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Stress release in oriented HIPS as observed by dynamic mechanical analysis

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Abstract

The transition from the glassy state to the rubbery state in a partially oriented *high-impact polystyrene* (HIPS) sample has been investigated by means of *dynamic mechanical analysis* (DMA), using three-point bending and parallel plate compression test modes. For samples without any thermal treatment an apparent increase of the storage modulus, $E'(T)$, was observed near the onset of the calorimetric glass transition temperature, followed by a strong decrease due to the dynamic glass transition. This peak was attributed to the stress release of the oriented material and almost disappeared for an annealed sample. The compression experiments were found to be more sensitive to the stress release phenomena than flexural experiments. Several experiments at different frequencies (from 0.5 to 20 Hz) showed that both the area and the height of the $E'(T)$ peaks increase linearly with the logarithm of frequency. The influence of the heating rate (for a fixed frequency – 1 Hz) was also analysed and the thermal calibration method used prior to those experiments is discussed. It was found that the strength of the $E'(T)$ peaks decreases with increasing heating rate and the corresponding loss peaks, $E''(T)$, shift to higher temperatures and become sharper. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: DMA; Polystyrene; Relaxation; Temperature calibration; Dynamic modulus; Glass transition

1. Introduction

The transition of polymeric materials from the glassy to the rubbery state has long been recognised as an important material property. The glass transition is a general feature of glass-forming materials and has been the object of experimental and theoretical studies for many years [1,2]. Because of the dramatic changes that occur during this transition, the glass transition temperature, T_g, can be observed by many means, including dilatometry, thermal measurements, dielectric spectroscopy and dynamic mechanical analysis (DMA) [3].

In DMA isochronal experiments the temperature dependence of the dynamic modulus ($E^*=E'+iE''$) and loss factor ($\tan\delta=E''/E'$) are measured during heating whilst the sample is excited at a particular frequency. On passing through the dynamic glass transition (α relaxation) the storage modulus, E', usually decreases strongly whereas the loss modulus curve, E'', is peak-shaped, due to the onset of large cooperative motions within the polymeric chains.

For amorphous polymers, it is known that most conventional processing techniques lead to oriented products [4]. Shear and extensional stress developed during processing induce some degree of molecular orientation which is frozen in when the temperature drops below T_g. This partially oriented state can be destroyed on subsequent reheating when the temperature approaches T_g, i.e., when molecular mobility allows the isotropisation of the preferable chain direction. During this process internal stresses within the material are released and one may expect changes in

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the mechanical properties and in the geometrical dimensions of the sample. Thus, beyond the conformational motions of the main-chain segments of the polymer (α relaxation), this stress release may also be detected by DMA in the vicinity of the calorimetric glass transition.

Polystyrene is an important but brittle material and its impact strength can be greatly enhanced by incorporating polybutadiene, leading to the well-known 'high-impact polystyrene', HIPS [5]. In the present work the effect of the stress release in oriented HIPS is analysed by DMA during heating experiments covering the glass transition region. Special attention is given to the effects of the frequency of the mechanical excitation and of the heating rate. The DMA technique has been widely used to study a variety of polystyrene-based materials, in addition to HIPS. These include copolymers, blends, ionomers, composites or interpenetrating polymer networks; a routine computer-aided literature search showed more than 150 publications on the subject during the past four years.

2. Experimental

The high-impact polystyrene used throughout this study was purchased from Goodfellow (LS162471NL) as 1 mm thick sheets.

The dynamic mechanical measurements were carried out using a DMA7e Perkin-Elmer apparatus with controlled cooling accessory, in the temperature range from +30°C to +140°C. High purity helium was used to improve heat transfer to the sample environment during the experiments.

For the three-point bending experiments rectangular specimens with typical dimensions of 5.5×4.7 mm were cut from the original sheet. The samples were placed over a 5 mm bending platform and a 5 mm knife-edge probe tip provided the mechanical excitation: in all experiments a static stress of 4×10^5 Pa and a dynamic stress of 3.5×10^5 Pa were imposed on the sample. Several frequencies, in the range from 0.5 to 20 Hz, were used.

For the compression experiment the sample, with dimensions of 4×4.7 mm, was placed between two 5 mm diameter stainless steel plates. The top plate imposed a static stress of 2.2×10^5 and a 1 Hz dynamic stress of 2×10^5 Pa. The experiment was carried out at 4 K/min.

3. Temperature calibration

The temperature sensor in the DMA apparatus is located close to, but separate (by an air gap) from, the sample. Therefore there is a temperature gradient between the two and it is important to know the sample temperature that corresponds to the value indicated by the sensor. This is especially relevant in this work, part of which is concerned with the effect of the heating rate. Temperature calibration was carried out by using the DMA instrument in a penetration mode, in which the displacement of a 3 mm spherical probe tip imposing a 10 mN static force into a small standard indium sample (from Goodfellow, 99.99999% purity) was monitored during heating at a specific rate. The onset of the probe displacement curve was compared with the known melting point of indium to correct the temperature axis of the DMA measurements. More details about this calibration procedure, in which different types of apparatus were tested, can be found elsewhere [6,7]. Moreover, some novel aspects about temperature calibration in this kind of equipment, such as calibration in cooling and the effect of the position of the indium sample with respect to the sample will be discussed in another paper.

Probe displacement curves are shown in Fig. 1 for experiments carried out at heating rates (β) of 0.5, 1,2,4 and 8 K/min. Many more experiments were actually carried out on the same indium sample; the curves in Fig. 1 are representative results for those heating rates. In fact, it was found that, for a specific heating rate, the onset temperature could vary by more than 1°C. These differences can be attributed to real temperature fluctuations in the furnace as well as experimental factors such as small changes to the geometries of the indium sample. Moreover, in some experiments the drop in the displacement curve was found to be confusing, making it difficult to determine the true onset temperature (see, for example, the 4 K/min curve in Fig. 1). It is, however, clear that the onset temperature increases with increasing β. This behaviour, also seen for temperature calibrations in other thermal analysis techniques (e.g. differential scanning calorimetry [3]), is due to the increasing thermal lag

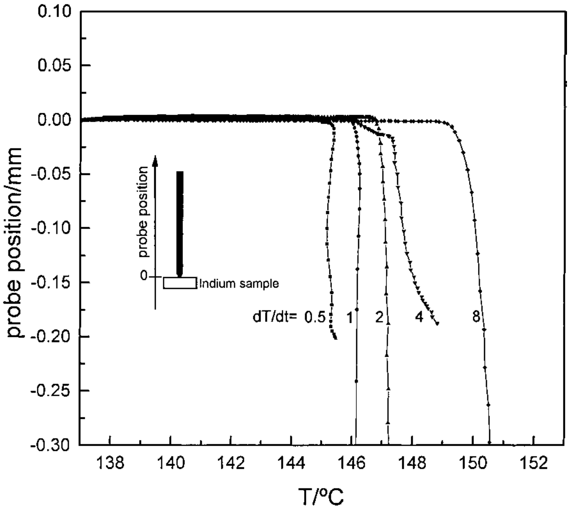

Fig. 1. Influence of the heating rate (K/min) on the penetration experiments on an indium sample. The zero value corresponds to the initial position of the probe tip (see inset figure).

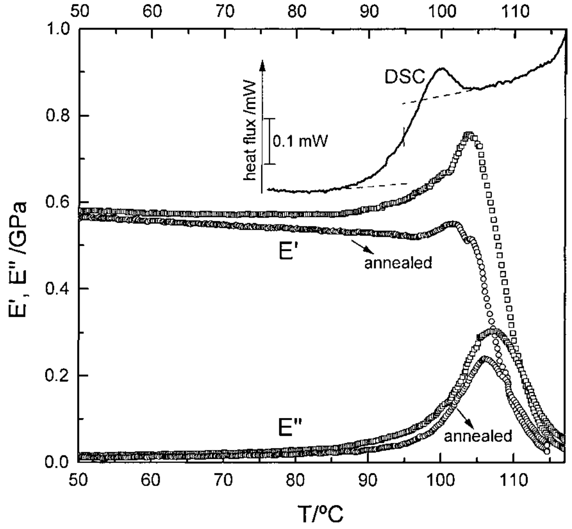

Fig. 2. Apparent strorage modulus (E') and loss modulus (E'') obtained for oriented (squares) and annealed (circles) HIPS samples in a three-point bending experimental mode. Both experiments were carried out at 4 K/min and 1 Hz. Solid line: differential scanning calorimetry experiment at 3 K/min; the temperature axis is the same as that of the DMA experiments.

between the thermocouple and the sample when β increases. It should be noted that the onset temperatures shown in Fig. 1 are considerably lower than the actual melting point of indium (156.6°C), especially for the low heating rates. This may be an indication that there is a considerable error in the calibration of the thermocouple itself or that complex helium fluxes into the furnace cause such differences.

4. Results and discussion

The results of two three-point bending experiments on HIPS at 4 K/min and 1 Hz are shown in Fig. 2. There is an apparent increase of the storage modulus, E', in the temperature range ~90°C to ~104°C for the 'as received sample' (square points in Fig. 2). This apparent stiffening of the sample can be attributed to an experimental perturbation resulting from the stress release within the sample leading to changes in sample geometry. In fact, during heating and close to the glass transition, the internal stresses are liberated as a result of the disappearance of the molecular orientation. This effect was clearly seen when an 'as-received' sample was freely heated up to about 120°C (above T_g). This annealed sample, now unoriented, was slowly cooled down to room temperature. It was observed that the thickness of the annealed sample increased by ~17% and smoothly shrank in length and in depth relative to their original dimensions. The change of the thickness of the sample was also investigated by monitoring the probe position over the 'as-received' sample during heating. In the first run an increase of the probe position was detected in the glass transition region whereas during the second run no substantial increase of the sample's thickness was observed – stress release was apparently complete during the first run.

It is clear that, during the DMA experiment on an 'as-received' sample, the stress release process leads to an increased sample thickness in the glass transition region. Sample dimensions, however, are introduced in the software before the experiment and are assumed to be constant. For the 'as-received' sample, therefore, the calculations of the viscoelastic parameters involving the sample's geometry are not correct in the glass transition region: E' is inversely proportional to the moment of inertia, I, which is, in turn, proportional to h^3, where h is the sample thickness. E' in the glass transition region is calculated with a constant h value which is less than the true figure, leading to a modulus that is higher than the real value. Of course, the dramatic decrease of the storage modulus through the dynamic glass transition eventually dominates any errors in h and the $E'(T)$ curve starts to decrease. For the case shown in Fig. 2, the drop of $E'(T)$ occurs near 102°C. We may expect that this temperature should be lower if no change of the sample thickness had occurred. The overall effect of the changed sample dimensions, due to the stress release within the oriented material, is the appearance of an apparent peak, in the $E'(T)$ results, called here the 'stress release peak', in the glass transition region. In future work changes in sample geometry on heating will be measured by careful dilatometric experiments. This information can then be used to correct the calculations of the viscoelastic parameters from the DMA experiments.

The stress release peak has almost disappeared for the annealed sample (circles, Fig. 2) confirming that the source of the peak lies in the changed sample dimensions. Note that the correct (relaxed) dimensions of the annealed sample were used for the calculation of E'. From the lower values of $E'(T)$ for the annealed sample it can also be concluded that the elimination of orientation leads to a softer material. The thermal treatment also affected the loss modulus curve: the area of the peak decreased and its maximum was shifted to a slightly lower temperature, i.e., the glass transition temperature as measured by DMA is apparently higher for the oriented material. The source of this effect, changed sample dimensions, has already been discussed.

The peak observed in the $E'(T)$ curve is not exclusive to HIPS and was also observed in our laboratory for other materials (e.g. extruded atatic polystyrene and injection molded polycarbonate) in which orientation was known to exist. Moreover, the explanation for the origin of these peaks in terms of the existence of orientation in the sample can be found in literature (e.g. [8]).

Differential scanning calorimetry experiments (DSC) were also carried out on a HIPS sample. A 23.96 mg annealed sample was studied in a DSC7 Perkin-Elmer calorimeter at 3 K/min. The heat flux curve is also shown in Fig. 2, where the temperature axis is the same as that for the DMA results. The peak in the heat flux curve, with a maximum at ~100°C, has a different origin to that for E' being caused by structural relaxation of HIPS due to thermal history [9]. The glass temperature was T_g=94.5°C, below the DMA glass transition at 1 Hz for which the maximum of the loss curve for the annealed sample is above 105°C. This is easily explained by the lower 'equivalent-frequency' of the DSC experiment [9]. It is interesting to notice that the onset of the segmental motions within the polymeric chains is about 85°C as seen by DSC. This temperature is also similar to the onset of the E' peak for the oriented sample, indicating that the isotropisation of the oriented chains correlates closely with the large cooperative motions characteristic of the glass transition.

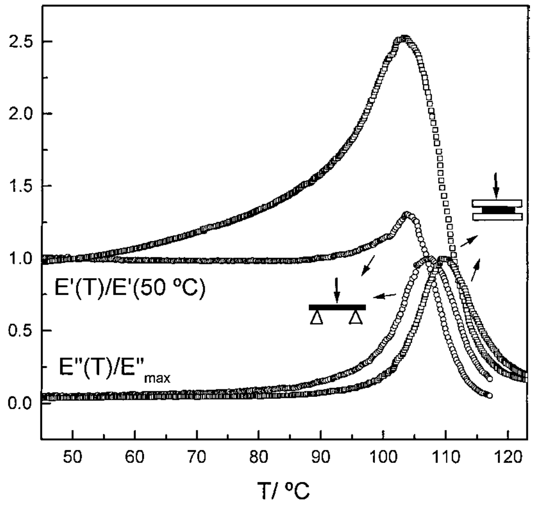

Fig. 3. DMA results for oriented HIPS obtained at different test modes: flexural (circles) and compression (squares). Both experiments were carried out at 4 K/min and 1 Hz. The storage modulus curves are normalised relative to the 50°C value and the storage modulus curves are normalised relative to their maximum value.

The results for flexural and compression experiments are compared in Fig. 3. The $E'(T)$ results are presented as normalised values relative to $E'(50°C)$. This procedure allows a better comparison between the two methods. The loss modulus results shown in Fig. 3 are also normalised relative to their maximum values (E_{max}'').

It is clear from Fig. 3 that compression experiments also lead to peaks in the E' vs. T data near T_g. As in flexural experiments, this effect may also be related to geometrical changes in the sample. During compression the sample thickness cannot increase because a static stress is imposed. The sample may even start to retract during the creep process that follow the dynamic experiment. Indeed, it was found that at the end of the experiment there was an increase in the effective sample area. Therefore, the decrease of the sample thickness, as well as the increase of the area, lead to an apparent compression modulus that is higher than the real value. We can then conclude that the errors in both experiments are caused by opposite geometric factors. For the specific case studied in this work, one concludes that for a compression experiment the change of the sample dimensions has a stronger influence on the viscoelastic parameters than for the three-point bending experiment because a more intense stress release peak was observed in the former case. This provides a good example of the dependence of the DMA results on the kind of mechanical excitation. It is also interesting to note that both experiments lead to normalised loss modulus curves with very similar shapes. However, the compression one is shifted to higher temperatures. This is compatible with the results in Fig. 2 in the sense that the increase of the strength of the stress release peak shifts the DMA glass transition to higher temperatures.

The effect of the dynamic stress frequency on the three-point bending experiments was also analysed. Six frequencies between 0.5 and 20 Hz were used and the corresponding storage modulus curves are shown in Fig. 4.

It can be clearly seen that as the frequency increases the intensity of the peak in the $E'(T)$ curves increases as well as its area. Moreover, as seen in Fig. 5, the plot of these two parameters as a function of the logarithm of frequency shows a nearly perfect linear relationship for both cases. This interesting behaviour must have a physical basis but this set of results is insufficient to demonstrate its origin. One hypothesis may be related to the fact that the dynamic glass transition temperature increases with increasing frequency, i.e., the drop of the true storage modulus occurs at higher temperatures for higher frequency experiments. Thus the influence of the changing sample geometry, which leads to an increase of the apparent storage modulus, can be extended to higher temperatures when frequency increases. More work is needed for an unambiguous confirmation of this idea.

Finally, the influence of the heating rate on DMA experiments was also analysed. Three different scanning rates were used for testing oriented samples: 2, 4 and 8 K/min. It is known that during the dynamic experiments, at a scanning rate β=dT/dt. the frequency f must be high enough in order that the temperature dependence of the response is not significantly smeared out by the heating process [1]. If the complex modulus needs to be resolved within temperature intervals ΔT, the frequency must satisfy

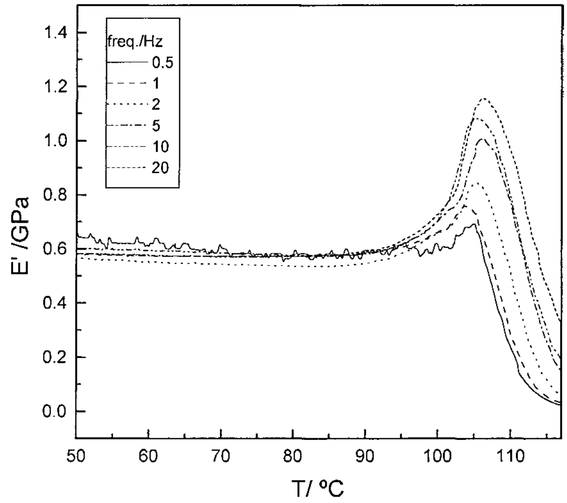

Fig. 4. Dependence of the storage modulus curves of oriented HIPS on frequency (three-point bending experiments at 4 K/min).

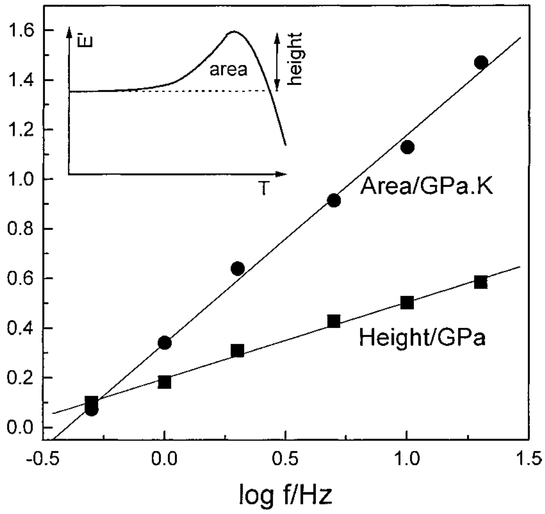

Fig. 5. Frequency dependence of the area (circles) and the height (squares) of the peak in the $E'(T)$ curves shown in Fig. 4. These two parameters are defined in the inset graphics.

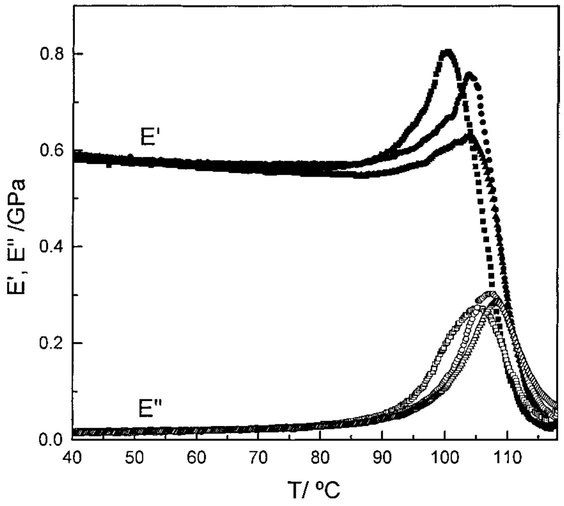

Fig. 6. Heating rate dependence of the storage modulus (filled symbols) and the loss modulus (open symbols) obtained from three-point bending experiments at 1 Hz. Heating rates: 2 (squares), 4 (circles) and 8 (triangles) K min^{-1}.

Eq. (1):

$$f \gg \beta/2\pi\Delta T. \qquad (1)$$

For β=8 K/min, the worst case, and for a temperature resolution of 0.2°C, we should have $f \gg 0.1$ Hz. Therefore, the frequency used, 1 Hz, should prevent that the temperature variance perturbs the dynamic experiment.

The results corresponding to the DMA experiments on HIPS are shown in Fig. 6. The temperature calibrations were taken into account for each heating rate. It is clear that the relaxation process shifts to higher temperatures with increasing heating rate (see temperatures of maximum loss modulus in Table 1). This behaviour was already reported [10] but in that work there was no evidence of a previous temperature calibration and the displacement of the processes in the temperature axis could be a result of that. Although this procedure was accomplished in the present work, we must be aware that the HIPS samples have a higher thermal resistance than indium. Thus a thermal gradient between the edges and the centre of the HIPS samples must exist; this thermal lag increases with increasing heating rate, leading to a shift of the relaxation processes to higher temperatures.

The $E'(T)$ curves in Fig. 6 also show that the stress release peaks decrease in magnitude with increasing β (see values of the area of the peaks in Table 1). This can be ascribed to the increase of the onset temperature at which the stress release process begins with increasing heating rate. In fact, as Fig. 2 suggests, the onset of the stress release process is highly correlated to the onset of the calorimetric glass transition process, which shifts to higher temperatures with increasing heating rate. Therefore the stress release peak in the $E'(T)$ curves, which occurs mainly between the onset temperature of the calorimetric glass transition process and the dynamic glass transition temperature should be attenuated for higher heating rates. As yet, this is only conjecture and, again, more work is needed in order to confirm it.

A comparison of E' and E'' curves shows that the strength of the stress release peaks influences the loss modulus peaks. In fact, the decrease of the E' peaks (with increasing heating rate) leads to sharper loss modulus peaks. Thus, information about the glass transition dynamics given by the loss modulus peaks may be effected by the stress release process. For example, a rough estimate of the activation energy in the temperature range of the loss peak can be obtained from the area of $E''(1)$ in a $1/T$ scale [11]:

$$\bar{E}_a = (E'_u - E'_r)\frac{R\pi}{2}\frac{1}{\int_0^\infty E''(T)\,\mathrm{d}(1/T)}, \qquad (2)$$

where E'_u and E'_r represent the limiting values of the

Table 1
Influence of the heating rate on the DMA results for oriented HIPS (see Fig. 6)

β (K min^{-1})	$T_{\max}(E')$ (°C)	Area of the E' peak (GPa K)	$T_{\max}(E'')$ (°C)	$\bar{E}_a$ (kJ mol^{-1})
2	100.0	0.98	105.2	324
4	103.5	0.34	107.2	350
8	103.8	0.090	108.2	392

The parameters analysed here are the temperatures of maximum E' and E'', the area of the E' peaks and the mean activation energy calculated by means of Eq. (2).

storage modulus at infinite and zero frequency, respectively, and R is the ideal gas constant. In the calculations a constant $E'_u - E'_r$ was used (0.545 GPa). The mean activation energies for the three heating rates are given in Table 1. As expected from Eq. (2), the decrease of the strength of the loss modulus peak leads to higher apparent activation energies. Note that these activation energy values must be lower than the true mean activation energy of the α-relaxation because we should expect an even sharper loss peak if no stress release occurred during heating.

5. Conclusions

From different dynamic mechanical experiments on oriented HIPS samples we can conclude that the stresses which are released within the samples during heating, and are due to molecular disorientation processes, have a strong influence on the results. The effects almost certainly originate in dimensional changes which lead to errors in the calculations of the viscoelastic parameters. Their magnitude, which is reflected by a peak in the storage modulus curve, $E'(T)$, is strongly dependent on the experimental conditions:

1. For the case studied in this work, compression experiments are more sensitive to stress release phenomena than flexural experiments. The stress release peaks observed in these two experimental modes seem to be caused by opposite changes in the sample dimensions.
2. The frequency of the mechanical stress shows a good correlation with the magnitude of the stress release peak, which increases linearly with increasing logarithm of the frequency.
3. The increase of the heating rate decreases the stress release peak and shifts the loss modulus peak to higher temperatures.

It can also be concluded that the onset temperature of the stress release process is close to the onset temperature of large molecular mobility, as seen by differential scanning calorimetry. This means that the time scale of this process is related to the experimental time scale corresponding to the heating process, in which the heating rate is the relevant variable, and not with the experimental time scale of the external dynamic excitation, which depends on the frequency of the dynamic stress imposed to the sample.

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