

Physical ageing response of polystyrene subjected to the large deformation: The increase in fictive temperature

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ABSTRACT

Film stretch was incorporated in the enthalpy relaxation experiment in order to examine physical ageing response of polystyrene subjected to large deformation. It was stretched in the midst of ageing step, where ageing temperature was located slightly higher than the onset of the glass transition shoulder to minimise the stretching effect on the enthalpy decay, and then heat capacity, $c_p(T)$, versus temperature curve was acquired by DSC (differential scanning calorimetry) as functions of the ageing time and stretch ratio. Pre-hold and post-hold stretches are both carried out, those are stretching-and-ageing and ageing-and-stretching, respectively. As a result, the stretching effect appeared as the shift of glass transition shoulder in $c_p(T)$ curve; its onset temperature increased with the increase in the stretch ratio. A remarkable discrepancy for the shift of glass transition shoulder was observed between the samples of pre-hold and post-hold stretches. The experimental $c_p(T)$ was reproduced by the modelling data calculated on the basis of Tool-Narayanaswamy-Moynihan framework to derive the data of fictive temperature (T_f). It was revealed that T_f isothermally increases with stretching. The amount of T_f increase depends on both the ageing time and stretch ratio. The discrepancy of the shift amount appeared between pre-hold and post-hold stretches was interpreted in terms of the increase in T_f .

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1. Introduction

Upon cooling glass forming systems, such as polymers, from above the glass transition to below it, they exhibit non-equilibrium behaviour. Local rearrangements in polymer chains take place under isothermal conditions, and the system comes asymptotically towards the equilibrium, which is well known as the structural relaxation or physical ageing. Changes in the physical properties that occur during the relaxation have attracted recent investigations of both academic and industrial interests including ultrathin film, interfacial effect with various substances, constructing layered structure, and confinement effect [1–4]. Also, the effects of stretch and the resultant chain orientation have been of interest from the practical point of view.

This paper is concerned with the enthalpy relaxation observed for a polymer in which the chain orientation by the stretch was induced within the ageing experiment. It was aimed to observe the progress of the relaxation subjected to deformations using

differential scanning calorimetry (DSC), which has a significance if the local rearrangement is influenced by the constrained situation caused by the stretch. Many research works have already been reported for material properties during the ageing and a comprehensive review can also be found [5]. According to them, physical ageing is roughly reflected by a decrease in specific volume, enthalpy, entropy, and creep compliance, and an increase in brittleness. This work also examines the consistency between these material properties, creep compliance in particular, and the DSC response to the combination of enthalpy relaxation and deformation by stretching. The changes in physical properties can be conveniently treated by the average relaxation time. It is a function of both structure and temperature [6,7]. It is an additional convenience to treat the structural state of the glassy polymer in terms of the fictive temperature (T_f), first introduced by Tool [8]. Nonlinearity appears in the evolution towards the equilibrium by allowing τ to be an explicit function of T_f and real temperature, as seen in the expression of Narayanaswamy [9,10].

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$$\tau = \exp \left\{ \ln(A) + \left(\frac{x\Delta h^*}{RT} + \frac{(1-x)\Delta h^*}{RT_f} \right) \right\} \quad (1)$$

A and Δh^* are constants and R is the ideal gas constant, the variable x ($0 < x < 1$) is an empirical parameter that partitions the temperature dependence and structural dependence of τ . Given these facts, it is expected to find some relationship between T_f and the structural change caused by the mechanical deformation, which contributes to the elucidation of property-structure relations.

In the enthalpy relaxation study, the calculation for τ with eq. (1) is frequently conducted to capture basic relaxation features [11–13], where T_f is determined simultaneously along the temperature program used to measure the relaxation property. This method was first developed by Moynihan and co-workers [14,15], which is thus frequently called as Tool-Narayanaswamy-Moynihan (TNM) model, to be used widely in the studies of structural relaxation.

While it has been known that TNM model is applicable to numerous polymers and polymer composites, and various glass properties, very little consideration was given to polymer glasses subjected to the deformation. In this regard, several calculation data have been presented to acquire a constitutive equation to describe the response of a polymeric material during arbitrary thermal and mechanical histories [16,17]. Rather, we are analysing the DSC response on the basis of T_f – T plot derived from the model calculation of TNM. Although T_f – T plot is not seen as frequently as the enthalpy(H)–temperature plot in the literature, it has an advantage to capture the departure from the equilibrium and the gradual approach to it in the physical ageing study. The similarity of the two relations of H – T and T_f – T can be deduced from the analogy between two equations of $c_p = (dH/dT)$ and $c_p^N = (dT_f/dT)$, where c_p^N is the normalised specific heat capacity [18]. In an attempt to acquire the details of T_f – T plot, a model calculation for $c_p(T)$, specific heat capacity, was carried out previously to reproduce the ageing experiment data of amorphous polystyrene [19].

Specifically, Fig. 1 illustrates the T_f – T relation of cooling process after the literature [18,20,21], in which the dotted line was

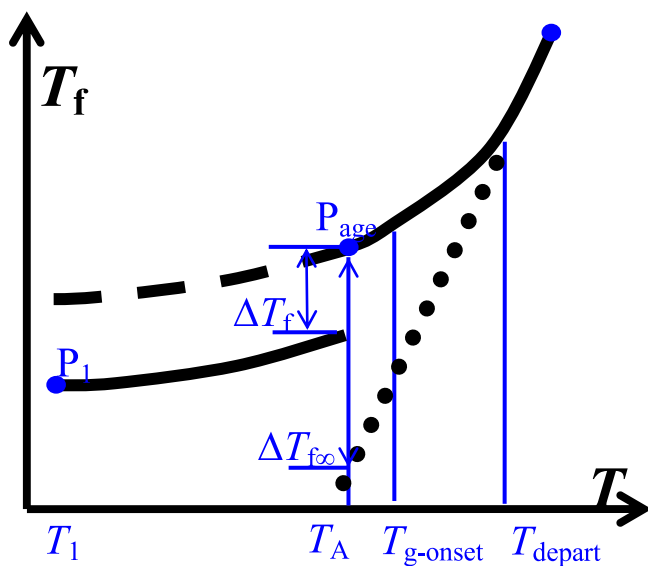


Fig. 1. Behaviour of the fictive temperature near the glass transition in the cooling process. The dotted line is the line of $T_f = T$. The dashed line is T_f – T plot observed in the ageing experiment of $t_A = 0$. Note that $T_{g\text{-onset}}$ can be determined from the heating scan.

extended from T_{depart} to extrapolate the equilibrium value of $T_f = T$. That is, T_f deviates from the equilibrium line at T_{depart} to the supercooling state when the polymer is cooled from a liquid of P_{liq} . The region of $T < T_f$, that is non-equilibrium state, can be seen in the left-side of the dotted line. Polymer is kept at constant temperature of T_A in the ageing experiment and T_f decreases according to the ageing time (t_A); P_{age} is the start of the ageing. ΔT_f denotes the decrease in T_f for t_A , and $\Delta T_{f\infty}$ is its limiting value; it reaches the equilibrium in the time of infinity. Alternatively, if it is not far below glass transition temperature (T_g), the equilibrium is reachable within observation time and no further change in T_f is possible. It is cooled further after the ageing period and then heated to observe DSC response, i.e., to measure the enthalpy recovery. T_f first crosses the dotted line in the heating process, and then further deviates from it to the region of $T_f < T$. Finally it catches up the equilibrium line by having a steeper slope upwards, where a shoulder-like increase in $c_p(T)$ and/or an overshoot appears in DSC curve. The start of this shoulder is commonly used for the location of the glass transition shoulder as the extrapolated onset temperature ($T_{g\text{-onset}}$) [21]. It is noteworthy that T_g is measured correctly only on cooling [22]. Also, note that T_A is given between the $T_{g\text{-onset}}$ and T_{depart} in this work so as to give a small value of $\Delta T_{f\infty}$, which will be discussed in the following section. Upon the temperature hold at T_A , T_f decreases; on the contrary, T_f increases when the sample is stretched isothermally at T_A , to which we paid an attention. If the increases in T_f were compared before and after the local rearrangement, it is expected to obtain information on the structural relaxation under the chain constraint. The analytical method we provide here is a measurement of T_f increase/decrease from the acquired $c_p(T)$ data, and thus does not measure the enthalpy itself. However, it exactly captures the relationship of the chain orientation by the stretch and the structural relaxation.

Regarding the increase in T_f by stretching at T_A , there is no existing data to show this phenomenon explicitly. However, it has been proposed at least in the enthalpy–temperature plot, that H isothermally decreases and increases by the temperature hold and the mechanical deformation, respectively [23]. Those reports to allude to T_f increase are seen for shear compliance, modulus and volume relaxation data [24–27]. It is also supported by DSC data obtained for stretched polystyrene films [28]. Deageing effect is reported as well for DSC curve with respect to compression deformation [29]. These existing data reminds us of the view that T_f increases by the stretch. This paper discusses on the basis of the fact that T_f increases, the difference in the shift of T_g -shoulder observed by DSC scans for both stretching-and-ageing, and ageing-and-stretching experiments.

2. Materials and methods

2.1. Sample and temperature program

A polystyrene pellet of G120K (Lot IF1606) was kindly supplied by Nippon Polystyrene. DSC scans of cooling and heating up to 350 °C showed no peaks, resulting from the crystallisation and melting, which suggests that the G120K sample does not show any property of a crystalline state. The film was fabricated using hot press machine at a pressure of approximately 20 MPa with thickness of 0.5 mm. $T_{g\text{-onset}} = 81$ °C was obtained for the film. The specimen with the size of 90 × 15 mm was cut out from the film and used for thermal ageing experiment with placing line markers for determining the stretch ratio ($d = L/L_0$), where L_0 and L are the distances between two markers before and after the stretch.

The temperature programs employed are schematically shown in Fig. 2; starting from a temperature of 200 °C, well above T_g (the former history was erased), the specimen was cooled to 84 °C of T_A

at a rate of $-12\text{ }^{\circ}\text{C}/\text{min}$, and then kept at T_A condition for the ageing process; it was quenched after a given ageing time and stored in a freezer at $-28\text{ }^{\circ}\text{C}$. Film chunks and the chuck holder, on which the specimen lies, were used to stretch with a handle stretcher while performing the ageing process. Views of the handle stretcher are available as the Supplementary Information. Stretching-and-ageing, ageing-and-stretching, both experiments were conducted while kept at T_A ; they are referred to as pre-hold and post-hold stretches, respectively. The indication of t_A includes the period required for the stretch. Immediately before the measurement, the specimen was taken from the freezer, cut into pieces, and then placed in a DSC cup to be used for the heating scan from the room temperature to $200\text{ }^{\circ}\text{C}$ with a rate of $5\text{ }^{\circ}\text{C}/\text{min}$. It was previously confirmed that the storage in a freezer has no influence on the heat flow curve. The DSC scans were conducted with a Seiko DSC-200 instrument with a method to overcome entropic shrinkage of samples to destabilise heat flow curves [28].

2.2. Model calculation

DSC curves for the samples of $d=1$ (i.e., those without stretching in the ageing) were analysed through $c_p(T)$ calculation based on TNM model. The stretched exponential form of eq. (2) was used as the relaxation function;

$$\phi = \exp[-(t_A/\tau_0)^\beta] \quad (2)$$

where $\beta = 0.399$, the value determined by the previous work, was used for the shape parameter [30]. In the $c_p(T)$ calculation, the evolution of the fictive temperature from one limiting case to another through the glass transition was calculated for any arbitrary set of temperature scans. The temperature scan was given to be exactly the same as the program of the ageing experiment which started in the equilibrium state at T_0 . The evolution can be calculated with eq. (3);

$$T_f(t) = T_0 + \sum_{i=1}^n \Delta T_i \left\{ 1 - \exp \left[- \left(\sum_{j=1}^n \frac{\Delta T_j}{Q_j \tau_j} \right)^\beta \right] \right\} \quad (3)$$

where ΔT_i is the temperature change corresponding to the i -th step and Q_j is the cooling rate or heating rate corresponding to the j -th step. The Boltzmann superposition summation over temperature appears instead of a corresponding summation over time [31]. The calculation yielded T_f data which was then converted to the heat capacity using eq. (4) in order to compare the calculation with the experimental data;

$$c_p(T) = c_{pg}(T) + \Delta c_p(T_f) \frac{dT_f}{dT} \quad (4)$$

where $\Delta c_p(T_f)$ is the difference in the heat capacity between the liquid and glassy states evaluated at T_f . The glass and liquid heat capacities (c_{pg} and c_{pl} , respectively) were determined for each curve in the range from approximately $T_g-10\text{ }^{\circ}\text{C}$ to $T_g-20\text{ }^{\circ}\text{C}$ for the glassy state, and from $T_g+10\text{ }^{\circ}\text{C}$ to $T_g+20\text{ }^{\circ}\text{C}$ in the liquid state.

The calculation data were used for the fitting procedure with the aim of reproducing five different DSC curves obtained. The curve fitting contains adjustable parameters of A , Δh^* and x ; in the calculation of eq. (1) $\ln(A)$ was used in practice instead of A . An iterative search routine for these parameters were used to determine the best set to reproduce heat capacity data with reference to the method of function minimisation; the successive substitutions of the parameters were carried out to find the minimum of the average square deviation defined as eq. (5).

$$\sigma_{ave} = \frac{1}{5N} \sum_{j=1}^N \sum_{i=1}^5 w(i) [c_{exp}(i,j) - c_{cal}(i,j)]^2 \quad (5)$$

The index i means the experimental scan while the index j denotes the points of each scan. More equations and variables, and

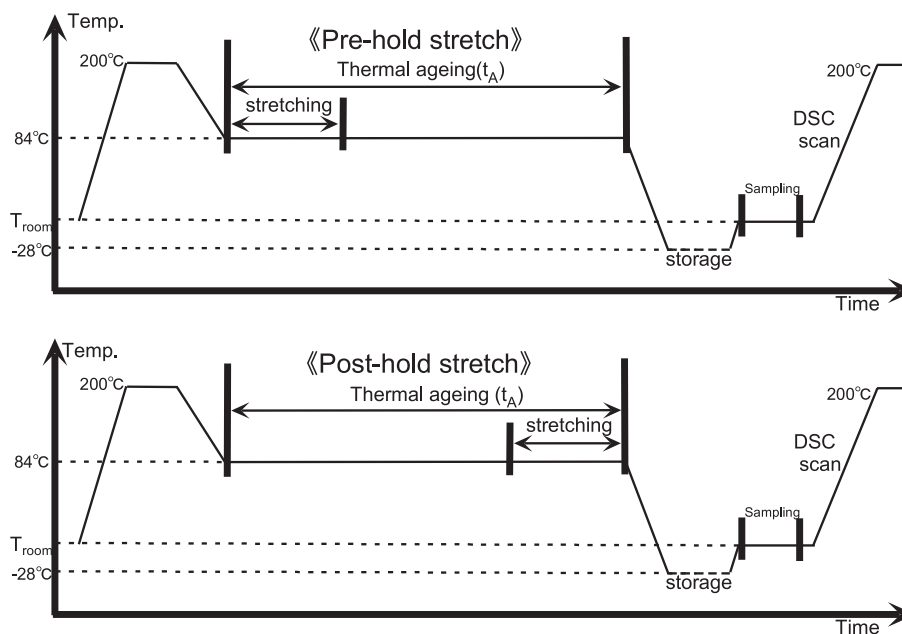


Fig. 2. Schematic diagrams of the pre-hold and post-hold stretches used to acquire DSC data of stretched films. While the temperature decreased from 200 to $84\text{ }^{\circ}\text{C}$, the specimen was fixed to the stretcher placed in an oven.

hence other matters to be considered, appear in the whole TNM framework (see refs. [32–35] and references cited therein).

In the $c_p(T)$ calculation for samples of $d > 1$, τ_0 need to be different from that of $d = 1$ in eq. (2). Moreover, it could vary depending on the pre-hold or post-hold experiments. Accordingly, it would be more reasonable to write $\phi'(d)$ and $\phi''(d)$ as the relaxation functions of pre-hold and post-hold experiments, respectively.

3. Results and discussion

Fig. 3 shows $c_p(T)$ plots acquired by the ageing experiments, which have a typical relaxation behaviour that larger enthalpy overshoot appears at longer t_A in the T_g -shoulder. The results of the data fitting with calculated $c_p(T)$ are also shown by the solid lines in Fig. 3. The parameters used for the calculation are $\ln(A) = -199$, $\Delta h^* = 595$ kJ/mol and $x = 0.71$.

Values of ΔH_t can be determined by the area bounded by $c_p(T)$ plots of $t_A = 0$ and given t_A . Those were 0.52, 0.97, 1.40 and 1.63 J/g for $t_A = 60, 120, 300$ and 1260 min, respectively, which were fairly small in comparison with those found in literature for polystyrene samples [36,37]; for example, $\Delta H_t = 0.81, 1.23, 1.93, 2.82$ and 2.96 J/g for $t_A = 24, 80, 300, 1000$ and 1900 min, respectively, in the ageing experiment at $(T_g - T_A) = 18^\circ\text{C}$ are reported in the previous DSC study [19]. The result obtained in this work can be ascribed to the experimental condition that T_A is located higher than $T_{g\text{-onset}}$, which implies the small ΔH_∞ condition mentioned in the introduction. Accordingly, the infinity value in the fictive temperature, $\Delta T_{f\infty}$, is

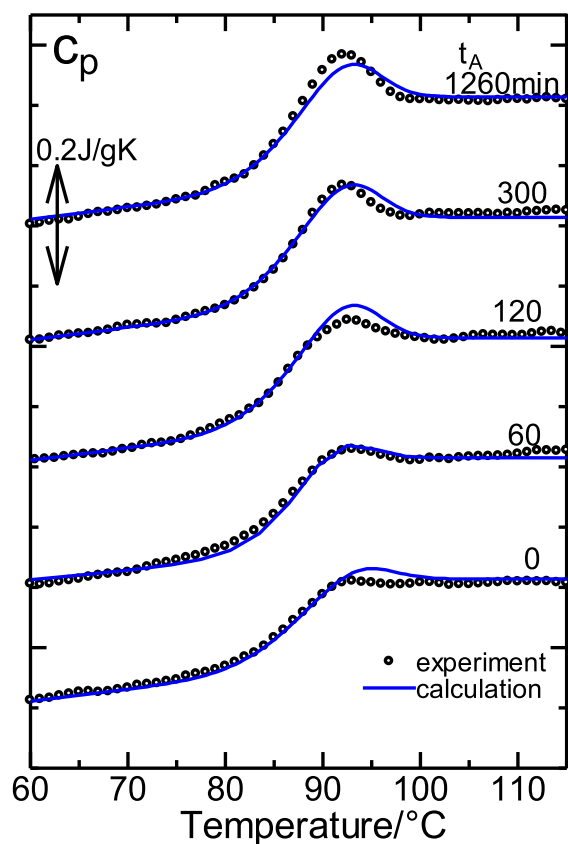


Fig. 3. $c_p(T)$ curves of G120K films without the stretch acquired by the heating scans after different ageing times, t_A , at $T_A = 84^\circ\text{C}$. The calculation curves were obtained with $\ln(A) = -199$, $\Delta h^* = 595$ kJ/mol, $x = 0.71$. Data are shifted vertically to be seen clearly.

considered small. It can be deduced that the decay amounts of T_f (indicated by ΔT_f in Fig. 1) in the sample before stretch and that after stretch will have little difference, which is meaningful in discussing the shoulder shift of the stretched sample in the text that follows.

Fig. 4(a) shows the results of heating scan after the ageing of $t_A = 60$ min for the films of pre-hold stretch; the T_g -shoulder shifted

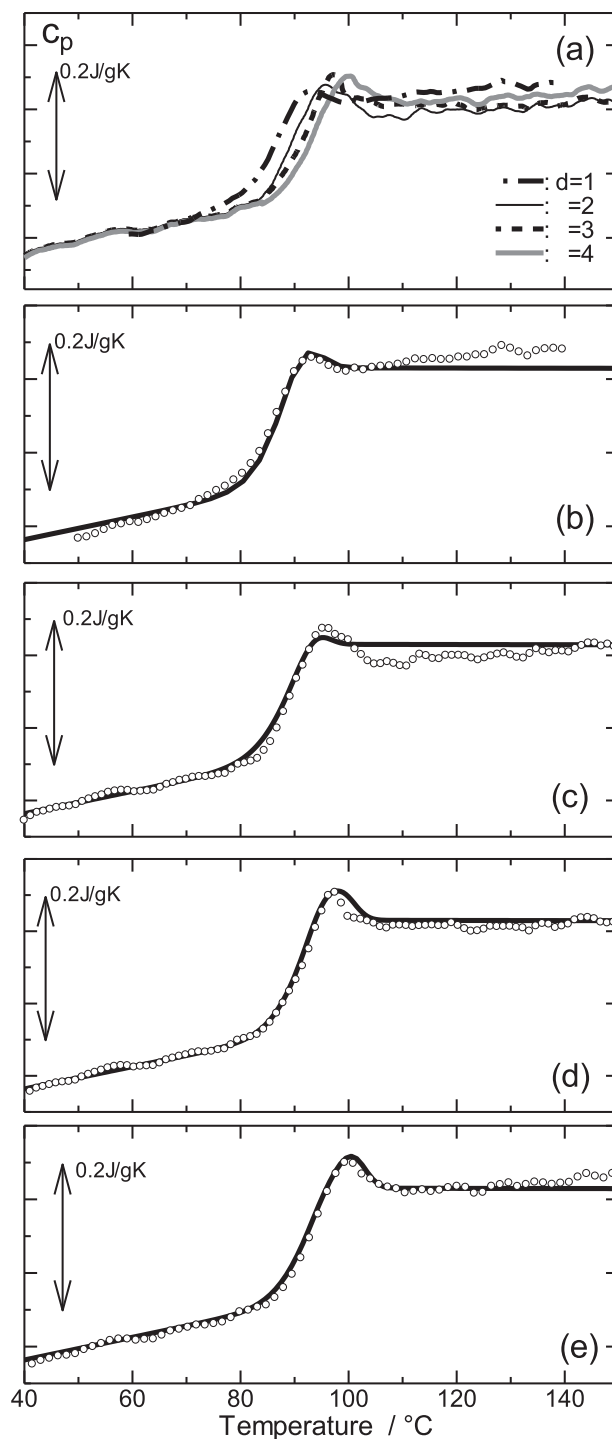


Fig. 4. (a) $c_p(T)$ curves of G120K films with the pre-hold stretch of various stretch ratios(d), acquired for the scans after the ageing of $t_A = 60$ min, $T_A = 84^\circ\text{C}$. The plots are shown separately by circles (\circ) in (b) $d = 1$, (c) 2, (d) 3 and (e) 4 with the calculation data of solid lines obtained by varying $\ln(A)$.

to higher temperature side as the increase in d . The results are phenomenologically in agreement with the shoulder shift of $\ln(A)$ variation seen in the model calculation using eqs. (1) and (3), where $T_{g\text{-onset}}$ increased with the increase in $\ln(A)$.

The shift of $T_{g\text{-shoulder}}$ shown in Fig. 4(a) might not directly be the increase in the glass transition temperature because it is measured correctly only on cooling. In order to examine the T_g increase in detail, the limiting fictive temperature (T_f') was calculated using eq. (6) for $c_p(T)$ data of Fig. 4(a), on the basis of the fact that several researchers have used T_f' determined from the heating $c_p(T)$ data to approximate T_g [38–40].

$$\int_{T_f'}^{T > T_g} (c_{pl} - c_{pg}) dT = \int_{T < T_g}^{T > T_g} (c_p - c_{pg}) dT \quad (6)$$

Values of T_f' determined for the pre-hold stretch of $t_A = 60$ min were summarised in Table 1 together with those of post-hold stretch. T_f' increased in the pre-hold stretch of $1 \leq d \leq 2.5$, and then levelled off against further increase in d . The increase in T_g is, as described below, related to the thermal stability which accompanies the chain orientation caused by the stretch. It can be considered from the result that the increase levelled off against d , that the effect is in a finite range in the pre-hold stretch. The relation between $T_{g\text{-onset}}$ and d in the post-hold stretch will be discussed later.

We need to look back here, the shoulder shift caused by varying $\ln(A)$ in the $c_p(T)$ calculation [19]. The shift takes place only in the vicinity of the parameter combination, those are three variables of $\ln(A)$, Δh^* and x , in which a fine curve fittings are seen between experimental and calculation $c_p(T)$ data. The shoulder shift due to $\ln(A)$ variation is attributed to T_f' , in other words, how much the samples depart from the equilibrium at T_f . This departure is mostly determined by T_f at the end of ageing period which is referred to as $T_{f\text{-end}}$ in this paper. Accordingly, it is necessary to inspect the processes from T_f at P_{age} to $T_{f\text{-end}}$ in order to interpret the result of Fig. 4(a).

There are two kinds of processes; the first one is the ageing alone and the second one is the series of the stretch and ageing. T_f decreases isothermally according to t_A in the process of ageing alone, which means that $T_{f\text{-end}}$ becomes lower than T_f of P_{age} . Subsequently, it goes through the region of $T_f < T$ to approach the line of $T_f = T$ when the heating scan is carried out. c_p overshoot most frequently appears in approaching. The overshoot shifts to higher temperature side and its amplitude becomes larger as the increase in t_A . When the process contains the stretch and ageing, it brings about T_f increase and T_f decrease, respectively. T_f increase gives rise to the increase in T_f' , and the approach to the $T_f = T$ line occurs at a higher temperature side in the subsequent heating scan, which results in the shift of the shoulder. It is noteworthy that the increase and decrease in T_f at T_A both work to shift $T_{g\text{-shoulder}}$ higher.

Although any relationship between the molecular structure and

$\ln(A)$ is not known, it is directly related to the relaxation time of the measure of rigidity with eq. (1). Film stretch and the resultant chain orientation causes the increases in thermal stability and the film rigidity which bring about the increase in τ , these relationships are qualitatively in agreement with the increase in $\ln(A)$. Needless to say, the physical meaning of A is primarily seen in the vibration period of molecules.

We attempted the model calculation concerning $c_p(T)$ data of Fig. 4(a) on the basis of the hypothesis that $\ln(A)$ may increase by the stretch; $\ln(A) = -199$ was used before the ageing, and the value slightly higher than -199 after the ageing. The calculation data reproduced well the shoulder shift and the position of the overshoot as shown in Fig. 4(b)–(e).

Next, the results of post-hold stretches are shown in Fig. 5(a); those are for samples of $t_A = 60$ min stretched after the temperature hold at 84°C . The shoulder shift was obviously more enhanced than the result of pre-hold stretch. The calculation curves have reasonably agreed with the experimental results, see Fig. 5(b)–(e), except that the shape of overshoot was not reproduced well in the $c_p(T)$ plot of $d = 4$. In addition, data of T_f in cooling steps (in which ageing and the stretch are included) obtained in the calculation of Fig. 5(b)–(e) were plotted in Fig. 6 to depict the decrease in T_f due to $t_A = 60$ and the subsequent increase due to the stretch. The increment becomes larger with the stretch ratio. As a result, it was shown that the increase in d give rise to the increase in $T_{f\text{-end}}$, and finally the increase in $T_{g\text{-onset}}$.

The shoulder shifts were summarised in Fig. 7(a) and (b) as the plots of $T_{g\text{-onset}}$ against d . Following two features can be mentioned for these results; the shift of post-hold is larger than that of pre-hold stretch, the shift of $1.5 \leq d \leq 2.5$ is significantly pronounced with the increase in t_A in the post-hold stretch. In order to interpret them, the behaviour of $T_{f\text{-end}}$ was examined for each experiment. In fact, $T_{f\text{-end}}$ can be written with the variables already defined in this paper.

$$T_{f\text{-end}} = T_A + (\Delta T_{f\text{-}\infty} + T') \times \phi' \text{ for pre-hold stretch,} \quad (7)$$

$$T_{f\text{-end}} = T_A + \Delta T_{f\text{-}\infty} \times \phi'' + T'' \text{ for post-hold stretch,} \quad (8)$$

where T' and T'' are the increments in fictive temperature due to the stretches of pre- and post-hold, respectively; T'' is the same as that indicated by the upward arrow in Fig. 6. The condition that T_A is higher than $T_{g\text{-onset}}$ of unstretched sample is used in this work, and the resultant ΔH_t becomes substantially small. Therefore, ΔT_f value is considered to be small in the ageing experiment, and there will be little difference in decay profiles of ϕ' and ϕ'' . Then, the behaviour of $T_{f\text{-end}}$ becomes interpretable with the approximation that $\Delta T_{f\text{-}\infty} \times \phi' \approx \Delta T_{f\text{-}\infty} \times \phi''$.

The comparison between T' and T'' can be accounted for with reference to the creep data reported for the viscoelastic evolution in the course of structural recovery during the ageing experiment [41–43]. According to them, the response against the large stress shows that the retardation in creep compliance increases with increasing amount of ageing [42]. This effect is well documented by Struik [44], and has been reported not only for polystyrene but also for several polymer glasses. That is, the structural relaxation evolves, and the increase in film rigidity also accompanies in our ageing experiment. To stretch more rigid material brings about larger increment in the internal energy, and simultaneously in fictive temperature. As a consequence, the relation of $T < T''$, and then $T \times \phi < T''$ can be derived. Thus, $T_{f\text{-end}}$ of post-hold stretch is larger than that of pre-hold stretch, which is a legitimate grounds for the result that $T_{g\text{-onset}}$ of post-hold stretch is higher than that of pre-hold stretch.

Table 1
Comparison of $T_{g\text{-onset}}$ and T_f' for pre-hold and post-hold stretches ($t_A = 60$ min).

d	pre-hold		post-hold	
	$T_{g\text{-onset}}/^\circ\text{C}$	$T_f'/^\circ\text{C}$	$T_{g\text{-onset}}/^\circ\text{C}$	$T_f'/^\circ\text{C}$
1.5	84.8 ± 0.3	85.2 ± 0.3	84.5 ± 0.2	84.9 ± 0.3
2	85.5 ± 0.7	85.6 ± 0.7	86.7 ± 0.3	87.0 ± 0.3
2.5	86.8 ± 0.7	87.1 ± 0.7	88.6 ± 0.3	88.9 ± 0.3
3	87.5 ± 1.0	87.8 ± 1.2	91.6 ± 1.0	92.0 ± 1.0
3.5	86.9 ± 1.4	87.3 ± 1.6	93.0 ± 0.2	93.3 ± 0.2
4	87.5 ± 0.2	87.9 ± 0.2	94.0 ± 0.2	94.4 ± 0.2

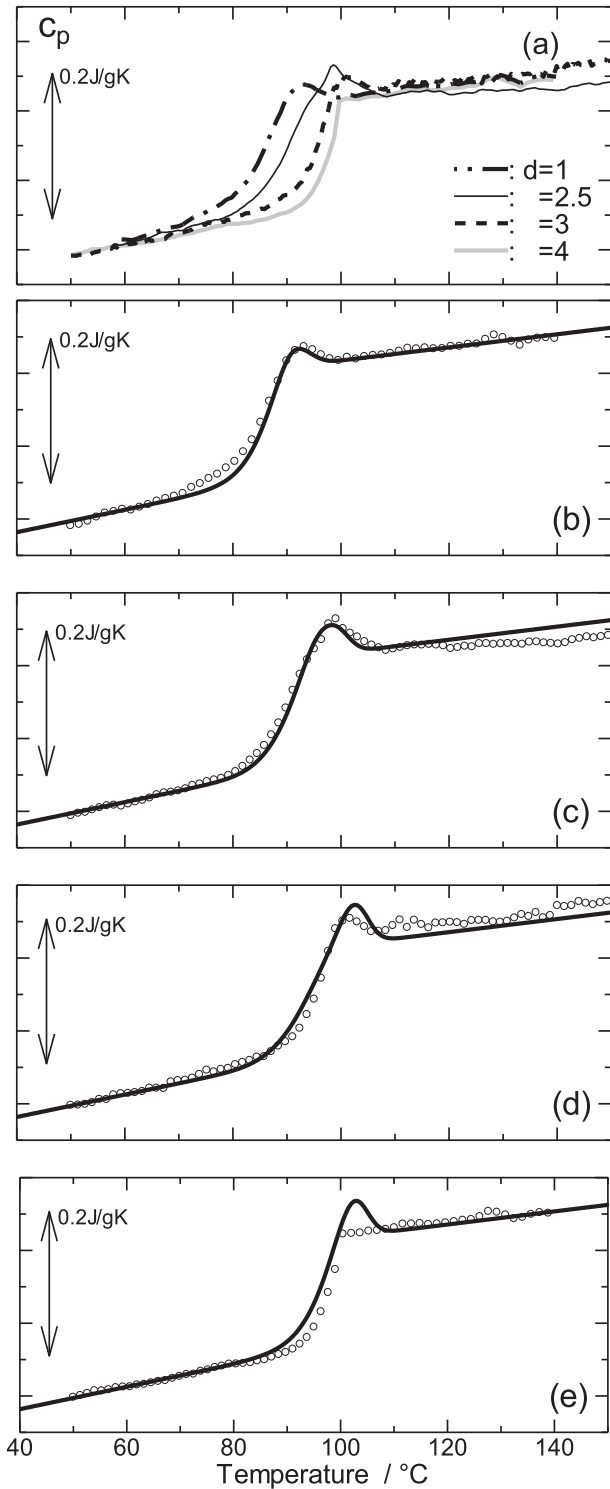


Fig. 5. (a) $c_p(T)$ curves of G120K films with the post-hold stretch of various stretch ratios (d), acquired for the scans after the ageing of $t_A = 60$ min, $T_A = 84$ °C. The plots are shown separately by circles (\circ) in (b) $d = 1$, (c) 2.5, (d) 3 and (e) 4 with the calculation data of solid lines obtained by varying $\ln(A)$.

The result of the significant shoulder shift in the post-hold stretch of $1.5 \leq d = 2.5$ shown in Fig. 7(b) can be attributed to the fact that the amount of T_f increase is raised by the evolution of structural relaxation against the stretching with the increasing amount of ageing. The amount of T_f increase appears to be saturated

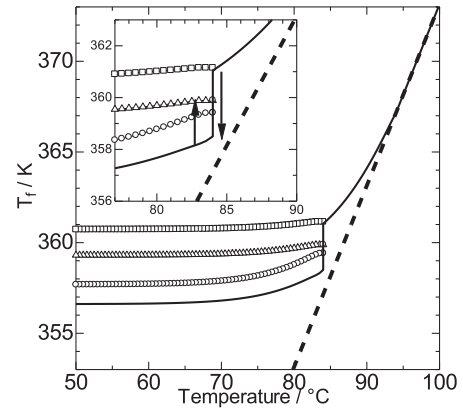


Fig. 6. Plots of T_f vs. T in cooling step for the post-hold stretch of $t_A = 60$ min $d = 1$ (—), 2.5 (\circ), 3 (\triangle), 4 (\square). In the inset, the plot was magnified around T_A . The downward arrow is the decrement of T_f due to the ageing, the upward arrow is the increment due to the stretch of $d = 3$. The line of $T_f = T$ (dashed line) is presented to guide the eye.

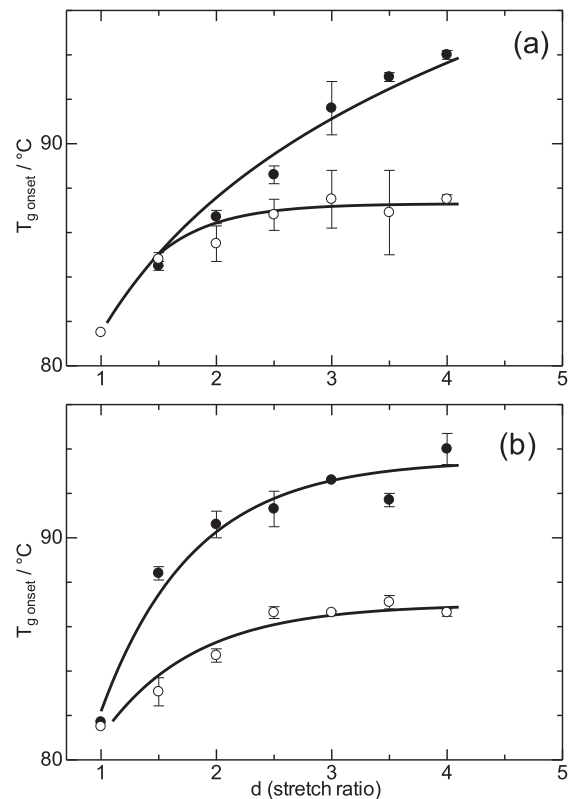


Fig. 7. The relations of $T_{g\text{-onset}}$ and the stretch ratio (d) determined for the pre-hold (\circ) and post-hold (\bullet) stretches. (a) $t_A = 60$ min, (b) $t_A = 300$ min.

against the further increase in d as the plateau region obviously exists in the plot around $d = 4$ of the post-hold stretch.

4. Concluding remarks

The effect of stretching was investigated in the enthalpy relaxation of isothermal ageing for polystyrene film, by conducting both the pre-hold and post-hold stretches. The response to the stretch appeared as the shift of T_g shoulder in the heating DSC scan, which was interpreted in terms of $T_f - T$ plot determined from the model

calculation based on the TNM framework. The increase in T_f caused by the film stretch was found, which implies the opposite of the asymptote towards the equilibrium during the isothermal ageing, and the primal reason for the shift of T_g shoulder. A significant discrepancy for the shift of T_g shoulder was also found between the experiments of the pre-hold and post-hold stretches. It was deduced from this result that the increase in film rigidity was brought about with the evolution of structural relaxation; to stretch more rigid film induces the larger increment in the internal energy and, as a result, the larger increment in fictive temperature. The result that the shift of T_g shoulder levelled off when the stretch ratio increased to some extent was interpreted in terms of the amount of T_f increase.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.polymer.2018.03.041>.

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