib Viscoanalyseur). The resulting polymer can withstand prolonged exposure at 180°C and short-term exposure at temperatures up to ca. 250°C.

* Corresponding author.

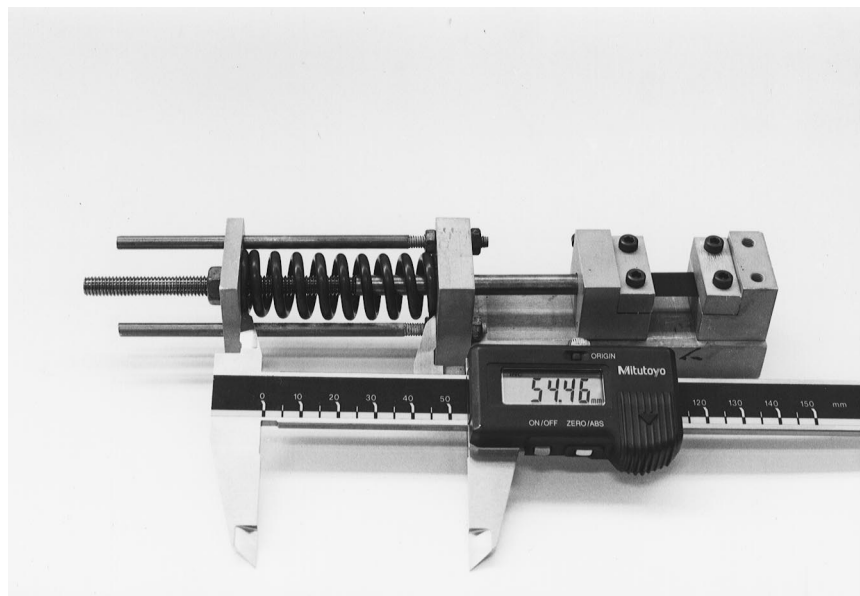


Fig. 1. Miniature creep rig.

2.2. Techniques

Rectanguloid test pieces for creep experiments were cut with dimensions $30 \times 10 \times 0.4$ mm such that glass-fibre support orientation was $\pm 45^\circ$ with respect to the direction of applied load (along the length of 30 mm). This was to limit the influence of the glass fibre fabric on creep behaviour [6]. (It was not found to be possible successfully to remove the fabric and reconstitute the polymer.) For these test pieces, 1 layer of adhesive film was sufficient.

Creep experiments were conducted in tension, using miniature spring-loaded creep rigs designed and made in the laboratory. These rigs, of which a picture of one is shown in Fig. 1, were inspired by apparatus used a number of years ago to test adhesive lap joints [7–9], although the present equipment is much smaller. Load is applied to the polymer in tension using a calibrated spring in compression. The strain of the polymer is measured with an electronic micrometer. The small (overall) strain resulting from creep allows a relaxation of the spring of ca. 2% of the initial stress and it is thus considered that applied load is essentially constant. Temperature control was assured by placing the creep rigs in a Memmert oven (in air) giving a regulation of $\pm 2^\circ\text{C}$.

Some creep tests were effected by fixing the temperature at 230°C and the applied stress, σ , at 22 MPa (ca. 50% of the failure load at this temperature), whilst varying creep time from 3 to 168 h. Others were done keeping the time to 24 h, but considering the test temperature (from 180 to 245°C) or the applied stress (from 0 to 30 MPa) as variables.

After each creep test, the test piece was rapidly cooled to ambient temperature using a jet of compressed air and then removed from its creep rig. The T_g of the polymer, in that condition, was then assessed using viscoelastometry (Metra-vib Viscoanalyseur). A frequency of 5 Hz in tension was

applied principally *in the direction of principal creep strain*. Some viscoelasticity experiments were also effected perpendicularly to the creep direction. Temperature scanning was effected at a rate of $5^\circ\text{C}/\text{min}$ from 25 to 370°C . The values of T_g were assessed from the maxima of the loss tangent, $\tan \delta$, curves.

A comparison was made between values of T_g obtained from test pieces having been loaded and those not having been loaded in creep, for equivalent conditions of time and temperature. In most cases, results below correspond to the mean of two samples. When tested, reproducibility was good.

3. Results and discussion

3.1. Influence of creep time

Fig. 2 demonstrates the evolution of T_g with time, t , for test pieces maintained at 230°C , both without applied load and with an applied stress, σ , of 22 MPa. In both cases, ageing leads to a decrease in T_g . However, for short times, T_g drops more rapidly for the *unloaded* polymer than that under load. This tendency becomes inverted after the order of 55 h of exposure at 230°C .

We infer from these results that two processes, acting more or less concomitantly, occur during high temperature creep: one is related to thermal degradation of the polymer and the other is a consequence of strain under applied load. In the early stages, thermal degradation would appear to be somewhat limited by creep, at least as far as can be appreciated from the evolution of T_g . Conversely, at longer exposure times, effects due to applied load and consequent creep strain become more important, favouring thermal degradation and leading to a (slightly) lower value of T_g .

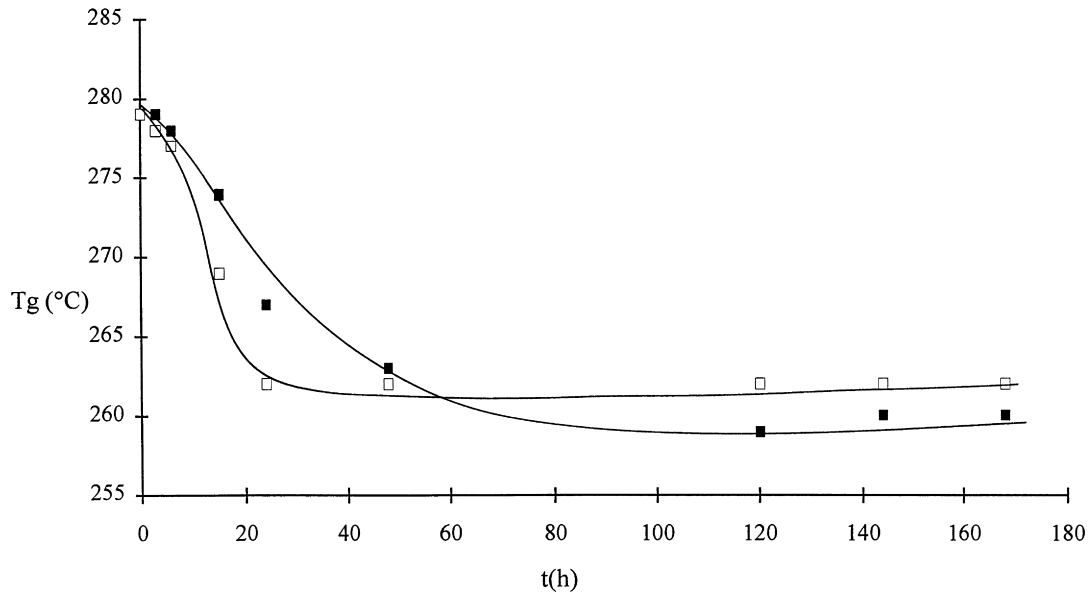


Fig. 2. Evolution with time, t , of glass transition temperature, T_g , for test pieces of epoxy-imide having aged without applied load (\square) and with an applied load of 22 MPa (\blacksquare), at 230°C.

In order to follow the effects of creep strain on the observed variations of T_g , we have considered, for each value of creep time t , the difference, ΔT_g , between measured T_g values, corresponding to the polymer under load, T_g (creep), and the polymer without applied load, T_g (aged), both at a temperature of 230°C.

$$\Delta T_g = T_g(\text{creep}) - T_g(\text{aged}) \quad (1)$$

In Fig. 3, we present ΔT_g as a function of the creep strain of the polymer under load. As can be seen, ΔT_g increases initially with creep strain, attaining a maximum of ca. +6°C, a value probably depending on the level of applied

stress and exposure temperature, and then decreases as the creep strain becomes more significant. Despite the relatively small variations of ΔT_g measured, values were found to be reproducible. They are thus taken to be the consequence of microstructural changes occurring in the epoxy-imide polymer during creep/thermal ageing.

We assume that two main processes occur leading to creep strain of the polymer, and modification of the macromolecular structure:

1. orientation and tensing of macromolecular chains,
2. scission of macromolecular chains.

From a qualitative point of view, process (1) may be

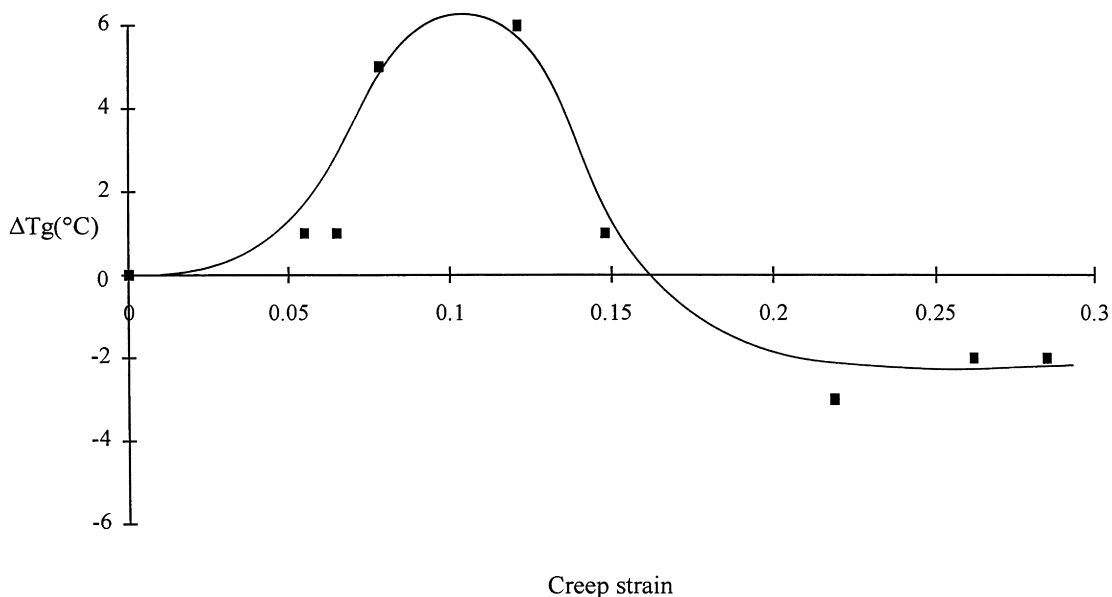


Fig. 3. Evolution of ΔT_g versus creep strain at 230°C and 22 MPa.

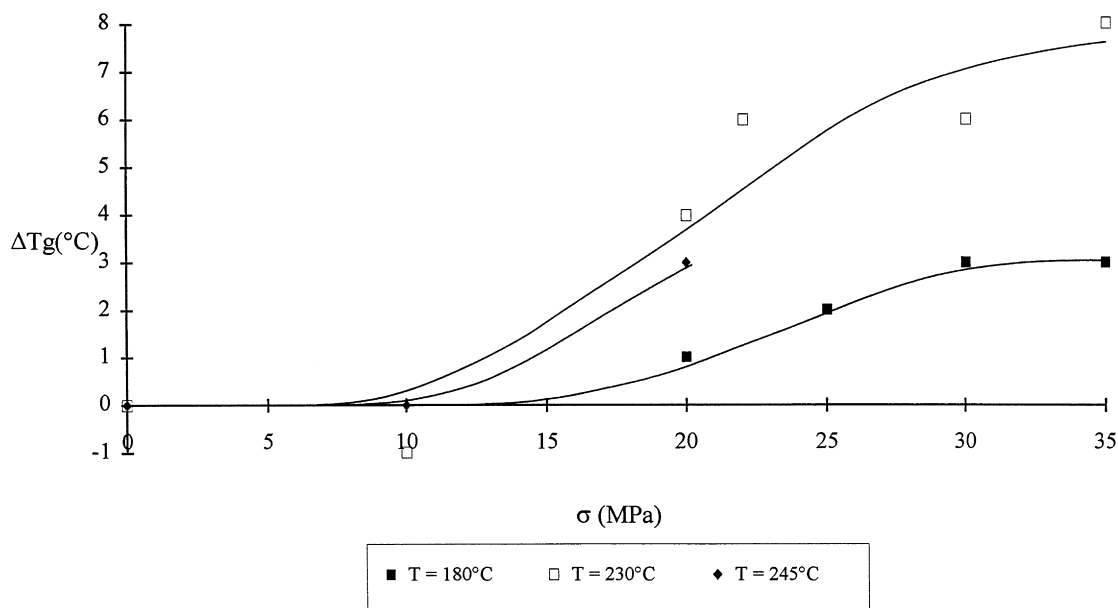


Fig. 4. Evolution of ΔT_g of test pieces having undergone creep for 24 h at 180, 230 and 245°C for different values of the initial applied stress, σ .

expected to be the more significant during the early stages of creep, whereas process (2) should become more important, and perhaps, dominate for larger values of creep strain.

Some viscoelasticity experiments were run on epoxy-imide samples after creep at 230°C, also at 5 Hz, but *perpendicularly* to the direction of creep load. *No difference* in T_g was observed between these tests and those conducted on the simply aged polymer, without applied load (for equivalent exposure times, t). The absence of any measurable differences in this case strongly supports our hypothesis of the influence of tensile creep on the variation of T_g .

3.2. Influence of temperature and stress

Fig. 4 shows the evolution of ΔT_g as a function of initial applied stress, σ , for three creep temperatures. Creep time is standardised as 24 h. An increase of ΔT_g accompanies an increase in σ . Indeed, an increase in stress, for a given temperature and creep time (24 h), leads to higher strain. Thus, when the creep stress is low, the polymer undergoes essentially effects of thermal degradation. The strain, being feeble, has a small influence on the variation of T_g associated with the degradation, and thus ΔT_g evolves little. At higher stress, by contrast, effects related to strain become more significant as can be seen by higher values of ΔT_g .

Temperature increase also influences ΔT_g (see Fig. 4). Nevertheless, when the creep temperature becomes too high, the increase in ΔT_g would seem to become attenuated as shown, albeit with limited evidence in this case, for 245°C. Higher temperatures favour polymeric strain by increasing viscous behaviour, but also the thermal degradation process. Thus, when the temperature is (relatively) too high, we may postulate that the increase in T_g related to strain of the macromolecular network is insufficient to

compensate the reduction in T_g provoked by (oxidative) scission of chemical bonds.

3.3. Reversibility of microstructural modifications

Some creep experiments were performed using the following protocol. Stresses, σ , of 0, 20 and 30 MPa were applied for 24 h to epoxy-imide samples maintained at 180 and 230°C (see Table 1). Values of T_g following this treatment, T_g (creep), were measured. Other samples of the polymer were allowed to recover subsequently with no applied stress for a further 72 h at their initial creep temperature. Their T_g was then measured, this value being denoted T_g (rec.). The application of stress leads to an increase of T_g [T_g (creep)] for both temperatures considered. The (relative) increase is more significant at the higher temperature, the material undergoing a higher strain. A period of recovery would seem to eliminate microstructural modifications occurring at 180°C (for the stresses and times in question), since T_g [T_g (rec.)] returns to its unloaded value. However, at 230°C recovery after loading leads to a T_g (rec.) significantly below its unloaded value (especially at the higher stress). Thus, during creep at 180°C, the polymer samples have *only* suffered the effects of strain responsible for an increase in T_g . After recovery, this strain has essentially disappeared and T_g has returned to its value corresponding to zero load.

In contrast, during creep at 230°C, strain is more significant and leads to a greater (relative) increase of T_g (creep). But after 72 h of recovery, T_g (rec.) has suffered a drop compared to its value following ageing alone. This strongly suggests irreversible microstructural changes due to creep, probably associated with the scission of macromolecular chains. The drop increases with applied stress: it seems

Table 1

Evolution of T_g of polymer having undergone creep for 24 h [$T_g(\text{creep})$] and creep and recovery subsequently for 72 h [$T_g(\text{rec.})$] for different values of stress, σ

Creep/recovery temperature (°C)	Stress, σ (MPa)	$T_g(\text{creep})$ (°C)	$T_g(\text{rec.})$ (°C)
180	0	268	268
	20	272	269
	30	274	268
230	0	261	261
	20	267	257
	30	269	252

plausible that chain scission due to creep strain adds to effects of thermal degradation.

We thus conclude that microstructural modifications undergone by the polymer may be of two types:

1. reversible when simply related to network deformation, and leading to a (relative) increase in T_g ,
2. irreversible when chain scission is implied.

At high temperatures and stresses, both processes are present.

4. Tentative interpretation and model

During creep, the polymer undergoes the effects both of high temperature and of applied stress. Thermal degradation of the material causes chain scission by an oxidation reaction [10], resulting in a reduction of T_g . As a consequence, the drop of T_g of samples having undergone creep may be related to an effectively reduced degree of crosslinking, simply caused by temperature and local environment. (It should be noted that oxidation does not *uncrosslink* the polymer, but chain scission leads to an equivalent effect.)

Comparing variations of T_g of samples after creep at 230°C with those simply aged, we may notice that, initially, creep *apparently* limits thermal oxidation effects. This has been followed using the parameter ΔT_g (Eq. (1)). As strain increases, ΔT_g increases to a maximum and then decreases. This phenomenon may be attributed to an evolution in the macromolecular network, which is at first essentially physical and which is then overtaken by a chemical effect. Under applied stress, molecular chains will tend to orientate in the direction of the applied load. This may lead to an *increase* in T_g , as has been observed with amorphous polymers [2,3]. Simultaneously, a small number of macromolecular chains may be so arranged that further elongation at a macro, or microscopic, level leads to local (chemical) failure and the creation of free radicals [11]. These latter may interact with oxygen in the local air environment leading to oxidation of the polymer [10]. Therefore, long-term creep may lead to an increase in the concentration of radicals produced ‘mechanically’. The polymeric

network will be significantly deformed and these reaction sites will be added in number to those corresponding to oxidation due simply to thermal degradation, thus exacerbating degradation of the material.

Although the processes will be simultaneous, orientation should be predominant at small creep strains with chain scission becoming increasingly important at longer times under load, leading to increased degradation.

We shall attempt to explain the observed changes of ΔT_g semi-quantitatively by using the above hypotheses. Let us consider a molecular chain of the epoxy-imide network between two crosslink points. Despite some random, curvilinear fluctuations (probably relatively limited in the case of a highly crosslinked material such as this), we may consider the effective linear distance between crosslinks to be length, d . Under the effect of applied load, this chain will orientate towards the load direction, leading to an effective (microscopic) elongation. The orientation of two neighbouring chains (i.e. with same or similar x , but different y or z coordinates) will reduce the space *between* them, although the overall volume of the repeat unit may remain constant, or even increase, due to elongation. This reduction in available space, or ‘free volume’, will limit the respective mobility of the neighbouring chains in question. In simplistic terms, let us suppose that the volume ‘available’ around a given chain of length d is initially oval with a maximum circular section of radius r_o , perpendicular to the direction of stress to be applied (shown schematically in Fig. 5). Application of load will lead to deformation of the ‘available’ volume, such that the radius r_o reduces to r and elongation occurs in the stressed direction.

The reduction in maximum radius, namely $(r_o - r)$, will be denoted Δ . Let us suppose that initially, any chain scission is a result mainly of thermal degradation. In this case, since ΔT_g increases, the main role played by creep is that of chain orientation. Let ϕ be the initial angle subtended between the polymer chain and the circle of radius r_o . For orientation effects to be significant, we must reasonably assume ϕ small compared to the angle after orientation, $\phi + \delta\phi$ (see Fig. 5). With this assumption we may take it that *effective* elongation on a local scale is principally due to chain orientation with only a small component due to actual strain of the molecular chain (for ϕ small, the component of applied load along the chain length will be negligible). For ϕ large, the converse is true: orientation will be (relatively) minor and strain of the intercrosslink molecular chain major (favouring scission). As ΔT_g is positive, experimentally, we treat the behaviour of chains of small ϕ as predominant in the early stages of creep.

With these simplifying hypotheses, we may express the relative reduction, δA , of the cross-sectional area of ‘available’ space, A , as:

$$\frac{\delta A}{A} = \frac{r_o^2 - r^2}{r_o^2} = \frac{r_o^2 - (r_o - \Delta)^2}{r_o^2} \quad (2)$$

where $r_o = d \cos \phi \approx d$.

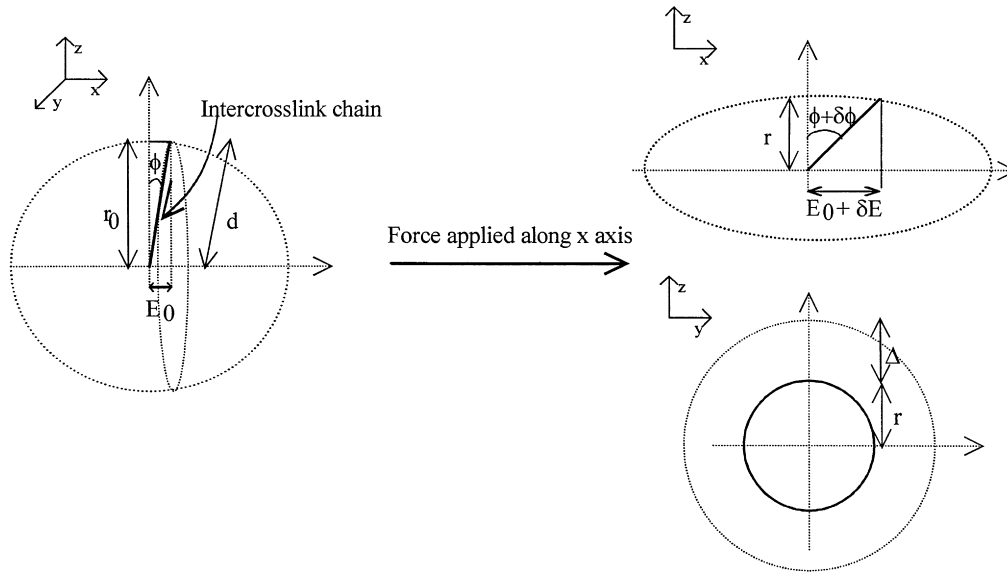


Fig. 5. Schematic representation of an intercrosslink chain orienting under the effect of an applied load in creep.

From Fig. 5, we have for $\phi \ll \delta\phi$:

$$\Delta \approx r_0[1 - \cos(\phi + \delta\phi)] \approx r_0[1 - \cos(\delta\phi)] \tag{3}$$

and defining E_0 and $E_0 + \delta E$ as the projections of d on the x axis, respectively, before and after orientation:

$$\cos^2(\delta\phi) \approx 1 - \left(\frac{E_0 + \delta E}{d}\right)^2 \approx 1 - \left(\frac{\delta E}{d}\right)^2 \tag{4}$$

for $E_0 \ll \delta E$. Combining Eqs. (2)–(4), we obtain:

$$\frac{\delta A}{A} \approx 1 - \cos^2(\delta\phi) \approx \left(\frac{\delta E}{d}\right)^2 \tag{5}$$

The term δE corresponds to elongation along the stressed axis due directly to orientation.

In order for variations due to chain orientation to be considered along the direction of applied load, and therefore associated (assuming affine behaviour) to macroscopic elongation of the polymer, it is necessary to take an effective average value of the projection of d on the x axis, denoted L :

$$L = \frac{\int_0^{\pi/2} d \cos\theta \cdot d\theta}{\int_0^{\pi/2} d\theta} = \frac{2d}{\pi}; \theta = \frac{\pi}{2} - \phi \tag{6}$$

We assume a simple equivalence, apart from a scale factor, between microscopic deformations in the polymeric network and those measured macroscopically. In addition, if we take it that the reduction of free volume between molecular chains is proportional to the reduction in area of ‘available’ space (Eq. (5)), we may express the variation of ΔT_g related to chain orientation as:

$$\Delta T_g \cong k_1 \left(\frac{2}{\pi} \varepsilon_m\right)^2 \tag{7}$$

where

$$\varepsilon_m \cong \frac{\pi}{2} \frac{\delta E}{d} \tag{8}$$

The terms ε_m and k_1 are respectively macroscopic, measured strain and a constant. This assumed linear relationship between variations in T_g and free volume has been previously suggested [12,13].

Thus creep strain, leading to orientation, plausibly leads to an increase in T_g . Nevertheless, the effects of steric hindrance and chain flexibility will probably physically limit the increase in ΔT_g . Our experimental results show ΔT_g attaining a maximum of $+6^\circ\text{C}$. With our present knowledge and this simple model, it is impossible for us to predict a theoretical maximal limit for ΔT_g : we shall therefore simply assume this value of $+6^\circ\text{C}$ for the experimental conditions used.

As creep continues further, ΔT_g decreases. This is clearly a sign of polymeric degradation. Sufficient molecular chains become oriented for elongation and then scission to become significant. Scission will occur at, say, a critical, microscopic strain, $\tilde{\varepsilon}_s$ (along the chain axis). When this occurs, ‘mechanical’ chain failure accompanies thermal scission and ΔT_g decreases.

Let us now consider the microscopic elongation of a chain together with its orientation, the overall sum elongation, E , being:

$$E = d(1 - \cos\theta + \tilde{\varepsilon}) \tag{9}$$

where θ is $(\pi/2 - \phi)$ in the general case, corresponding to the simplifying assumption that orientation is complete and $\tilde{\varepsilon}$ is the subsequent strain. If $\tilde{\varepsilon}$ reaches $\tilde{\varepsilon}_s$, scission occurs (see Fig. 6).

When the orientation angle corresponds to a critically small value, θ_c , for a given elongation, E , then chain failure will occur as $\tilde{\varepsilon} \rightarrow \tilde{\varepsilon}_s$. (For chains of $\theta > \theta_c$, strain is below

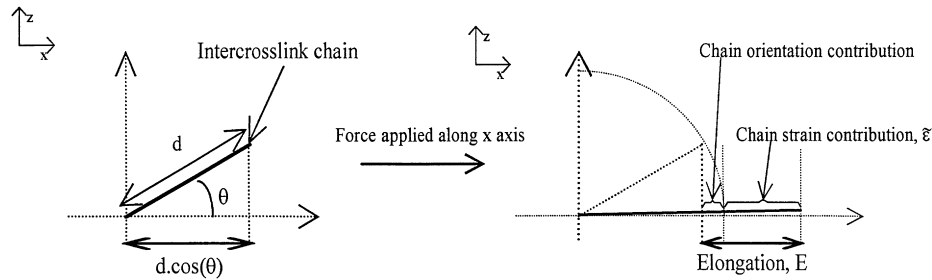


Fig. 6. Schematic representation of the orientation, elongation and scission of a macromolecular chain under macroscopic creep strain.

failure value and still possible; for those of $\theta < \theta_c$, failure may have occurred for smaller E .) This will occur for a variable fraction of the network chain population, depending on the overall state of strain of the polymer (cf. Eq. (6)), and given conditions of temperature and environment.

The fraction of fractured chains, f_r , at elongation E corresponds to the fraction having completely oriented to the direction of stress involving an angle of θ_c or less and is given by:

$$f_r = 2 \frac{\theta_c}{\pi} = \frac{2}{\pi} \cos^{-1} \left[1 + \tilde{\epsilon}_s - \frac{E}{d} \right] \quad (10)$$

We apply the approach of Fox and Losheak [4], which consists of expressing the evolution of T_g of a polymer as an affine function of the degree of crosslinking. Normalizing the ratio E/d with the length L (cf. Eq. (8)), we obtain:

$$\Delta T_g \cong \Delta T_g(\text{max.}) - k_2 \cdot \frac{2}{\pi} \cos^{-1} \left[1 + \tilde{\epsilon}_s - \frac{2\epsilon_m}{\pi} \right] \quad (11)$$

where $\Delta T_g(\text{max.})$ is taken as $+6^\circ\text{C}$ and k_2 is a constant.

The scission of chains during creep undoubtedly facilitates the orientation of other chains. Nevertheless, the maximum gain of ΔT_g is given by $\Delta T_g(\text{max.})$, since it is improbable that the material could attain a T_g higher than in the undegraded state. The problem of steric hindrance may severely modify the details of our simplified model.

Eqs. (7) and (11) have been employed using the

experimental results of ΔT_g and creep strain. An adjustment was made to obtain the best fit and the resulting constants found were $k_1 = 1274 \text{ K}$, $k_2 = 33 \text{ K}$ and $\tilde{\epsilon}_s = 7.7 \times 10^{-2}$, taking $\Delta T_g(\text{max.})$ as $+6^\circ\text{C}$. The results and corresponding calculated line are shown in Fig. 7.

An increase in temperature accelerates the degradation process whilst also favouring creep. This explains why the effect of strain may still be more marked than that of thermal degradation: this is observed in Fig. 4 with the increase of ΔT_g being greater after creep for 24 h at 230°C . However, at 245°C , ΔT_g begins to fall for equivalent conditions. Presumably thermal degradation is getting the upper hand. Despite faster creep leading to orientation, greater strain rates and thermal activation probably lead to more rapid production of free radicals.

Stress and strain are directly related: creep strain at a given time is lower for a smaller applied stress. Thus, at low loads, orientation phenomena are slower and the main microstructural modifications are due to oxidative ageing of the polymeric network. An increase in stress leads to a more rapid molecular orientation and thus a greater increase in ΔT_g .

Chain orientation seems to be an essentially reversible phenomenon given sufficient recovery time, whilst chain scission is irrecoverable. This could explain why, at lower temperatures and sufficiently short times (180°C and 24 h), a variation of ΔT_g is observed but disappears after recovery (72 h).

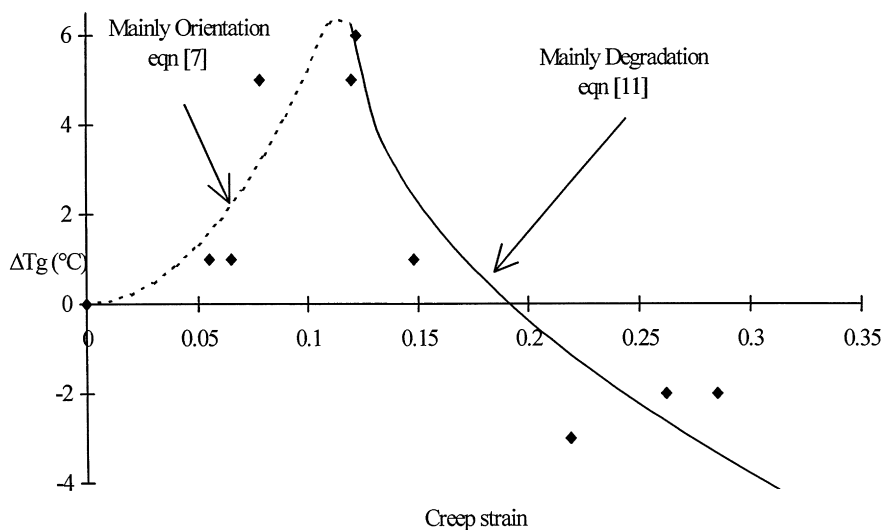


Fig. 7. Results of Fig. 3 of ΔT_g versus creep strain at 230°C and 22 MPa, together with calculated lines obtained from Eqs. (7) and (11).

Clearly our treatment is simplified and both major effects will be to some extent concomitant: our treatment of orientation alone leading to increasing ΔT_g followed by chain scission alone causing a drop in ΔT_g is somewhat naïve. In addition many ideal simplifications are included in the development. Nevertheless, we feel that the basic physics of chain orientation and scission are at the heart of this interesting experimental observation of differing trends for variations in the glass transition temperature after creep, depending on conditions of time, stress and temperature.

5. Conclusions

An experimental study of the variation of glass transition temperature, T_g , of an epoxy-imide polymer during creep under various conditions of temperature, stress and time has shown some unexpected behaviour. Compared to the polymer simply aged without applied load, the relative change in T_g , ΔT_g , initially increases and then later decreases such that at long creep times, T_g is lower for the stressed material. The physics is clearly complicated, but we hypothesize that the initial increase in ΔT_g is due mainly to macromolecular chain orientation leading to an effective reduction of free volume. Concomitantly, chain extension and thermal degradation due to environmental oxygen lead to chain scission and a reduction in T_g . For longer times, chain scission due to mechanical loading adds to thermal effects and, as a result, T_g is lower for the stressed polymer. We have developed a simple theoretical model, dividing ageing time into two sections. The initial creep time is treated as if orientation

is the predominant phenomenon whilst for longer times, chain scission overrides. The microstructural modifications brought about by these two mechanisms are exacerbated by increased temperature.

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