Dynamic mechanical behaviour of oriented poly(tetramethylene terephthalate) as a function of static extension

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The dynamic mechanical behaviour of oriented poly(tetramethylene terephthalate) tapes has been studied as a function of the static extension of the sample. It was found that both the α and β relaxations showed maximum intensity at an intermediate level of strain. This is consistent with a simple two site model, where the site occupancy depends only on the static extension.

INTRODUCTION

Although the dynamic mechanical behaviour of poly(ethylene terephthalate) has been the subject of extensive investigations[1–4], there have been few studies of other poly(n-methylene terephthalates), apart from a comparative examination of the α and β relaxations in an attempt to identify the molecular origins of the relaxation processes[5]. This early study was prompted by the observations that changes in the infra-red spectrum of poly(ethylene terephthalate) which occurred on crystallization or orientation could be attributed to rotational isomerism in the glycol residue[6]. This raised the possibility that either or both of the α and β relaxations (which are also active in dielectric relaxation) could be associated with conformational changes from *trans* to *gauche* and *vice-versa.* It was concluded from dynamic mechanical, infra-red and broadline n.m.r. studies that both relaxation processes in poly(ethylene terephthalate) related to motion in the glycol residue, the α relaxation involving major reorientation and the β relaxation some more restricted motion, which could not be specified in detail.

In this paper the dynamic mechanical behaviour of oriented poly(tetramethylene terephthalate) (4GT) is described. Particular attention has been given to the changes in storage and loss compliance as a function of an applied static extension. In this respect the work described here relates to previous recent studies of 4GT, where the primary concern was with the interpretation of the stress–strain curve in terms of structural changes[7–9]. It was shown that a plateau region, where the nominal stress is almost independent of strain from 4–10% extension, corresponds to the transformation of the crystalline regions from the α to the β structure. In the β structure the molecular chain is close to its fully extended length, whereas in the α-structure the chain is appreciably contracted. The transformation from the α to the β form occurs primarily by a discontinuous change in the conformation of the glycol residue, and it was shown by X-ray diffraction that a given level of strain corresponds to a given proportion of each crystalline form. There were also corresponding changes in the infra-red and Raman spectra[8,10], and whilst these changes primarily reflected the changes in the crystalline regions observed in the X-ray measurements there were also changes in bands assigned to vibrations of molecular chains in the non-crystalline regions. This suggests that comparable conformational changes occur in the non-crystalline regions when samples are strained. This conclusion was confirmed by a comparison of the mean crystalline lattice strain with the overall sample strain[11]. At low overall strains the mean crystalline lattice strain is about half the overall strain, but increases to be comparable with the overall strain at high strains. These results suggest that the conformational changes in the non-crystalline regions must be at least equivalent to those in the crystalline regions over a wide range of strains.

In our recent work[11] we made a particular study of loading and unloading behaviour, and observed remarkable hysteresis effects with regard to the α–β crystal transformation which could be very effectively described in terms of a mean-field model, analogous to the Weiss theory of ferromagnetism. In the present paper we will discuss the very large changes in storage and loss compliance which occur on extending 4GT. The results can adequately be described by a simple two site model in which the site occupancy is determined by the level of extension, so that for the dynamic mechanical behaviour it is not necessary to invoke cooperative effects in the first instance.

EXPERIMENTAL

Preparation of samples

The samples were in the form of oriented tape 20 μm thick and 1.22 mm wide. The tapes were prepared as follows. First, 4GT polymer was melt-extruded at 280°C through a rectangular die and quenched into water at ambient temperature. This isotropic tape was then drawn bet-

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ween rollers moving at different speeds over a heated cylinder at 90°C and then a heated plate at 160°C to a nominal draw ratio of 5:1 (conventional pin and plate drawing). To stabilize the samples further, these tapes were subsequently annealed at constant length for 20 h at 200°C in a vacuum oven.

This procedure produces material with well-developed crystallinity and high crystalline orientation as revealed by wide-angle X-ray diffraction. The birefringence of the drawn and annealed samples was 0.16 ± 0.01, and a density estimate of crystallinity based on a crystalline density of 1.39 g cm^{-3} was about 40%. Quantitative X-ray measurements of mean crystallite size and orientation for these identical samples are reported in a previous publication[11], following more qualitative description of the X-ray diffraction patterns which had already been given[7]. A comprehensive account of the general mechanical behaviour of such materials, including recovery and shrinkage, together with the effects of annealing on the stress–strain curves has also been given[9].

Separate batches of oriented tapes, prepared under similar conditions as described above, were used for the high and low temperature dynamic mechanical measurements. The two batches were similar in properties, and slight differences observed in their mechanical behaviour do not affect the major effects which are being studied in this investigation, as will be clear from the results obtained.

Dynamic mechanical measurements

The dynamic mechanical measurements were performed at 10 Hz on samples 5 cm long. The measurements from room temperature to 125°C were performed on a previously-described apparatus[12], and those below room temperature on a second, which was similar in principle but more suitable for samples of greater stiffness. In both cases, the sample is subjected to a sinusoidal strain produced by a vibrator. The stress in the sample is measured by a non-bonded strain gauge transducer and the strain by a similar gauge connected to the vibrator by a calibrated spring. The storage and loss compliances were determined by comparing the relative magnitude of the in-phase and out-of-phase components received by the transducers monitoring the stress and strain, respectively, using a Solartron 1172 frequency response analyser as the phase-sensitive detection system.

The sample was enclosed in a temperature chamber constructed from polyurethane foam, and the required temperature obtained by passing a gas stream through the chamber. For low temperatures, a stream of cold nitrogen gas was boiled-off from a storage dewer and heated to the required temperature by passing it over a resistance wire heating element. High temperatures were obtained from a stream of compressed air which was blown through the same heater and temperature enclosure.

The dynamic mechanical results were obtained for different levels of static extension of the sample. Initially, for the high temperature measurements, the static extension was set indirectly by estimating the static load required from previously-measured relaxed stress–strain curves for 'similar samples' and then extending the sample until this load was indicated by the static output of the load cell attached to the sample. For the low temperature measurements, however, it proved possible to measure the static extension of the sample directly using vernier calipers or by using feeler gauges between studs attached to the clamps and similar studs on the frame supporting the apparatus.

It was not possible, however, to measure the static strain during a temperature run and it was therefore decided to leave the nominal extension of the sample at its room temperature setting. The true strain therefore increased slightly by an estimated 1–2% due to sample contraction during the low temperature runs and decreased slightly during the high temperature runs. The slight uncertainty introduced by this approach is common to all samples and does not detract from the qualitative observations and analysis presented here.

In addition to these measurements at fixed extension as a function of temperature, measurements were made as a function of static extension at room temperature. In these measurements, the extension was first increased and then decreased to check for hysteresis effects and the complete cycling procedure was also performed at two different rates.

RESULTS

The storage compliance J' and the loss compliance J'' were measured as a function of temperature for different static extensions. The results for low temperature (1, 4 and 10% extension) are shown in *Figures 1a* and *1b*, and for high temperatures (1, 7 and 13% static extension) in *Figures 2a* and *2b*.

It can be seen that both the α and β relaxations show a large dependence of J' and J'' on static extension and that there is a consistent pattern over the whole temperature range. Both J' and J'' first rise as the static extension is increased, and then fall, as do tan δ and the imaginary part of the modulus.

The room temperature extension cycling results are shown in *Figures 3a* and *3b*. It can now clearly be seen that J' and J'' show maximum values at 5% static extension. It

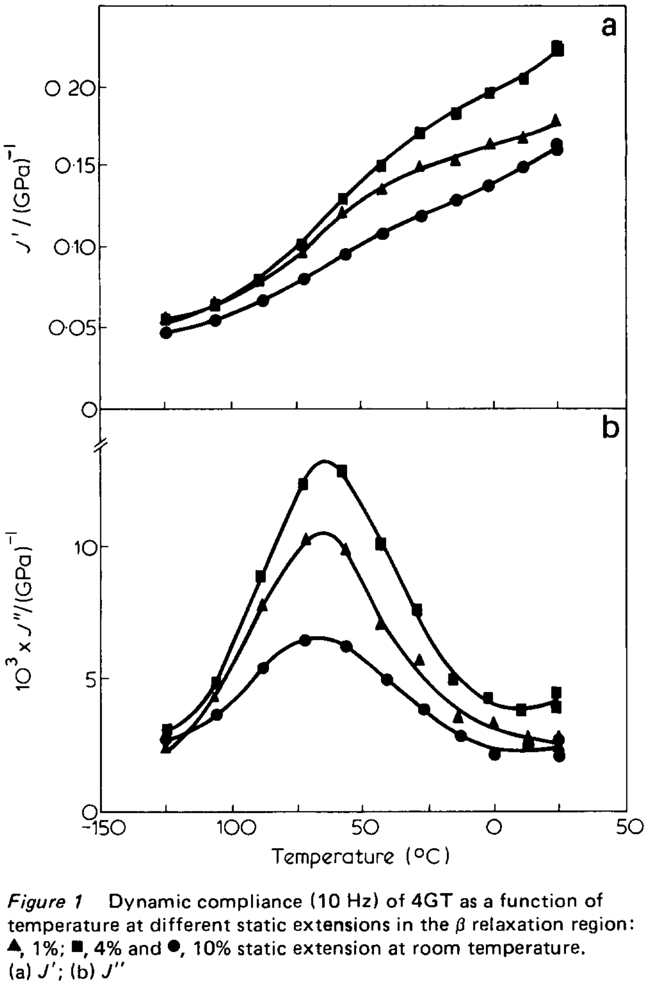

Figure 1 Dynamic compliance (10 Hz) of 4GT as a function of temperature at different static extensions in the β relaxation region: ▲, 1%; ■, 4% and ●, 10% static extension at room temperature. (a) J'; (b) J''

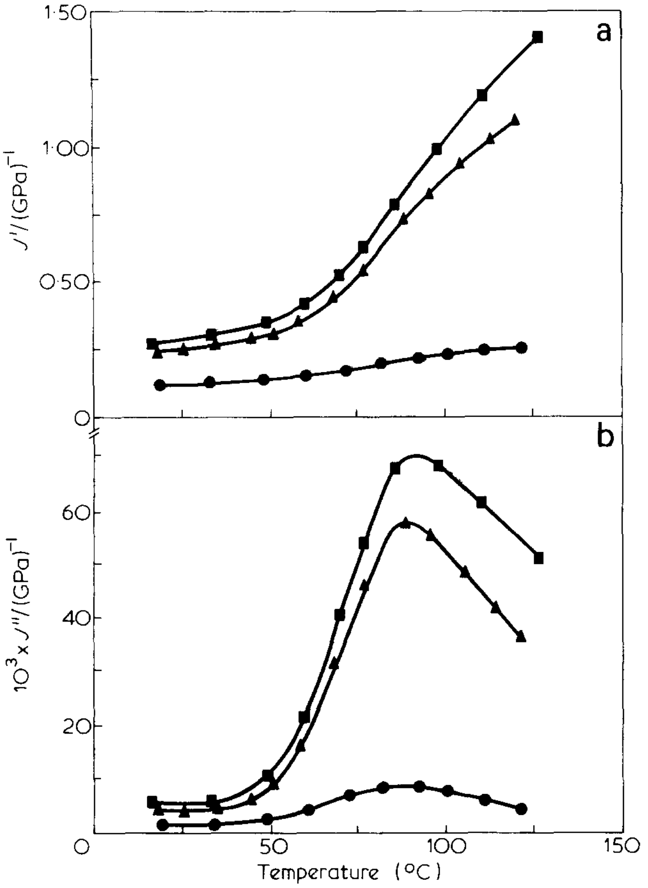

Figure 2 Dynamic compliance (10 Hz) of 4GT as a function of temperature at different static extensions in the α relaxation region. ▲, 1%; ■, 7% and ●, 13% static extension at room temperature. (a) J'; (b) J''

is also noteworthy that the dynamic compliance measured as a function of extension, as distinct from load, shows little hysteresis.

DISCUSSION

It is clear from the results that to a good approximation J' and J'' are functions of the static extension only. From our previous structural studies it can be concluded that the basic change caused by extension of the sample is the change from the crumpled to extended conformation of the molecules in both crystalline and non-crystalline regions. It is likely, however, that the dynamic behaviour reflects primarily the properties of the non-crystalline regions and we therefore consider for simplicity the predictions of a model based upon a collection of identical elements each of which may exist in a long or short form. We do not, at this stage, wish to consider the complexities introduced by the two phase nature of the sample. If we denote the fraction of elements in the state 'i' by f_i then the mean length of the elements is given by:

$$l = f_1 l_1 + f_2 l_2 \tag{1}$$

Denoting the length at room temperature and zero stress by l^0 we may define an incremental compliance (J) by:

$$J = \frac{1}{l^0} \cdot \frac{\Delta l}{\Delta \sigma} = \frac{(l_1 - l_2)}{l^0} \cdot \frac{\Delta f_1}{\Delta \sigma} \tag{2}$$

The quantities Δf_1 and $\Delta\sigma$ may be real variables when defining a 'relaxed' static incremental compliance or complex variables defining a complex compliance when considering the dynamic behaviour of the model. This may be calculated from the usual rate equation for the two site model as follows:

$$\frac{\mathrm{d}f_1}{\mathrm{d}t} = -\frac{1}{\tau_0 \exp\left(\frac{V}{kT}\right)} \left\{ f_1 \exp\left(\frac{W}{kT}\right) - f_2 \exp\left(\frac{-W}{kT}\right) \right\}, \tag{3}$$

where V is the mean barrier height and $2W$ is the energy difference between the two sites. The effect of an applied stress is to change this energy difference since the longer form will be favoured in the presence of a tensile stress. For simplicity we assume a linear dependence of the form:

$$W = W_0 - \sigma(l_1 - l_2)A \tag{4}$$

where A is a constant with the dimensions of area. Since the applied stress consists of a static component σ^s and a time dependent component σ^t then $2W$ and the f_i show a similar behaviour. We therefore write:

$$\sigma = \sigma^s + \sigma^t$$

$$W = W^s + W^t$$

$$f_i = f_i^s + f_i^t \tag{5}$$

The long time solution of the rate equation requires:

$$\frac{f_1^s}{f_2^s} = \exp(-2W^s/kT) \tag{6}$$

where

$$W^s = W_0 - \sigma^s(l_1 - l_2)A \tag{7}$$

We may solve for the dynamic behaviour if we assume that the time dependent variables are small perturbations of this static state. To be more specific, we assume that terms in $f_1^t\, W^t/kT$ are negligible and that $\exp(W^t/kT) \simeq 1 + W^t/kT$. Substituting equations (5) into the rate equation (3) and using (6) and (7) to eliminate W^s and σ^s then yields the following rate equation:

$$\frac{\mathrm{d}f_1^t}{\mathrm{d}t} = -\frac{1}{\tau}\left\{ f_1^t - \frac{2\sigma^t(l_1 - l_2)}{kT} A f_1^s f_2^s \right\} \tag{8}$$

where

$$\tau = (f_1^s f_2^s)^{1/2} \tau_0 \exp(V/kT) \tag{9}$$

To calculate the complex compliance we substitute $\sigma^t = \sigma_0 \exp(i\omega t)$ and $f_1^t = f_0 \exp(i\omega t)$ into equation (8) and obtain the final desired result:

$$J^* = \frac{(l_1 - l_2)}{l^0} \cdot \frac{f_0}{\sigma_0} = \frac{2(l_1 - l_2)^2}{kT} \cdot \frac{A}{l^0} \cdot \frac{f_1^s f_2^s}{1 + i\omega\tau} \tag{10}$$

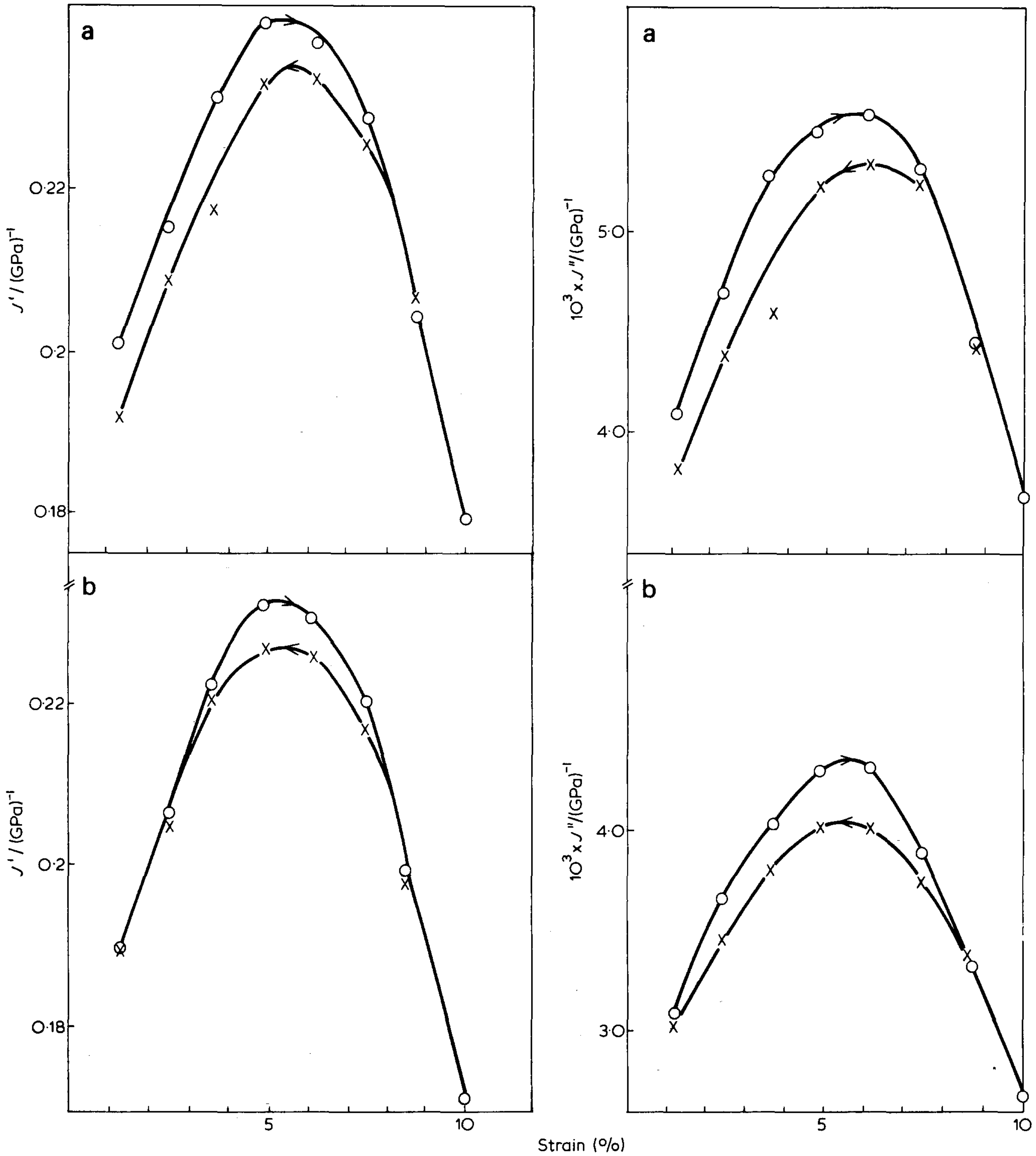

Figure 3 Dynamic compliance (10 Hz) of 4GT as a function of static extension at room temperature. O, Strain increasing; x, Strain decreasing. (a) 5 min between strain increments; (b) 25 min between strain increments

Hence

$$J' = \frac{2(l_1 - l_2)^2}{kT} \cdot \frac{A}{l^0} \cdot \frac{f_1^s f_2^s}{(1+\omega^2\tau^2)} \tag{11}$$

and

$$J'' = \frac{2(l_1 - l_2)^2}{kT} \cdot \frac{A}{l_0} \cdot \frac{f_1^s f_2^s \omega\tau}{(1+\omega^2\tau^2)} \tag{12}$$

Inspection of the above shows that for any mean value of ω both J' and J'' are maximized when $f_1^s = f_2^s = 0.5$ since we must maintain $f_1^s + f_2^s = 1$. Thus if the elements are predominantly in the short form in the absence of an applied stress then J' and J'' will first rise as the sample is extended until there are equal numbers of molecules in the 'long' and 'short' forms after which point J' and J'' will then fall with further extension of the sample.

This model roughly describes the observed results and is an intuitively appealing description of the phenomenon in view of the known stress-induced crystalline phase transition. However, it does ignore several basic problems.

(1) Do the dynamic data reflect processes occurring in the crystalline regions or amorphous regions or both?

(2) How can the single model above explain the strain

dependence of both the α and β relaxations?

(3) Is it necessary to use a model which reproduces the observed hysteresis in the static stress–strain data for a complete description of the dynamic phenomena?

We have investigated more complicated models involving correlated motion which reproduce the hysteresis in the stress–strain data and the crystalline phase transition[11] and which link the α and β relaxation processes in simple amorphous systems[13]. It is likely that a synthesis of these ideas with a correct recognition of the two phase nature of the sample will provide the framework for a more complete understanding of the phenomena reported above.

CONCLUSIONS

The dependence of the dynamic mechanical behaviour of 4GT can be interpreted in terms of a simple two site model, where the site occupancy relates to the level of static strain. Related structural studies show that the structural changes which occur on extension principally involve the conformation of the tetramethylene residue[7,8,10]. In the first instance then, these results suggest that both the α and β relaxations involve molecular motions of at least this part of the molecular chain. This is consistent with previous conclusions[3,5] but has not hitherto received such dramatic confirmation. It is more remarkable to note that the effect of static strain is very similar for both the α and β relaxations. This leads us to speculate whether these relaxations are not in fact separate branches of a single relaxation, as has been previously proposed for glassy polymers[13]. In this respect it is perhaps most likely that although the conformational changes occur on extension in both the crystalline and amorphous regions of the polymer, the dynamic mechanical behaviour primarily reflects the changes in the amorphous regions. This aspect of the subject is worthy of further study.

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