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Physical aging of shape memory polymers based upon epoxy-thiol "click" systems

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ABSTRACT

The physical aging behaviour of two epoxy-thiol shape memory polymers has been studied: diglycidyl ether of bisphenol-A cross-linked with pentaerythritol tetrakis, denoted 4-thiol, with a calorimetric glass transition temperature, T_g, of 51 ºC; and the same system modified with tri(2,3-epoxypropyl)isocyanurate in a 30 wt% proportion, denoted 4-thiol-30%iso, with T_g = 63 ºC. The aging of both polymers has been measured by torsional creep for aging temperatures between room temperature and the T_g of each polymer. The creep behaviour of each polymer is characterised by a discrete distribution of relaxation times, which shifts with aging time according to a double logarithmic aging rate, μ, and with aging temperature according to an activation energy. The distribution of creep relaxation times for 4-thiol is rather symmetrical, and slightly narrower than that for 4-thiol-30%iso, which is also skewed to longer times. The dependence of μ on temperature displays a peak as the aging temperature reduces below T_g, and is sharper for 4-thiol, in accordance with the narrower distribution, as predicted by a theoretical model based upon structural relaxation kinetics. The other parameters defining the aging behaviour, namely the reduced activation energy ($\Delta h^*/R$ = 92 kK for 4-thiol and 82 kK for 4-thiol-30%iso) and the non-linearity parameter of structural relaxation (x = 0.35 for 4-thiol and 0.25 for 4-thiol-30%iso), have been determined experimentally and are compared with the predictions of the theoretical model. These parameters can be used to predict the effects of physical aging on the shape memory response.

KEYWORDS

epoxy-thiol; physical aging; shape memory.

1. INTRODUCTION

Shape memory polymers (SMP) are a class of smart materials that can be deformed into a temporary shape, which is essentially stable and normally under zero external load (free recovery), and can subsequently recover their original state by the application of an appropriate stimulus. To achieve this shape memory effect the material must pass through some kind of transition, and the most common examples of SMPs are those that are thermally activated when the material passes through its glass transition region. While the shape memory effect has been known now for many decades, it is only relatively recently that interest has grown considerably, particularly with respect to the ability to tune the response of the material through the use of new compositions and the development of phenomenological models. A large number of recent reviews bear testimony to the increasing activity in this area [1-12].

In this context, some particular aspects of the shape memory effect and of the application of thermally activated SMPs are of interest in the present work. First, for many applications, the procedure is to fix the temporary shape and then to store the material for an extended period of time before applying the external stimulus, namely heating above the glass transition temperature T_g, in order to recover the original shape. For such materials, the storage period takes place at temperatures below T_g, and hence the effects of physical aging should be considered. As pointed out by Rousseau [4], though, there have been few studies of the effects of aging on the shape memory response of polymers. Tobushi et al [13] investigated the shape recovery of polyurethane foam SMPs stored for long periods at 60 ºC below T_g and, perhaps unsurprisingly for such low aging temperatures, found no significant strain recovery during aging for up to 6 months. More recently, Yakacki and co-workers [14,15] showed that the free recovery behaviour of methacrylate-based SMPs was significantly influenced by storage periods of up to one year at a temperature 36 ºC below T_g; in particular, the onset temperature for shape recovery increased by up to 9 ºC and the maximum rate of shape recovery increased by almost an order of magnitude. An important conclusion reached by these authors [14,15] was that aging could potentially be used as a method for shape-memory response optimisation. There is, therefore, not only scope for tailoring the response of the SMP by controlling the physical aging of the fixed form, but also a need to take this effect into account in any practical application in which long storage times are anticipated.

The second aspect of the shape memory effect of interest here is the modelling of the behaviour in order to predict the shape memory response as a function of the several material and experimental parameters involved, the latter including in particular the effects of aging. Many models have been proposed for the shape memory effect of polymers, based upon a thermomechanical constitutive model [16,17] or, more commonly, thermoviscoelasticity [18-24], but the effects of aging have been included less often [19,20,22]. In order to include the effects of aging in a theoretical model, to be described in a separate paper, it is clearly necessary to obtain values for the characteristic parameters which describe the physical aging process, such as the aging rate and the

activation energy [25,26]. We show here how these parameters are obtained for a specific SMP based upon epoxy-thiol "click" systems.

Within the class of epoxy-based SMPs, epoxy-thiol "click" systems represent an example of how new compositions can enable the tuning of the shape memory response [27]. "Click" chemistry is a relatively novel methodology which promotes efficient, versatile and selective reactions [28-30], and the epoxy-thiol "click" mechanism is particularly interesting due to the formation of hydroxyl and thioether groups in a single step, which can be further transformed into other polymeric structures [31,32]. Such epoxy-thiol systems have been shown recently to display a promising shape memory response under demanding conditions, for example exhibiting enhanced stress levels in comparison with other epoxy-based SMPs [33-35]. As these epoxy-thiol thermosets have relatively low glass transition temperatures, in the range from 45 ℃ to 75 ℃ approximately, the possible effects of aging during storage at room temperature are of considerable interest. The purpose of the present paper is therefore to characterise the physical aging behaviour of these epoxy-thiol thermosets, by means of torsional creep measurements, with a view subsequently to incorporate the relevant parameters into a thermoviscoelastic model in order to predict the shape memory response under any programming and shape recovery conditions.

2. EXPERIMENTAL

2.1. Materials

The specimens for the torsional creep measurements were kindly provided by A. Belmonte, and were prepared following the procedure described in reference [33]. The epoxy resin was a commercial diglycidyl ether of bisphenol-A (DGEBA, GY240, Huntsman, Everberg, Belgium), with a molecular weight per epoxy equivalent of 182 g/equiv, and the cross-linking agent was pentaerythritol tetrakis (3-mercaptopropionate) (4-thiol), with a molecular weight per thiol equivalent of 122.17 g/equiv (Sigma-Aldrich, St. Louis, MO, USA). A tri(2,3-epoxypropyl)isocyanurate (iso), with a molecular weight per epoxy equivalent of 99.09 g/equiv was used as a modifier in a 30% weight proportion, i.e. 30:70 wt% iso:DGEBA, maintaining a stoichiometric proportion of thiol and epoxy groups (epoxy:thiol ratio equal to 1:1). An encapsulated imidazole (LC-80, AC Catalysts, Linden, NJ, USA) was used as a latent initiator in a proportion of 0.5 phr. The reagents were used as received without further purification.

Two formulations were prepared, with the proportions of the reagents indicated in Table 1, by manual mixing of the components in a glass beaker, and the mixtures were then carefully poured into an open Teflon mould to make samples in the form of a rectangular strip with approximate dimensions: thickness, $y = 1.6$ mm; width, $b = 7.5$ mm; length, $l_0 = 40$ mm. The samples were cured isothermally in an air-circulating oven for one hour at 120 ℃, followed by a post-cure of one hour at 150 ℃. The expected network structures

for the samples without and with the iso modifier are illustrated in Schemes 1 and 2, respectively, in reference [33].

Table 1. Weight percentages (wt%) of each component in epoxy-thiol systems

Formulation	DGEBA	thiol	iso	LC-80
4-thiol	59.7	40.0	0	0.3
4-thiol-30%iso	38.0	45.4	16.3	0.3

2.2. Torsional creep measurements

The rectangular parallelepiped sample for creep measurements was clamped in the torsional creep apparatus, which has been described in detail elsewhere [36] and is shown schematically in Figure 1. This apparatus consists essentially of a coil suspended between the poles of a permanent magnet and fixed rigidly to a torque tube, the other end of which is clamped to the top of the specimen. The bottom of the specimen is clamped rigidly to the frame of the apparatus, leaving a free length l between the clamps, and the coil and torque tube are counterbalanced such that there is no net axial force on the sample. A constant current from a stabilised power supply (L50/05, Farnell, Leeds, UK) is passed through the coil in order to provide a constant torque on the sample for the creep experiment. The coil constant k in the equation relating the torque Ω to the applied current I:

$$\Omega = k I \tag{1}$$

is found by calibration with a material (aluminium) with a known shear modulus, G. The resulting angle of twist is measured by reflecting a light beam off the concave mirror rigidly attached to the torque tube, the focussed light spot being followed continuously by the photocell of a Graphispot (GR VAT, Setaram, Paris, France) chart recorder at several metres distance from the mirror.

Figure 1 goes here

The maximum shear stress, τ_{max}, occurs along the centre line of the broader face of a rectangular cross-section sample of width b and thickness y, and is given by:

$$\tau_{max} = \Omega/c_1 b y^2 \tag{2}$$

and the angle of twist, ϕ, of the sample with free length l between the grips is given by:

$$\phi = \Omega l/c_2 b y^3 G \tag{3}$$

where the coefficients c_1 and c_2 depend only on the ratio b/y and can be found in appropriate tables [37]. For the samples used in these creep experiments, for which $b/y =$

4.69, the values of c_1 and c_2 are both 0.288. The creep compliance, $J(t)$, at time t is therefore obtained from the linear displacement, $\delta(t)$, at time t measured on the photocell chart recorder at a distance L from the concave mirror of the creep apparatus, by the equation:

$$J(t) = 0.288 \, by^3\delta(t)/2LlkI \qquad (4)$$

The torsional creep apparatus is designed such that the sample can be enclosed by a copper sheath and immersed in a thermostatically controlled bath (TE-160, Techne, Chelmsford, UK) containing silicone oil, the temperature of the sample being measured by a thermocouple within the copper sheath and close to the sample surface. This allows the creep response to be monitored over a range of temperatures. The procedure for determining the physical aging behaviour at any temperature, T_a, below T_g was as follows. First, the sample was heated to above T_g in order to erase any previous thermal history and to establish an equilibrium structural state (rejuvenation). The sample was then cooled "in situ" to the aging temperature, T_a. The cooling rate was facilitated by passing a flow of cold water through a copper coil immersed in the bath, the average cooling rate being 0.6 °C/min, and the time required to reach the aging temperature was between 30 minutes and 1 hour, depending on the aging temperature; this difference in cooling times is insignificant in comparison with the subsequent aging times, which were up to almost 200 hours.

Creep experiments at low strain (< 0.2%) were performed at approximately equal logarithmic intervals of aging time (typically 1, 2, 4, 8, 24, 48, 96, 198 hours) according to the protocol of Struik [25]. This limits the creep time to one tenth of the aging time; thus, for the duration of any creep experiment the sample can be considered to be in a quasi-equilibrium structural state, while the typical doubling of the aging times allows sufficient time (9 times the creep duration) for full recovery to occur. It should be noted that the shortest aging time of 1 hour can be of the same order as the time required to cool to T_a from above T_g. Under these circumstances the definition of such a short aging time is imprecise, and one might expect the analysis of the results to be affected. This will be demonstrated when the results are further analysed below.

3. THEORETICAL ASPECTS

Physical aging occurs because the average relaxation time, for creep in the present case, increases with time as a consequence of the gradual approach of the sample towards an equilibrium structural state, where the structure is defined by, for example, the specific volume or enthalpy [25,26]. The initial non-equilibrium state is determined by the aging temperature, T_a, and the cooling rate from the rejuvenation temperature. The kinetics of the structural recovery at T_a has been widely studied and has been rather successfully modelled [38,39] so as to include the well-known characteristic features of structural recovery: (i) the relaxation time depends on both temperature and structure, the structure usually being characterised by the fictive temperature, T_f; (ii) there is a distribution of

relaxation times. The first of these features is usually referred to as non-linearity, and can be quantified in terms of a parameter x ($0 \leq x \leq 1$) in the Tool-Narayanaswamy-Moynihan (TNM) equation [40]:

$$\tau(T, T_f) = \tau_0 \exp\left[\frac{x\Delta h^*}{RT} + \frac{(1-x)\Delta h^*}{RT_f}\right] \qquad (5)$$

in which $\tau(T,T_f)$ is the relaxation time in the glassy state defined by temperature T and fictive temperature T_f, and τ_0 is the relaxation time in equilibrium at infinite temperature. This equation assumes that, in equilibrium ($T = T_f$), the relaxation time follows an Arrhenius behaviour with an apparent activation energy, Δh^*, which is a reasonable approximation over a relatively limited temperature interval.

The second characteristic feature of structural recovery, that there is a distribution of relaxation times, can be incorporated either as a discrete distribution, as in the KAHR model [38], or by means of the KWW stretched exponential formalism [41,42], which is mathematically more convenient. The KAHR model assumes that there is a distribution of N structural states (or elements) in the glassy sample, each characterised by its departure from equilibrium, δ_i ($1 < i < N$), which can be related to its fictive temperature, $T_{f,i}$, and by its relaxation time, τ_i. Each element relaxes according to a kinetic equation involving δ_i and τ_i, while each relaxation time τ_i depends on the global glassy state, characterised by T_f, following equation (5), implying a mean field approach and being consistent with thermorheological simplicity. In contrast, the KWW formalism makes use of a stretched exponential function:

$$\tau = \tau_r \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right] \qquad (6)$$

where τ_r is a reference relaxation time and the so-called non-exponentiality parameter β ($0 \leq \beta \leq 1$), characterises the width of the distribution of relaxation times, the smaller is β the wider being the distribution. In this KWW equation (6), the relaxation time τ depends on temperature and structure according to the TNM equation (5).

The combination of the TNM equation and the KWW stretched exponential allow the response of the sample to any thermal history to be modelled as a function of the various experimental and material parameters. As an illustration, we have modelled the set of aging experiments in which the sample is cooled at 0.6 ºC/min from above T_g, taken as the temperature at which the average relaxation time in equilibrium is 100 s, to different aging temperatures, between 5 and 40 ºC below T_g, and determined how the average relaxation time increases with aging time at each of these temperatures. The results are shown in Figure 2, on a double logarithmic plot, for the following set of material parameters: $\beta = 0.4$, $x = 0.6$, $\Delta h^*/R = 85$ kK, and the different curves correspond to the different aging temperatures, from $T_g - 5$ ºC at the bottom to $T_g - 40$ ºC at the top.

Figure 2 goes here

The typical range of aging times accessible experimentally is from 1 to 200 hours, indicated by vertical dashed lines in Figure 2. Hence it can be seen that the aging rate, quantified by the slope of the curves between these two vertical dashed lines, is zero at the highest aging temperature, and then first increases as the aging temperature decreases, reaches a maximum value (in the present case at $T_a = T_g - 25$ ℃), and then decreases again, and would eventually reach zero again at sufficiently low aging temperatures. This behaviour is characteristic of physical aging [25], and the theoretical model allows the dependence of the aging rate to be studied as a function of the various material parameters (β, x and Δh^*) for comparison with the observed experimental results to be presented below.

Figure 3 goes here

As an illustration, Figure 3 shows the effects of each of these parameters separately. For these purpose, the slope of the curves between these two vertical dashed lines representing the typical limits of experimental aging times in Figure 2 is taken simply from a straight line joining the start and end points. In Figure 3a, where the effect of β is shown, it can be seen that as the distribution becomes narrower (increasing β), the maximum value of the aging rate increases and the peak becomes slightly narrower, while the temperature of the peak remains constant. In contrast, Figure 3b shows that the effect of decreasing x, in other words of increasing contribution of the structure (fictive temperature) to the relaxation time, is much stronger: the peak is broadened significantly and shifted to lower temperatures, while the maximum value of the aging rate increases. Finally, the effect of decreasing the activation energy, shown in Figure 3c, is simply to shift the whole peak to lower temperatures without any change in shape. The experimental results described in the next section will be interpreted in the light of these theoretical predictions.

The aging rate as defined above represents the shift of the structural relaxation time distribution with the increase of aging time at constant temperature. If the creep relaxation times are influenced in the same way as the structural relaxation times, then the aging rate defined above would be equivalent to the shift rate, μ, first defined by Struik [25]. In this context, it is noticeable that the values of the aging rate illustrated in Figure 3 are all less than unity, and indeed there is no combination of β, x and Δh^* for which the aging rate would be greater than unity. A search in the literature confirms that the value of μ is nearly always less than unity, as illustrated by the following examples for amorphous polymers for which the structural relaxation analysis above applies. Sullivan and co-

workers found values in the range 0.6 to 0.8 for unidirectional glass fibre reinforced epoxy vinyl ester composites [43] at temperatures between 15 ℃ and 100 ℃ below T_g, and in the range from 0.6 to 0.9 for various glass reinforced thermoset composites [44], including a value of 0.8 for a sheet moulding compound and 0.7 for a polycarbonate (PC) composite; Wang et al [45] investigated continuous fibre reinforced composites and found values of μ in the range from 0.3 to 0.7 over a wide range of aging temperatures, from 10 ℃ to 70 ℃ below T_g for a cyanate ester and for 90º composites, although these authors do report a much higher value of 1.1 for the ±45º composites; Tomlins [46] found average values of 0.89 and 0.90 for polyvinyl chloride (PVC) and epoxy, respectively, aged at room temperature, well below their respective T_gs; Robertson et al [47] investigated the aging of an amorphous polyimide, and report values of μ of 0.65, 0.85, 0.80 and 0.40 for temperatures 63 ℃, 53 ℃, 33 ℃ and 13 ℃ below T_g, respectively; Robertson and Wilkes [48] studied the aging behaviour of blends of atactic polystyrene and dimethyl phenylene oxide at temperatures 30 ℃ and 60 ℃ below their respective T_gs, and found values of about 0.9 and 0.7 for the pure polymers and a value as low as about 0.5 in some blends; from the graphs presented by Echeverria et al [49] for the aging of amorphous selenium, values of μ can be estimated and are found to be in the range from 0.4 to 0.7 for aging temperatures between 10 ℃ and 15 ℃ below T_g; Arnold and Venditti [50] report a value of μ of 0.78 for the aging of polyethylmethacrylate bone cement at 37 ℃, 10 ℃ below T_g; Kuznychov et al [51] also find similar results for acrylic bone cement aged at 37 ℃, reporting values of μ of 0.77 and 0.75 for two different grades, which reduce to 0.55 and 0.56 at a higher stress level; Arao et al [52] find a value of μ of 0.71 for a carbon fibre reinforced epoxy resin aged at 80 ℃, 60 ℃ below the T_g of about 140 ℃; finally, in our own earlier work on polycarbonate [36] we found a value of μ of 0.87 for the aging of polycarbonate determined by creep at 125 ℃, approximately 20 ℃ below T_g.

There are some, though few, exceptions where the value of μ is greater than unity. Struik [25] clearly shows polycarbonate reaching values well in excess of unity, in contrast to the value of 0.87 given immediately above [36], and the value of 0.7 found by Sullivan et al [43] mentioned above for a fibre composite based on PC. Nicholson et al [53] find values of μ very close to, and occasionally greater than, unity for polyimide aged at temperatures between 15 ℃ and 25 ℃ below T_g, while Guo and Bradshaw [54] report values of μ slightly greater than unity for polyetheretherketone and polyphenylene sulphide when aged at temperatures 35 ℃ below their respective T_gs.

In summary, the theoretical model analysis presented above suggests that the aging rate can approach unity, depending on the combination of the parameters β, x and Δh^*, but should not exceed it, and this appears to be supported in general by the results presented in the literature. This observation supposes, of course, that the creep relaxation times are affected by aging in the same way as the structural relaxation times, though this is by no means universally accepted; for example, there is still debate about whether or not the time scales for volume and enthalpy relaxation are equivalent. Nevertheless, we base the

model upon this supposition, and below we show how the experimental results compare with the model predictions.

4. EXPERIMENTAL RESULTS AND DISCUSSION

4.1. 4-thiol

First it was necessary to establish the appropriate rejuvenation temperature for this sample. The calorimetric glass transition temperature of the 4-thiol sample was determined by Differential Scanning Calorimetry (DSC), and was taken as the fictive temperature corresponding to a cooling rate of 10 ºC/min, giving a value of 51.0 ºC. In comparison, the peak of tan δ in Dynamic Mechanical Analysis (DMA) experiments at a frequency of 1 Hz, often taken as a measure of the glass transition temperature, T_g (1 Hz), is given as 59.7 ºC by Belmonte et al [33]. This higher value is a consequence of the timescale for the DMA measurement being much shorter than that for the DSC measurement. In fact, it should be noted that the glass transition is characterised not just by the glass transition temperature but also by the width of the transition, which depends on the width of the distribution of relaxation times, discussed in the Theoretical section and quantified by the non-exponentiality parameter β, for example, in the KWW formalism. The transition region can be as wide as 20 K or more [55,56].

Accordingly, the 4-thiol samples were rejuvenated at a temperature of 60 ºC. The aging temperatures selected for this sample were 31.7, 37.7, 42.2, 47.3 and 51.6 ºC, and the aging time of zero was taken when the sample first reached the aging temperature after cooling from the rejuvenation temperature.

It may be worth making a few comments about the choice of these aging temperatures. First, they were not selected such as to be at specific values of T_g-T_a, partly because of the impossibility of defining a unique value of T_g (e.g. note the difference between the calorimetric and DMA values, considered above); instead they were chosen to cover a range of T_g-T_a values, from zero to about 20 K. Second, it may appear strange that an aging temperature of 51.6 ºC should be chosen, being above the calorimetric T_g. However, not only, as is also noted above, can the transition region be as wide as 20 K or more, such that a non-equilibrium state will exist for a finite (if short) period of time just above T_g, but also there are different kinetics (and different T_gs) for the relaxation of different properties, for example enthalpy and volume. To our knowledge, there is not as yet any clear answer as to which, if either, of these two properties control the physical aging as monitored by the mechanical response in creep.

Figure 4 goes here

A typical example of a set of creep curves for different aging times is shown in Figure 4 for the aging temperature of 47.3 ℃. The characteristic shifting of the creep curves to longer times as the aging time increases can be seen. These curves can be superposed by horizontal shifting, thus defining a shift factor, a_δ, and leading to a master curve, which is shown in Figure 5. The superposition of the creep curves for aging times of 1, 2, 20 and 48 hours onto the reference curve for the aging time of 164 hours can be seen to be good. Both horizontal and vertical shifting can also be used, and generally gives a slightly better master curve, but the differences in the resulting shift factors are not significant and so we adopt here the simpler procedure of horizontal shifting only. This procedure has been adopted also by other workers, illustrated by references [57] and [58], for example, though other procedures have also been proposed [59].

Figure 5 goes here

A plot of the shift factor versus the ratio of the reference aging time (164 hours) to the actual aging time for each aging temperature, on a log-log scale, is represented in Figure 6 for the aging temperature of 47.3 ℃. Here it can be seen that there is a good linear relationship, the slope of which defines the double logarithmic aging rate [25], μ, in this case equal to 0.37. The one point which deviates somewhat from the best fit line corresponds to the shifting of the shortest aging time, 1 hour. There are two reasons why there can be significant uncertainty in this measurement: first, the creep duration is only 6 minutes and therefore represents only a very small part of the master curve in Figure 5, and for this part there is very little time-dependence, in other words the creep curves are almost horizontal and consequently subject to some error in attempting to make a horizontal shift to superpose them; second, the cooling time is of the same order of magnitude as the aging time, and hence the precise definition of an aging time is difficult.

Figure 6 goes here

The double logarithmic shift factor, or aging rate, is determined at the five different aging temperatures used for this sample, and the results are shown as the blue diamonds in Figure 7, where the curve is drawn to guide the eye. The qualitative similarity between the experimental results of Figure 7 and the theoretical predictions of Figure 3 are evident. In fact, a rather good fit of the theoretical model, indicated in Figure 7 by the green triangles, to the experimental data can be obtained by the combination of the following parameter values: $\beta = 0.8$, $x = 0.4$, and $\Delta h^*/R = 85$ kK. However, a realistic quantitative comparison would require the determination of the important material parameters for this

4-thiol sample, in particular the distribution of relaxation times and the apparent activation energy. This is considered later.

Figure 7 goes here

Whereas the aging behaviour at each aging temperature has been characterised by an aging shift rate, the effect of temperature can be characterised by time-temperature superposition of the creep curves at different temperatures. This superposition should ideally be made for creep curves for which the same structure applies, in other words for creep curves with the same fictive temperature. However, the dependence of the fictive temperature on the aging time is not known "a priori", and therefore in practice it is convenient instead to superpose the creep curves obtained for the same aging time at each temperature. For short aging times, the structures defined by constant aging time and by constant fictive temperature will be approximately the same, but these two become increasingly different as the aging time increases; indeed, at very long aging times the structure attains the equilibrium state at each temperature, which is clearly very different from states defined by a constant fictive temperature. Nevertheless, we adopt this procedure, and for each temperature we use the common aging times of 2, 24 and 168 hours, though the aging time of 2 hours is rather short and, for the reasons already discussed above, will give rise to greater uncertainty. The results of the superposition for the aging times of 24 and 168 hours are shown in Figure 8, for the reference temperature of 51.6 °C.

Figure 8 goes here

In each case it can be seen that the master curve produced covers the whole relaxation from glassy to rubbery state, and both master curves are fit with a KWW stretched exponential function with the same value of $\beta = 0.65$, with average relaxation times of 240 s and 500 s for the aging times of 24 h and 168 h, respectively. The quality of the fit of the KWW function to the master curves is good over only a part of the relaxation; in particular, the last part of the relaxation involves relaxation times that are significantly longer than those of the KWW distribution. This illustrates the drawback of using the KWW distribution; even though it is mathematically convenient for describing physical aging and structural relaxation, it does not properly describe the processes occurring at long times. An alternative procedure is to model the master curves using a discrete distribution, and the distribution that gives a good fit to the data is shown in Figure 9.

Figure 9 goes here

This discrete distribution has four elements per decade, and the relaxation strengths are normalised such that their sum is unity. The distribution for the aging time of 168 h is simply shifted to longer times than that for the aging time of 24 h, without any change of shape, which is consistent with a thermorheologically simple system. The magnitude of the shift is 0.284 on the log scale, compared with the logarithm of the aging ratio which is 0.845. The distribution can be seen to be rather symmetrical, in comparison with the KWW distribution which is skewed towards the short relaxation times, and hence the discrete distribution gives more weight to the longer relaxation times. The fit obtained with this distribution is excellent for both aging times, as can be seen in Figure 8, where the theoretical creep curve for each aging time is indicated by the black squares.

The magnitude of the horizontal shift used to construct the superposed master curve can be plotted as a function of the reciprocal temperature in order to determine an activation energy. Such an Arrhenius plot is shown in Figure 10 for each of the three aging times (2, 24 and 168 h), taking 42.2 ºC as the reference temperature and omitting the lowest aging temperature of 27.8 ºC for which there was some uncertainty in the calculated shifts as a consequence of the small amount of time-dependence in the creep response. The results for the two longer aging times, 24 h and 168 h, are in rather good agreement, and give reduced apparent activation energies of 91 and 92 kK, respectively, while the shorter aging time of 2 h gives a significantly lower value of 79 kK. The interpretation of this activation energy needs to be made carefully, though.

Figure 10 goes here

If the creep curves for constant fictive temperature had been superposed, then the activation energy would correspond to that at constant structure, which from the TNM equation can easily be shown to be equal to $x\Delta h^*$, where x is the non-linearity parameter, rather than Δh^*, which represents the temperature dependence of the relaxation time(s) in equilibrium. On the other hand, if the time-temperature superposition is made, as it is here, by shifting creep curves at constant aging times, then the activation energy determined from a plot such as that in Figure 10 will depend on the aging time; as the aging time increases, the apparent activation energy will increase from one representing a constant structure or constant fictive temperature, i.e. $x\Delta h^*$, to one representing an equilibrium structure, i.e. Δh^*. This can, in fact, be demonstrated with the theoretical results presented in Figure 2. For any given aging time, a plot of the log(average relaxation time) versus the reciprocal temperature will give the apparent activation energy. Such a plot is shown in Figure 11 for three aging times: $t_a = 1$ s, representative of a very short aging time; $t_a = 4.61$ h, within the experimental aging time range; and $t_a =$

3.2 years, a very long, though rather impractical, aging time. The apparent activation energy is determined from the slope, and clearly takes different values for the different aging times, but there is a systematic and predictable variation. The reduced apparent activation energy for $t_a = 1$ s is found from the corresponding slope in Figure 11 as 53.0 kK. The input values to the Matlab programme to calculate the results shown in Figure 2 were $x = 0.6$ and $\Delta h^*/R = 85$ kK, and hence $x\Delta h^*/R = 51.0$ kK, in very good agreement, because at such short aging times the sample is in a non-equilibrium state of approximately constant fictive temperature at each temperature. For the aging time of an experimental order of magnitude, 4.61 h, the slope can be seen to change asymptotically from a value coincident with that for the aging time of 1 s at low aging temperatures to a value coincident with that for the very long aging time at higher aging temperatures. For this longest aging time, the slope at low aging temperatures is less than that at higher aging temperatures, because there is insufficient time at these low aging temperatures for the sample to approach equilibrium. On the other hand, at higher aging temperatures there is sufficient time to reach equilibrium, and the slope in this region, indicated by the dashed line and coincident with the slope for the aging time of 4.61 h, corresponds to a reduced apparent activation energy of 85.2 kK, equal to the input value. This behaviour is the origin of the difference in the values of the apparent activation energy found from the experimental results presented in Figure 10, from which we conclude that the reduced apparent activation energy for the 4-thiol sample is approximately 92 kK.

Figure 11 goes here

4.2. 4-thiol-30%iso

The same experimental and analytical procedure was followed for the 4-thiol-30%iso sample as was used for the 4-thiol sample. The calorimetric glass transition temperature of the 4-thiol-30%iso sample was determined by DSC to be 63.3 ℃, in comparison with T_g (1 Hz) = 75.4 ℃ quoted by Belmonte et al [33]. Accordingly, the 4-thiol-30%iso samples were rejuvenated at a temperature of 96 ℃. The aging temperatures selected for this sample were 27.8, 36.2, 45.7, 55.6, 60.3 and 68.1 ℃, and the aging time of zero was again taken when the sample first reached the aging temperature after cooling from the rejuvenation temperature.

Figure 12 shows a typical set of creep curves, obtained for the aging temperature of 55.6 ℃ and for aging times from 1 to 96 h, which can be shifted horizontally to give the master curve shown in Figure 13.

Figure 12 goes here

Figure 13 goes here

The double logarithmic shift factor determined at the six different aging temperatures is shown in Figure 14. It can be seen that the behaviour is qualitatively very similar to that displayed by the 4-thiol sample in Figure 7, but quantitatively it is somewhat different: the maximum aging rate is only between 0.5 and 0.6 here in comparison with a value of approximately 0.8 for the 4-thiol sample, and there appears to be a plateau rather than a peak as the aging temperature decreases. In fact, the aging rate behaviour shown in Figure 14 for the 4-thiol-30%iso sample can be reasonably well fit by the theoretical model with the parameter values $\beta = 0.30$, $x = 0.30$, and $\Delta h^*/R = 85$ kK, as shown in Figure 14. A more meaningful fit of the theoretical model to the experimental data, however, would require the use of experimentally determined values of the important parameters, namely the distribution of relaxation times and the apparent activation energy. The determination of these parameters is now considered.

Figure 14 goes here

In the same way as for the 4-thiol sample discussed above, the creep curves at different aging temperatures and for any given aging time can be superposed by time-temperature superposition, using horizontal shifting only, to produce a master curve. This is illustrated for the 4-thiol-30%iso sample in Figure 15 for an aging time of 96 h at each aging temperature. The master curve displays the whole relaxation, from unrelaxed to relaxed compliance, which can be fit with the KWW stretched exponential function. The best fit of this function, with $\beta = 0.55$ and $\tau_r = 50$ s at the reference temperature of 68.1 °C, above the calorimetric glass transition temperature of 63.3 °C, is shown and, similar to the situation for the 4-thiol sample, it can be seen that although there is a very good fit for times up to about the mid-point of the relaxation, the long-time portion of the relaxation is not well described. On the other hand, an excellent fit over the whole relaxation can be achieved by the use of a discrete distribution, which is shown in Figure 16 for comparison with that for the 4-thiol sample.

Figure 15 goes here

Figure 16 goes here

The distributions for the two different samples are referred to different conditions: an aging time of 168 h at the reference temperature of 51.6 °C for the 4-thiol sample, and an aging time of 96 h at the reference temperature of 68.1 °C for the 4-thiol-30%iso sample. In order to compare the two distributions on the same graph, the relaxation times have

been normalised by dividing by the respective KWW relaxation time, namely 500 s for 4-thiol and 40 s for 4-thiol-30%iso. It can immediately be seen that the 4-thiol sample has a significantly narrower distribution than that for 4-thiol-30%iso, and in particular that the distribution for the latter sample has a long time tail not present in the 4-thiol sample. This observation is consistent with the lower value of β in the KWW fit to the data for 4-thiol-30%iso (β=0.55) in comparison with that for the 4-thiol sample (β=0.65), and is also consistent with the observations made above concerning the dependence of the aging rate on the aging temperature.

The activation energy for the 4-thiol-30%iso sample can be determined from the time-temperature superposition procedure which gives rise to master curves such as that shown in Figure 15. The dependence of the horizontal shift factor on the aging temperature is shown in an Arrhenius plot in Figure 17 for four different aging times, the reduced activation energy for each aging time being given in the inset. It can be seen that, similar to the situation for the 4-thiol sample, the highest activation energy is found for the longest aging time, and so, for the reasons elaborated above, we take 82 kK to be the reduced activation energy for the 4-thiol-30%iso sample.

Figure 17 goes here

4.3. Comparison of 4-thiol and 4-thiol-30%iso

 Besides the different temperature regions of their viscoelastic response, characterised for example by their glass transition temperatures, that for 4-thiol-30% iso being some 12 ℃ higher than that for 4-thiol, the important differences between these two systems lie in their distributions of creep relaxation times and in their apparent activation energies. From Figure 16 it is clear that the 4-thiol-30%iso sample has a significantly broader distribution of creep relaxation times than does the 4-thiol sample, and furthermore that it is asymmetric, being skewed to longer times. This would correspond to the 4-thiol-30%iso sample having a smaller KWW exponential factor, β, and this is indeed what is found when fitting the master curves for each system for any given aging time: in Figure 8 the best fit KWW function for 4-thiol was obtained with β = 0.65, while in Figure 15 the best fit for 4-thiol-30%iso was obtained for β = 0.55.

A similar comparison can be made with respect to the aging behaviours, as depicted in Figures 7 and 14 for 4-thiol and 4-thiol-30%iso, respectively. In these Figures the dependence of the aging rate on temperature is rather well fit by the theoretical model with respective values of β of 0.80 and 0.30; although there is a larger difference between these two values of β than is found from the creep curves, the trend is the same, implying a broader distribution for the 4-thiol-30%iso sample.

The reduced apparent activation energies are found as 92 kK and 82 kK for 4-thiol and 4-thiol-30%iso, respectively, from the temperature dependence of the creep curves of these two samples at selected aging times. It is assumed in the theoretical model that the creep response follows the structural relaxation times, which can also be determined from the enthalpy relaxation behaviour monitored by Differential Scanning Calorimetry (DSC). In this respect, it should be noted that these materials are fully amorphous; in semi-crystalline polymers, the existence of both rigid and mobile amorphous fractions can complicate the kinetics of the structural relaxation process, as has been pointed out recently [60]. Such DSC experiments (to be presented elsewhere) give reduced apparent activation energy values of $\Delta h^*/R = 201$ kK and $\Delta h^*/R = 158$ kK for the 4-thiol and 4-thiol-30%iso samples, respectively, where the higher value for 4-thiol is to be noted. The uncertainty in these values of the reduced activation energies is typically around 10%, and hence, from a consideration of both the creep and DSC results, the difference between the 4-thiol and 4-thiol-30%iso samples is considered to be significant in that the former has a higher activation energy.

In the aging behaviours shown in Figures 7 and 14, the fit of the theoretical model also requires the non-linearity parameter x, which is found to be 0.40 and 0.30 for 4-thiol and 4-thiol-30%iso, respectively, when the KWW distribution function is used. This implies a greater degree of non-linearity in the response of the 4-thiol-30%iso sample, in other words a greater dependence of the relaxation times on the structure, or fictive temperature. This can be appreciated by comparison of the experimental aging rates as a function of temperature with the theoretically predicted effect of the non-linearity parameter shown in Figure 3; higher values of x result in a sharper peak, which is what is found for the 4-thiol sample.

The discrete distributions shown in Figure 16, rather than the KWW function, can be input into the theoretical model, together with the apparent activation energies for each system, to provide a more direct comparison of the theory and the experimental aging results. This will still require an input value of the non-linearity parameter, x, for which we do not have an independent experimental determination, and this input value is obtained by trial and error. The results are shown in Figures 18 and 19 for 4-thiol and 4-thiol-30%iso, respectively.

Figure 18 goes here

Figure 19 goes here

It is worth stressing here that the only adjustable parameter in the theoretical model to obtain the results shown in Figures 18 and 19 is the non-linearity parameter x. In addition, however, there are some assumptions that have been made in the analysis of the experimental data and in the development of the theoretical model. In the first case, the

master curves at each aging temperature were obtained by horizontal shifting only of the creep curves at different aging times. This is equivalent to assuming that the relaxed and unrelaxed compliances are unaffected by aging. In the second case it is assumed that there is a direct correspondence between the structural relaxation times, whose variation is modelled theoretically, and the creep relaxation times. The rather good agreement between theory and experiment seen in Figures 18 and 19 suggests that these assumptions are reasonable. Furthermore, the values of x required for a good fit of the theory (incorporating the experimentally determined discrete distributions) to the experimental data, 0.30 for 4-thiol and 0.25 for 4-thiol-30%iso, are in reasonable agreement with those obtained with the KWW distribution. In particular, they show the same trend of decreasing x as the molecular structure changes from 4-thiol to 4-thiol-30%iso. Bearing in mind the discussion related to Figure 11, the reduced activation energy for the creep response should lie between $x\Delta h^*/R$ and $\Delta h^*/R$, depending on the fictive temperature corresponding to the selected aging time. The values of $x\Delta h^*/R$ are 60 kK and 40 kK for 4-thiol and 4-thiol-30%iso, respectively, consistent with the earlier observation that the measured values of 92 kK and 82 kK should lie between these values of $x\Delta h^*/R$ and the values of $\Delta h^*/R$, which are 201 kK and 158 kK for the 4-thiol and 4-thiol-30%iso, respectively.

Both of these systems, 4-thiol and 4-thiol-30%iso, have been shown to display significant physical aging, as monitored by creep measurements, at or close to ambient temperature. The effects of physical aging in these materials, potentially useful for shape-memory applications, are therefore likely to be of some importance if these materials are to be stored for prolonged periods of time in their deformed state at ambient temperature prior to the recovery of their original state on heating. Consequently it is of some interest to be able to predict the effects of aging on the shape memory response. The discrete distributions of creep relaxation times, the activation energies, the relaxed and unrelaxed compliances, and the glass transition temperatures, all experimentally determined for each system, together with the values for the non-linearity parameter x found by comparing theory and experiment in Figures 18 and 19, represent all the parameters necessary for the modelling of the shape recovery behaviour based upon a linear viscoelastic model in which aging effects are included. This is the subject of a future paper.

5. CONCLUSIONS

The above results for the aging of 4-thiol and 4-thiol-30%iso samples, as determined by torsional creep measurements, can be summarised as follows. Both materials present aging behaviours below T_g which are qualitatively similar and in accord with theoretical predictions based on the kinetics of structural recovery in the glassy state, but which are quantitatively significantly different. For both systems the creep curves for different aging times at any given aging temperature can be superposed by horizontal shifting to form a good master curve, from which the double logarithmic aging rate can be determined.

The creep of 4-thiol involves a rather symmetric distribution of relaxation times which, for a given aging time, shifts with temperature according to a reduced activation energy of 92 kK. The creep of 4-thiol-30%iso involves a somewhat broader distribution of relaxation times, skewed to longer times, with a reduced activation energy of 82 kK. The double logarithmic aging rate, μ, varies with aging temperature in a different way for the two systems, presenting a somewhat sharper peak in the 4-thiol system. This is consistent with the 4-thiol sample having a narrower distribution of relaxation times. The comparison of the aging rate for each system with the predictions of the theoretical model allows the non-linearity parameter, x, of structural relaxation to be determined, the optimised values being 0.30 for 4-thiol and 0.25 for 4-thiol-30%iso.

Both systems display significant physical aging effects at room temperature, and hence the prediction of the physical aging behaviour is of practical importance for these systems. The experimentally determined parameters for the aging behaviour of each system have been determined according to the above procedures, and are now available for input into a linear viscoelastic model to predict the effects of aging on the shape-memory response of these systems.

ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

Figure 1. Schematic illustration of the torsional creep apparatus.

Figure 2. Log-log plot of average relaxation time during aging as a function of aging time at the temperatures relative to T_g indicated. The vertical dashed lines represent typical experimental limits of aging times: 1 hour (left-hand) and 200 hours (right-hand).

Figure 3. Aging rate as a function of T_a–T_g showing the effects of the different parameters: (a) $\Delta h^*/R$=85 kK, x=0.6, β values shown in inset; (b) $\Delta h^*/R$=85 kK, β=0.4, x values shown in inset; (c) β=0.4, x=0.4, $\Delta h^*/R$ values shown in inset.

Figure 4. Creep curves of creep compliance as a function of log(creep time) for the 4-thiol sample at the aging temperature of 47.3 ºC. The different aging times are indicated in the inset.

Figure 5. Master curve for the superposition of creep curves for different aging times at 47.3 ºC. The reference aging time is 164 hours.

Figure 6. Plot of log(shift factor) versus log(reference aging time/aging time) for 4-thiol sample aged at 47.3 ºC.

Figure 7. Double logarithmic aging rate, μ, as a function of the aging temperature for the 4-thiol sample: blue diamonds, experimental data; green triangles, model prediction using KWW distribution with β=0.8, x=0.4 and $\Delta h^*/R$=85 kK.

Figure 8. Time-temperature superposition of creep curves obtained at the temperatures indicated for aging times of 24 hours (upper figure) and 168 hours (lower figure). Full line is fit of KWW function, and black squares represent the master curve corresponding to the discrete distribution of Figure 10. Reference temperature 51.6 ºC.

Figure 9. Discrete distribution of relaxation times for 4-thiol sample, for aging times of 24 hours (red squares) and 168 hours (blue diamonds) at the reference temperature of 51.6 ºC.

Figure 10. Arrhenius plot of time-temperature superposition shift factor, on a logarithmic scale, as a function of the reciprocal temperature for the different aging times indicated: 2 h, green triangles; 24 h, red squares; 168 h, blue diamonds. The reference temperature is 42.2 ºC.

Figure 11. Arrhenius cross-plot from data presented in Figure 2, showing variation of the average relaxation time with the aging temperature for fixed values of the aging time: t_a = 1 s, blue diamonds; t_a = 4.61 h, red squares; t_a = 3.2 years, green triangles. Full line is best fit to the data for t_a = 1 s; dashed line is best fit to first four points for t_a = 3.2 years

Figure 12. Creep curves for 4-thiol-30%iso sample at the aging temperature of 55.6 ℃ and for aging times as indicated.

Figure 13. Master curve obtained by horizontal shifting of creep curves in Figure 12.

Figure 14. Double logarithmic shift factor for 4-thiol-30%iso sample as a function of aging temperature: blue diamonds, experimental data; green triangles, model predictions using KWW distribution with $\beta=0.30$, $x=0.30$ and $\Delta h^*/R=85$ kK.

Figure 15. Master curve for 4-thiol-30%iso sample for aging times of 96 h at the temperatures indicated. The reference temperature for shifting is 68.1 ℃. The full line shows the best fit of the KWW function, with $\beta = 0.55$ and $\tau_r = 50$ s. The blue squares show the fit obtained with the discrete distribution shown in Figure 16.

Figure 16. Comparison of discrete distributions for 4-thiol (blue diamonds) and 4-thiol-30%iso (red squares) samples. The relaxation times have been normalised with respect to the best fit KWW relaxation time for each sample.

Figure 17. Arrhenius plot of time-temperature superposition shift factor, on a logarithmic scale, as a function of the reciprocal temperature for the 4-thiol-30%iso sample, for the different aging times indicated: 8 h, purple crosses; 24 h, green triangles; 48 h, red squares; 96 h, blue diamonds. The reference temperature is 45.7 ℃.

Figure 18. Double logarithmic aging rate, μ, as a function of the aging temperature for the 4-thiol sample: blue diamonds, experimental data; red squares, model prediction using discrete distribution with $x=0.30$ and $\Delta h^*/R=92$ kK.

Figure 19. Double logarithmic shift factor for 4-thiol-30%iso sample as a function of aging temperature: blue diamonds, experimental data; red squares, model predictions using discrete distribution with $x=0.25$ and $\Delta h^*/R=82$ kK.