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Thermochimica Acta 431 (2005) 149–154

thermochimica acta

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Heat flows on the heating process after aging of glassy poly(methyl methacrylate) measured by temperature modulated differential scanning calorimeter

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Received 31 October 2004; received in revised form 9 January 2005; accepted 27 January 2005
Available online 5 March 2005

Abstract

Reversing and non-reversing heat flows on the heating process after isothermal aging of glassy atactic poly(methyl methacrylate) was measured by temperature modulated differential scanning calorimeter. The reversing and non-reversing heat flows of the non-aged sample were subtracted from those of the aged sample to investigate only the isothermal aging effects. The difference between the aged and non-aged sample was most significant in the sample aged at 100 °C in both the reversing and non-reversing heat flows. Starting temperature of the difference in the non-reversing heat flow became higher with the aging temperature. On the other hand that of the reversing heat flow was around 70 °C irrespective of the aging temperature. Based on these results it is suggested that recovery of the molecular mobility at the glass transition occurs by two steps.

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Keywords: Glass transition; Aging; Poly(methyl methacrylate); Temperature modulated DSC; Heat flow

1. Introduction

It is known well that irreversible heat absorption is observed in the glass forming polymers on the heating process after aging around the glass transition temperature [1]. This phenomenon has been utilized as a measure of aging in the glassy sate. Differential scanning calorimetry (DSC) has been used to measure the irreversible heat absorption. However, the amount of the heat absorption is not easily estimated from the results of DSC because of ambiguity in drawing the base line. In order to solve this problem temperature modulated DSC (TM-DSC) has been utilized by many authors. The heat flow to the sample could be successfully separated into the reversing and non-reversing heat flows. The irreversible heat absorption after aging was clearly observed in the non-reversing heat flow and the ambiguity in drawing the base line was much reduced because the non-reversing heat flow was almost zero outside of the glass transition region. Development of TM-DSC was a notable progress in instrument for the study of aging of the glassy state.

However, there remain two difficulties in TM-DSC measurement. One is originated in the essential properties of the glassy state. Since aging progresses depending on temperature and time we have to take account of thermal history of the sample. In order to investigate aging at a fixed temperature aging at other temperature should be avoided. However, for measurement of the irreversible heat absorption on the heating process by TM-DSC temperature has to be scanned at a finite, practically rather slow, underlying heating rate. Time required for cooling is not negligible as well. These thermal histories cause additional aging effect. The other is related to the way to calculate the non-reversing heat flow, that is,

$$\text{non-reversing heat flow} = \text{total heat flow} - \text{reversing heat flow}. \quad (1)$$

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0040-6031/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2005.01.063

Temperature of the step in the reversing heat flow accompanying the glass transition depends on the modulation frequency while that of the total heat flow depends on the underlying heating rate. Since the modulation frequency and the underlying heating rate are independent parameters from each other the steps are not identical with each other [2]. This difference between the total and reversing heat flows appears in the non-reversing heat flow together with the irreversible heat absorption.

In this work we applied TM-DSC to aging of atactic poly(methyl methacrylate) (at-PMMA). Samples were isothermally aged at various temperatures around the glass transition temperature for a fixed time to study temperature dependence of the aging effect. TM-DSC study of the glass transition of at-PMMA was carried out successfully and usefulness of TM-DSC was clearly shown [3]. In Ref. [3] the authors paid attention to change in the as measured heat flow traces with aging time. In this work we paid attention to difference between the heat flow of the aged sample and that of the non-aged sample, which has the same thermal history with the aged sample excepting the aging, in order to minimize the effects of the additional thermal history and discrepancy of the step temperature. Some results of the reversing heat flow were presented in else where in comparison with the results from dielectric measurement [4]. In this paper aging temperature dependence of the reversing and non-reversing heat flows investigated in detail.

2. Experimental

At-PMMA (Mw = 93,300, Mw/Mn = 2.01) was used. At-PMMA pellet was heated on a hot plate and pressed just after passing the glass transition temperature to form a film of 150 μm thick. A disk shaped sample (2.20 mg) was cut from the film and put in an aluminum pan with an aluminum lid. After crimping the pan the bottom surface of the pan was slightly ground to remove the deformation due to the crimping. A commercial instrument, MDSC2920 (TA Instruments), was used for TM-DSC measurement. Firstly the sample was heated to 220 °C to make it equilibrium. After five minutes the sample was cooled to the aging temperature, T_a, at 10 K/min and aged for 6 h. After the aging the sample was cooled to 10 °C at 10 K/min. Heating process started without delay at 5 K/min. Period and amplitude of the temperature modulation were 30 s and 0.5 K, respectively. After the sample was heated to 220 °C next temperature cycle started with a different T_a. The isothermal aging was made at temperatures between 80 and 140 °C. The non-aged sample was measured as well for comparison. Nitrogen gas was flowed at 30 ml/min to avoid degradation of the sample.

3. Results and discussion

Before detailed data analysis applicability of Eq. (1), which is just assumed in many cases, was checked on the basis of the experimental results. Generally the heat flow to the sample can be expressed by the next equation:

$$J = C(\beta)\beta + (C'(\omega) - \mathrm{i}C''(\omega))\mathrm{i}\omega\tilde{T}\,\mathrm{e}^{\mathrm{i}\omega t} + F(T_0 + \beta t) + F'_{\mathrm{T}}(T_0 + \beta t)\tilde{T}\,\mathrm{e}^{\mathrm{i}\omega t}, \tag{2}$$

where J is the heat flow to the sample. The first term on the right hand side is the heat flow accompanying the steady heating at a constant rate of β. $C(\beta)$ is equivalent to the heat capacity obtained by the conventional DSC which depends on β around the glass transition temperature. The second term is the heat flow accompanying the periodic temperature change at the rate of $\mathrm{i}\omega\tilde{T}\,\mathrm{e}^{\mathrm{i}\omega t}$ in which $\tilde{T}$, ω, i and t are amplitude, angular frequency, the square root of -1 and time, respectively. $C'(\omega) - \mathrm{i}C''(\omega)$ is the complex heat capacity depending on ω [5]. The third and fourth terms are heat flow caused by spontaneous change in the sample such as enthalpy recovery on the heating process after aging around the glass transition temperature, irreversible chemical reaction, melting and crystallization from the superheated or supercooled state and so on. The heat flow due to the spontaneous change is expressed in approximation to the first order of the temperature modulation; the third and fourth terms correspond to the zeroth and the first order terms, respectively. T_0 is the temperature at $t = 0$.

Eq. (2) is rewritten as

$$J = C(\beta)\beta + F(T_0 + \beta t) + \mathrm{i}(\omega C'(\omega) + \varphi''(\omega))\tilde{T}\,\mathrm{e}^{\mathrm{i}\omega t} + (\omega C''(\omega) + \varphi'(\omega))\tilde{T}\,\mathrm{e}^{\mathrm{i}\omega t}, \tag{3}$$

where we take account of the case that F'_{T} is a complex quantity expressed as $\varphi' + \mathrm{i}\varphi''$. When the rate of the spontaneous change follow the temperature change without delay F'_{T} is given by the temperature derivative of F (T) and $\varphi'' = 0$ [6]. F'_{T} was found to become a complex quantity at the melting temperature of polymers [7] and it was theoretically deduced by Toda and Saruyama [8]. The sum of the first and second terms on the right hand side is the total heat flow. The sum of the third and fourth terms is called cyclic component of the heat flow. For successful separation of the heat flow to the reversing and non-reversing heat flows it is necessary that $C''(\omega)$, φ' and φ'' are negligible and the absolute value of the cyclic component divided by $\omega\tilde{T}$ is equal to $C'(\omega)$. Contribution from the fourth term can be checked by measuring the phase shift in the cyclic component. If the contribution from the fourth term is not negligible there will be notable phase shift. Upper curves of Fig. 1 show the phase of the cyclic component on the heating process after annealing at 105 °C (solid) and after cooling without annealing (dashed). They agreed well with each other and exhibited only shallow dips around the glass transition. The depth was less than 5 degrees irrespective of the annealing condition which was small enough to be neglected. The values of the phase angle are not corrected for the instrumental parameters but the depth will not be changed significantly after the correction. Contribution from φ'' was checked by comparing the revers-

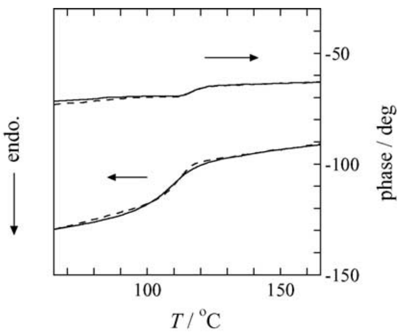

Fig. 1. The upper curves are the phase of the cyclic component on the heating process after annealing at 105 °C (solid) and after cooling without annealing (dashed). The lower curves are the reversing heat flow of the cooling process without annealing (solid) and the following heating process (dashed).

ing heat flows on the heating and cooling processes since the enthalpy recovery occurs only on the heating process. The lower curves of Fig. 1 are the reversing heat flow of the cooling process without annealing (solid) and that of the following heating process (dashed). They agreed well with each other. As will be shown later the enthalpy recovery occurred on the heating process even in this case. This result suggested that the heat flow due to the enthalpy recovery did not cause φ'' which could not be neglected. Therefore it was confirmed that $C'(\omega)$ was obtained from the cyclic component. In order that the non-reversing heat flow calculated by Eq. (1) agrees with $F(T_0+\beta t)$, $C'(\omega)$ has to agree with $C(\beta)$ since the reversing heat flow is given by $C'(\omega)\beta$. This point will be discussed below. Expression of the heat flow by the sum of the heat flow due to the heat capacity and that due to the spontaneous change was introduced by Reading and coworkers in early papers about TM-DSC [9–11]. Eqs. (2) and (3) are written in more detailed form than the original expression taking account of the complex heat capacity [5] and complex nature of F'_{T} [7,8].

Fig. 2 shows the total, reversing and non-reversing heat flow traces of the non-aged sample. For comparison linear correction is made for the total heat flow so that the trace at temperature lower than the glass transition temperature, T_g, agrees with the reversing heat flow trace. It can be seen that the shape as well as the position of the stepwise change are different in the two heat flow traces. Accompanying change in the underlying heating rate or the modulation frequency the step position of the total or reversing heat flow shifts, respectively, but the shape of the step stays almost unchanged. Therefore it can be said that the dip in the non-reversing heat flow trace contains contribution from the irreversible heat absorption due to the aging. However, to estimate each contribution to the dip from the aging and the discrepancy of the step position is difficult. The total and reversing heat flow traces are not identical with each other at temperatures higher than T_g. The origin of this discrepancy was not identified but good reproducibility of the heat flow traces was confirmed in repeating measurements with the same condition. Therefore it can be said that the discrepancy does not seriously affect the data analysis below.

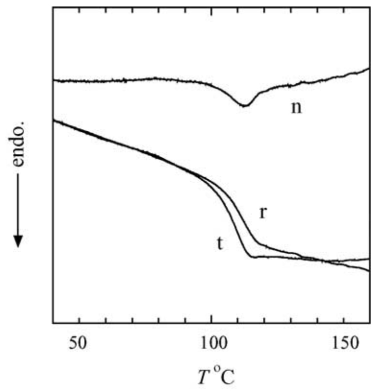

Fig. 2. Total (t), reversing (r) and non-reversing (n) heat flow traces of the heating process of the sample without isothermal aging.

In order to extract the effect of isothermal aging from the observed non-reversing heat flow we subtracted the heat flow of the non-aged sample from that of the aged sample. Fig. 3 shows the non-reversing heat flow traces; Fig. 3a and b show traces as measured and after subtraction, respectively. The traces of $T_a = 115\,°\mathrm{C}$ and higher in Fig. 3b are almost flat. This shows that the sample was in equilibrium state at temperatures down to 115 °C on the cooling process. The traces of $T_a = 80$ and 85 °C in Fig. 3a have double dips and the trace of $T_a = 90\,°\mathrm{C}$ exhibits wavy tail on the high temperature side of the dip. The double dips and the wavy tail are not seen in Fig. 3b. In Fig. 4 traces of $T_a = 80$ and 85 °C are compared with that of the non-aged sample. The non-aged trace agrees very well with the high temperature dip of the double dips of the $T_a = 80$ and 85 °C traces. Based on this result we assume that the effect of the isothermal aging is additive to the aging effect during the temperature scan and the non-reversing heat flow due to discrepancy of the step positions is independent of T_a. Shape, depth and position of the dips in Fig. 3b change smoothly over the whole range of T_a. This supports the above assumption. The dip is deepest around $T_a = 100\,°\mathrm{C}$. Shape of the dip is almost symmetric. The minimum of the dip moves to higher temperature as T_a becomes higher. Difference between the starting temperature of the dip and T_a decreases as T_a becomes higher; it was 10 K for $T_a = 80\,°\mathrm{C}$ and almost zero for $T_a = 105\,°\mathrm{C}$.

Fig. 5 shows the reversing heat flow traces; a and b correspond to those of Fig. 3. The traces in Fig. 5b are vertically extended twice. The traces of $T_a = 110\,°\mathrm{C}$ and higher are almost flat. The traces of $T_a = 105\,°\mathrm{C}$ and lower exhibit peaks. Since contribution from irreversible heat emission to the reversing heat flow is negligible the peaks can be attributed to change in the heat capacity during the isothermal aging. As can be seen in Fig. 5b the effect of the heat capacity change was observed only around T_g. This shows that the heat capacity of the glassy state did not change during the isothermal aging. What changed is the heat capacity of the degrees of freedom characteristic of the molten state. Such degrees of freedom are released gradually as the temperature increases

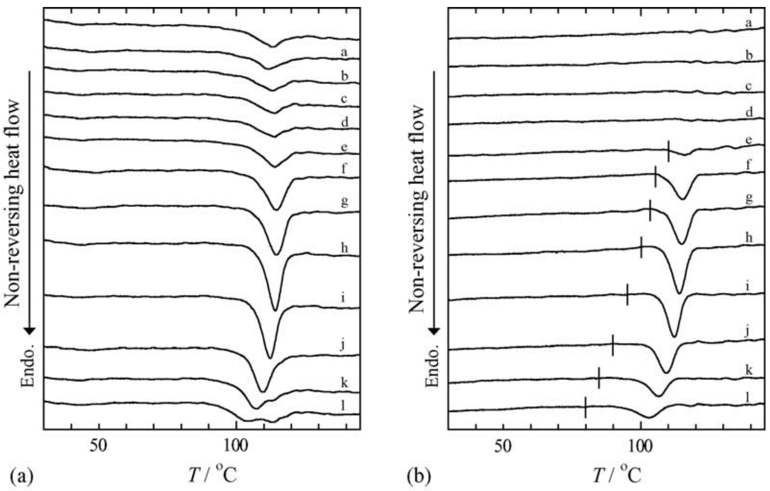

Fig. 3. Non-reversing heat flow traces after isothermal aging at a: 140 °C, b: 130 °C, c: 120 °C, d: 115 °C, e: 110 °C, f: 105 °C, g: 103 °C, h: 100 °C, i: 95 °C, j: 90 °C, k: 85 °C and l: 80 °C. (a) Observed traces. The top trace is that of the non-aged sample. (b) The curves are obtained by subtracting the non-aged trace from the aged traces in a. Short vertical lines show the position of T_a.

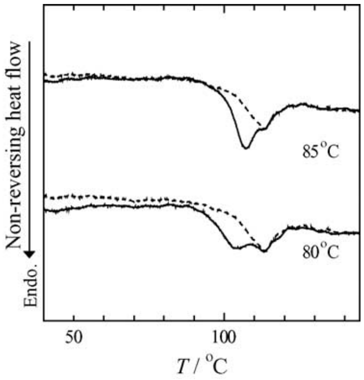

Fig. 4. Comparison between the non-reversing heat flow traces of $T_a = 80$ and 85 °C (solid curve) with the trace of the non-aged sample (dashed curve).

after passing T_g. The peaks of Fig. 5b mean that the amount of released degrees of freedom is less in the aged samples than in the non-aged sample at temperature just above T_g. This is consistent with an idea that the molecules packed in more stable state begin to move at higher temperature than those in the non-aged sample. T_a dependence of the height and position of the peak is similar to the case of Fig. 3. The peak is highest around 100 °C. The peak position moves to higher temperature as T_a becomes higher. However, the shape of the peak is not symmetric but with long tail on the lower temperature side.

Fig. 6 shows the total heat flow traces before (a) and after (b) subtraction of the non-aged trace. By subtraction of the non-aged trace it became easier to see the effects of the isothermal aging. However, the origin of the peaks just before the dips cannot be elucidated from Fig. 6b. Subtraction of the

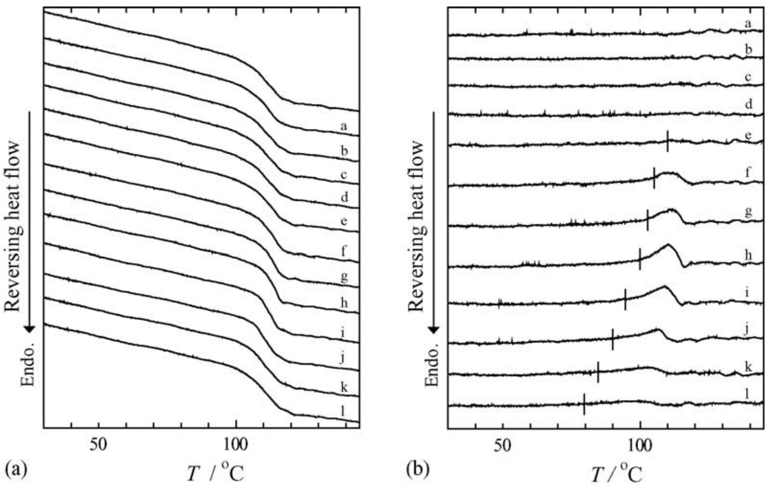

Fig. 5. Reversing heat flow traces after isothermal aging at a: 140 °C, b: 130 °C, c: 120 °C, d: 115 °C, e: 110 °C, f: 105 °C, g: 103 °C, h: 100 °C, i: 95 °C, j: 90 °C, k: 85 °C and l: 80 °C. (a) Observed traces. The top trace is that of the non-aged sample. (b) The curves are obtained by subtracting the non-aged trace from the aged traces in (a). Short vertical lines show the position of T_a.

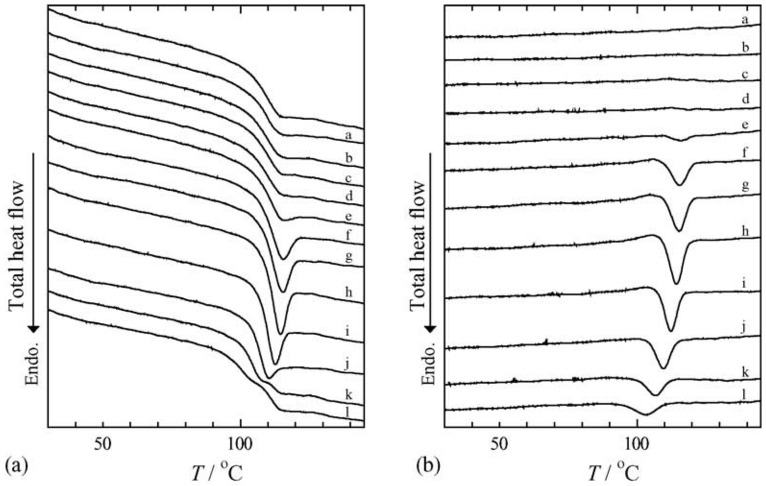

Fig. 6. Non-reversing heat flow traces after isothermal aging at a: 140 °C, b: 130 °C, c: 120 °C, d: 115 °C, e: 110 °C, f: 105 °C, g: 103 °C, h: 100 °C, i: 95 °C, j: 90 °C, k: 85 °C and l: 80 °C. (a) Observed traces. The top trace is that of the non-aged sample. (b) Curves are obtained by subtracting the non-aged trace from the aged traces in (a).

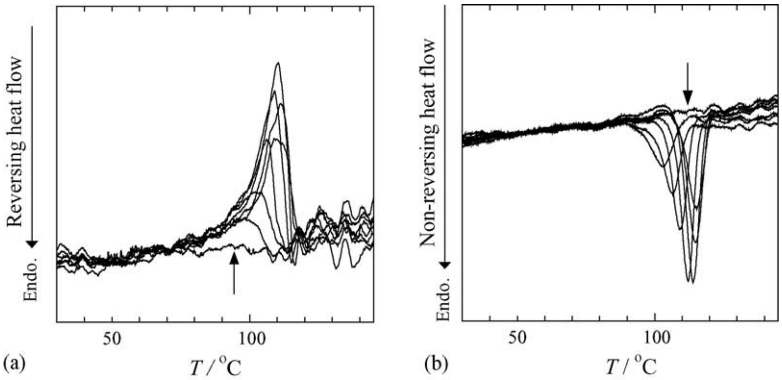

Fig. 7. (a) Reversing and (b) non-reversing heat flow traces after subtraction of the non-aged trace. Traces of $T_a = 80$, 85, 89, 95, 100, 103 and 105 °C are superimposed on the trace of $T_a = 140$ °C (indicated by arrows).

non-aged sample will be a useful method to study change in the aging effects accompanying changing the aging condition, but this method should be utilized with separation of the heat flow into the reversing and non-reversing heat flows.

Fig. 7 shows the reversing and non-reversing heat flow traces after subtraction of the non-aged trace superimposed on the trace of $T_a = 140$ °C which is shown as the base line. Each trace is vertically moved to coincide with the base line at 50 °C. It can be seen that all peaks in Fig. 7a start around 70 °C and the peak top position depends on T_a. On the other hand starting temperature of the dip in Fig. 7b depends on T_a. In both Fig. 7a and b the end point of the peak or the dip does not exceed 120 °C. It is reasonable to say that both the peak of the reversing heat flow and the dip of the non-reversing heat flow are attributed to release of the degrees of freedom characteristic of the molten state. Results shown in Fig. 7 suggest that the release of the degrees of freedom occurs by two steps. The first and second steps are related to the peak of the reversing heat flow and the dip of the non-reversing heat flow, respectively. If aging does not occur release of the degrees of freedom will take place without irreversible heat absorption. This type of releasing process is considered to take place in the annealed sample as well but the amount of the released degrees of freedom is reduced. This suggests that the starting temperature of the peaks of the reversing heat flow is the starting temperature of this type of releasing. This is the first step of the release. It is considered that the degrees of freedom fixed during aging need activation energy to be released. According to this idea the starting temperature of the dip corresponds to the starting temperature of this type of releasing. This is the second step of the release. This simple phenomenological model is directly deduced from the experimental results. However, the molecular process underlying this phenomenological model is left to be studied.

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