



Slow dynamics in thermal expansion of polyvinyl acetate thin film with interface layer

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Abstract

The experimental observation of an unusual thickness change in polyvinyl acetate (PVAc) thin films during the temperature cycle across the glass transition temperature (T_g , ~ 31 °C) is reported. After sufficient thermal treatment at the high-temperature side of T_g , an unexpected lack of thickness change can be observed during cooling in the rubbery state; with further cooling beyond T_g , the thickness of the PVAc thin film can increase abruptly. However, the thermally responsive behaviors recover to normal during the heating process. The thickness does not change in the glassy state and then increases in the rubbery state. In the present research, these asymmetric thermally responsive behaviors of PVAc thin films were confirmed by an X-ray reflectivity technique in repeated experiments. To clarify the mechanism, the relationship between the unusual thickness change and the fine structural changes in PVAc thin films was considered. It is proposed that an interface layer might exist and vary with the conditions of the polymer thin-film system, causing an unusual thickness change in the polymer thin film with the variation in temperature.

Introduction

A polymer thin film is an interesting system, the properties of which can change considerably because of the changes in the structure at the interface, particularly those of the glass transition [1–7]. In the past decades, many researchers have observed that thin-film systems of polymers exhibit a fairly different nature compared with that of the bulk, for example, changes in the glass transition temperature (T_g) under different interface conditions and the dewetting of an ultrathin film in the glassy state [8–14]. In these unusual phenomena, negative thermal expansion (NTE) is an interesting and confusing behavior observed in polymer ultrathin films [15, 16]. Some materials exhibit a suppression of thermal expansion, or even contraction, instead of an increase in volume during heating, and this phenomenon has promising applications in the further development of

high-precision instruments. However, the research on polymer thin-film systems is still limited, especially on the thermal expansion process.

In 1993, Orts et al. [17] reported the unusual temperature-dependent thickness of polystyrene (PS) ultrathin films on silicon. In their research, the thickness change in different PS ultrathin films with temperature was studied by the X-ray reflectivity technique, which is based on the interference analysis of the reflections from each interface and is extremely sensitive to the layered structure along the depth of the film at an angstrom-to-nanometer scale [18]. In 1994, Reiter et al. [12] also observed an increase in the isothermal thickness of PS ultrathin films and proposed that this phenomenon occurs during the dewetting process. In 2002, the reversible NTE in PS ultrathin films in a glassy state was first studied by Mukherjee et al. [19] with a synchrotron beamline, which further extended the investigation of the usual phenomena. In 2004, another polymer thin-film system, polycarbonate ultrathin films, was studied by Soles et al. [20] to determine the mechanism of NTE in polymer thin films. In their report, the effect of a hydrophobic/hydrophilic interface was first studied on the NTE of a polymer ultrathin-film system. In 2005, Kanaya et al. concluded their work on the NTE of a PS ultrathin-film system, and two different NTE behaviors with different kinetics were proposed [21–23]. In a recent study, the

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authors reported a new finding on the NTE of a polymer thin-film system. Another two NTE behaviors were confirmed in polyvinyl acetate (PVAc) thin films with different thicknesses from 10 to 100 nm, and a multilayer structure was proposed for the mechanism of the NTE in polymer thin-film systems [24]. During the past 25 years, with the continuous generation of experimental data, research regarding the mechanism of NTE has constantly advanced. Particularly in the past 15 years, the ultraslow thin-film thickness change associated with the NTE of polymer thin-film systems has become one of the most important research topics.

In the present study, further research on the NTE in PVAc thin films was conducted. The thin film (67 nm) was prepared on a silicon wafer with a native silicon dioxide layer. Some new phenomena were observed: in the temperature cycle between 45 and 19 °C, (i) when the PVAc thin film was kept above its T_g for sufficient time, the coefficient of thermal expansion (CTE) significantly decreased in the rubbery state at the initial state; (ii) however, after passing the glass transition of the PVAc thin film from the rubbery state to the glassy state, the NTE was clearly observed with cooling; and (iii) one interesting finding was that when the cooling finished and the heating started, the thermal expansion behaviors of the PVAc thin film recovered to normal, i.e., the thickness change was small in its glassy state and then abruptly increased as the temperature crossed T_g . Based on this observation, it is proposed that an interface layer might exist and vary with the conditions of the polymer thin-film system, causing the unusual thickness change of the polymer thin film with temperature.

Experimental

Commercial PVAc powder (Sigma-Aldrich Co., USA) was used for the sample preparation. The number-average and weight-average molecular weight were approximately $M_n = 59$ and $M_w = 107$ k. The polydispersity, M_w/M_n , was ~ 1.8 , which could still be considered safe to avoid the inhomogeneous aggregation of the components with different molecular weights in the polymer thin film [25]. The PVAc thin film was prepared on a silicon (100) wafer (SUMCO Co., Japan, cut to the size of 15×15 mm and then cleaned by nitric acid) by spin coating (SC-400, Oshigane Co., Ltd., Japan) with a 2-wt% PVAc toluene solution (Wako Chemical, Japan) at a rotation of 4000 rpm for 40 s. After spinning, an annealing was conducted at 45 °C for more than 113 h until the thickness of the PVAc thin film did not change.

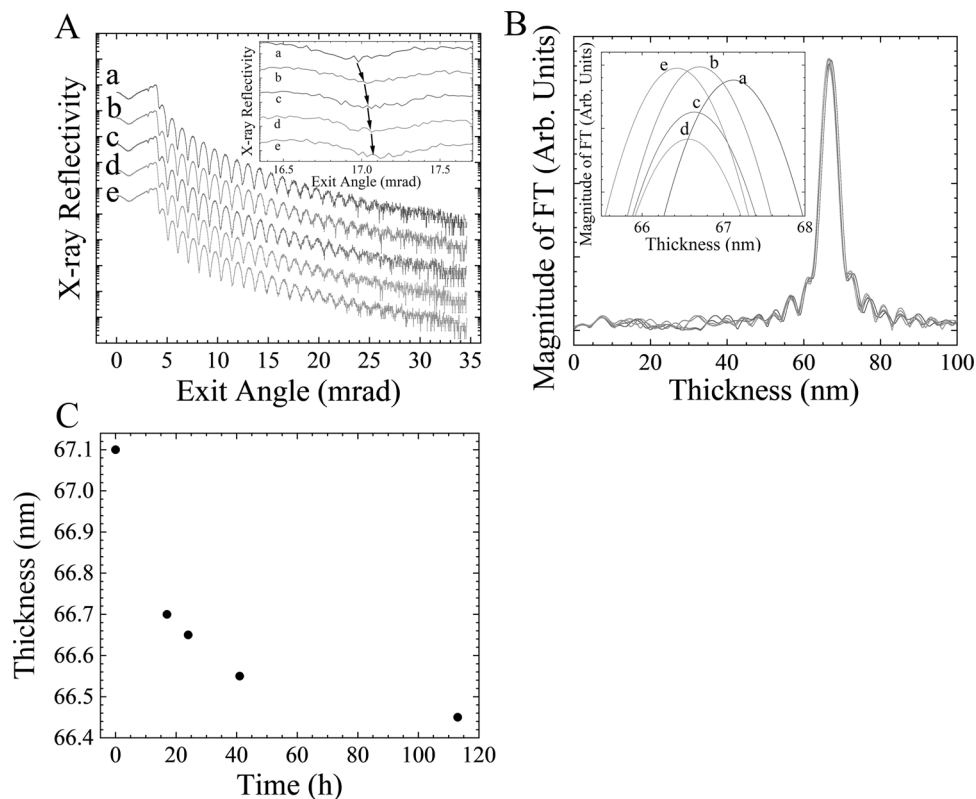
To study the thickness change of PVAc thin films with temperature, the thin films were monitored by a customized

multichannel X-ray reflectometer in temperature cycles from 45 to 19 °C, which made real-time static data collection in the laboratory possible [24, 26–28]. The temperature scan strategy was set at 2 °C perstep, and each step took 9 min, including the temperature-changing stage (~ 0.5 min) and suspending stage (~ 8.5 min). The valuable data collection was started at the fourth minute and stopped at the seventh minute of each step to avoid temperature fluctuations. The same experiment was repeated twice for each sample, and before the second temperature scanning, the sample was kept at 45 °C for 4 days to provide a stable initial state. For the thickness analysis, all X-ray reflectivity data were preferentially analyzed by Fourier transform (with a range of scattering vector, q_z of 0.03 – 0.16 nm $^{-1}$) [29–31].

Discussion

In the experiment, to clarify the relationship between the NTE and fine structural changes that are not yet known in the polymer thin-film system, first, the thickness change from annealing was confirmed. In Fig. 1a, the collected X-ray reflectivity curves for the PVAc thin film during the annealing process (at 0, 17, 24, 41, and 113 h) are presented with an offset. Browsing the Kiessig fringes from a to e , the clear amplitude of the oscillation indicates the stable interface conditions during the annealing (at 45 °C) [32, 33]. Meanwhile, the decrease in the frequency of oscillation can also be confirmed in the insert graph, which indicates a decrease in the thickness of the PVAc thin film [29–31, 34, 35]. At the high-angle range (>25 mrad), it appears as if a second higher frequency exists and reduces the visibility of the high-angle fringes; however, considering the low signal-to-noise ratio, it was proposed that these signals are mainly from noise. Therefore, all X-ray reflectivity data were preferentially analyzed in a q_z range of 0.03 – 0.16 nm $^{-1}$. In Fig. 1b, the Fourier transform of the X-ray reflectivity fringes observed in the annealing are plotted with a step of 0.05 nm, and the main peak position indicates the thickness of the PVAc thin film. As shown in the inset graph in Fig. 1b, the thickness of the PVAc thin film gradually decreases during the annealing. In Fig. 1c, the thickness of the PVAc thin film is plotted against time for 113 h. Noticeably, the thickness decrease of the PVAc thin film during the annealing can be considered to include two steps: the rapid thickness decrease in the first 17 h and the slow thickness decrease during the next 100 h. These two steps are not the two kinetics processes because the sorting out of all the kinetics during annealing with only five data plots is impossible. Within the first 17 h, the thickness decreases rapidly by 0.6% from 67.1 to 66.7 nm, which could be related to the evaporation of residual toluene and the disappearance of free holes in spin-coated polymer thin films with annealing [36]. In the general

Fig. 1 **a** X-ray reflectivity curves of a PVAc thin film during annealing at 45 °C: (A) at 0 h, (B) at 17 h, (C) at 24 h, (D) at 41 h, and (E) at 113 h—the inset graph displays the magnified fringes ~17 mrad. **b** The Fourier transform (FT) of the interference fringes observed in the X-ray reflectivity profiles—the inset graph displays the magnified peak of the FT magnitude with thickness. **c** The thickness change (calculated by FT) of the PVAc thin film during annealing. All X-ray reflectivity curves are presented on a base-10 logarithmic scale with an offset



prethermal treatment, the annealing can be completed with the directional creep of the polymer chain from the bulk area toward the inner free hole, which is considered fast and irreversible, similar to the first step shown in Fig. 1c. During the next 100 h, the thickness decreases slowly, only by 0.4% from 66.7 to 66.45 nm, which was rarely noticed or studied in the past. In related reports, Kanaya suggested that this ultraslow thickness decrease is a type of thickness recovery process caused by the different CTEs between the polymer thin film and its substrate [21–23]. However, in subsequent research, different experimental phenomena indicated that this process should be more complex [24]. It was proposed that this type of ultraslow thickness decrease could be caused by the formation of an interface layer. When the polymer thin film is kept in its rubbery state, the touching events between Kuhn segments and the substrate could increase with temperature and time, reducing the free volume near the interface, and resulting in one tight layer with a 2D-distributed polymer chain parallel to the surface of the substrate. As a result, the total thickness gradually becomes smaller with the increase of the thickness of the interface layer in the rubbery state. This slow thickness decrease can still be suspected of including other monotonous kinetics processes, such as the evaporation of residual toluene. However, in the following experiment results, it is shown that these monotonous kinetics processes do not

contribute to the new findings in this experiment because there is no decay in the behaviors of PVAc ultrathin films with the temperature cycle.

In Fig. 2, the thickness change of the PVAc thin film during the temperature cycle between 45 °C and 19 °C is presented. The temperature scan started at 45 °C, varied up to 19 °C, and then returned to 45 °C. This process was repeated twice to confirm the performance. An asymmetric and reproducible thickness change of the PVAc thin film is observed in the temperature cycle. In the cooling process, the thickness of the PVAc thin film can remain stable at first. When the temperature becomes lower than T_g , which is reported to be 31 °C in the bulk system, the thickness increase can occur abruptly as the temperature crosses the T_g with further cooling. The NTE can be confirmed in the PVAc thin films in the glassy state with cooling, and another interesting find is that there is no thickness change of the PVAc thin film in its rubbery state with cooling. Furthermore, in the heating process, the behavior of the thickness change is reversed and appears similar to that of the bulk. The thickness of the PVAc thin film remains stable at the low-temperature side and then increases quickly at the high-temperature side. The CTE of the PVAc thin film was calculated and is presented in Table 1. Considering the thickness change for the short temperature range, all processes were treated as having a linear relationship, and the

T_g value was set to 31 °C to simplify the calculation. Table 1 shows that, in the heating process, the CTEs of the PVAc thin films are close to zero in the glassy state and $\sim 230\text{--}310\text{ ppm K}^{-1}$ in the rubbery state, which are less than half the CTE of the PVAc bulk [37]. As is evident, the tendency of the thermal expansion of the PVAc thin film is the same as that of the bulk state in the heating process, but the CTE is suppressed. Finally, another point that is

noteworthy is that the initial thicknesses of the PVAc thin films are close prior to each temperature scan. This responds to the second step, as shown in Fig. 1, in which a slow isothermal thickness decrease is observed when the sample is kept at 45 °C.

In the studies on the interface interaction between a polymer thin film and substrate, Kanaya confirmed that the interface interaction can significantly affect the T_g of polymer thin films [38–40]. In these experiments, the T_g at different depth positions in a stacked, deuterated, and hydrogenated PS and poly(methyl methacrylate) (PMMA) multilayer was studied by neutron reflectometry. One of the interesting finds was that the T_g in the polymer thin-film system can change with depth, and near the interface between the polymer and substrate, only a limited thickness change in the bottom sublayer can be observed within the experimental temperature range. As shown in Fig. 2, similar behaviors of PVAc thin films can be confirmed in the cooling process when the temperature is more than 31 °C, and it is assumed that an interface layer dominates the performance of the PVAc thin films in this cooling process. In the proposed mode for the NTE of polymer thin-film systems, the interface layer can form in its rubbery state with a slow kinetics process and consists of polymer chains parallel to the surface of the substrate [24]. The proposed interface layer is different from that of isotropic polymer materials. Because the distribution of the polymer chains in the interface layer gradually changes from 3D to 2D and parallel to the surface of the substrate, it is proposed that the interface layer has a higher atomic bond area density in-plane. As the temperature becomes less than T_g , the CTE of polymers can be exclusively governed by the vibrational contribution; therefore, the interface layer, which contains more atomic bonds, has a larger CTE in horizontal directions than it does in its adjacent layer (the transition layer). In this experiment, the interface layer grows slowly with sufficient thermal treatment at 45 °C, and its CTE is suppressed by the interface interaction in the rubbery state. As shown in Fig. 3, no thickness change in the rubbery state with cooling is observed. When the temperature is below the T_g , the PVAc ultrathin film could be further frozen with the anisotropic structure formed in the rubbery state, and the different CTEs in the horizontal direction between the interface layer and transition layer

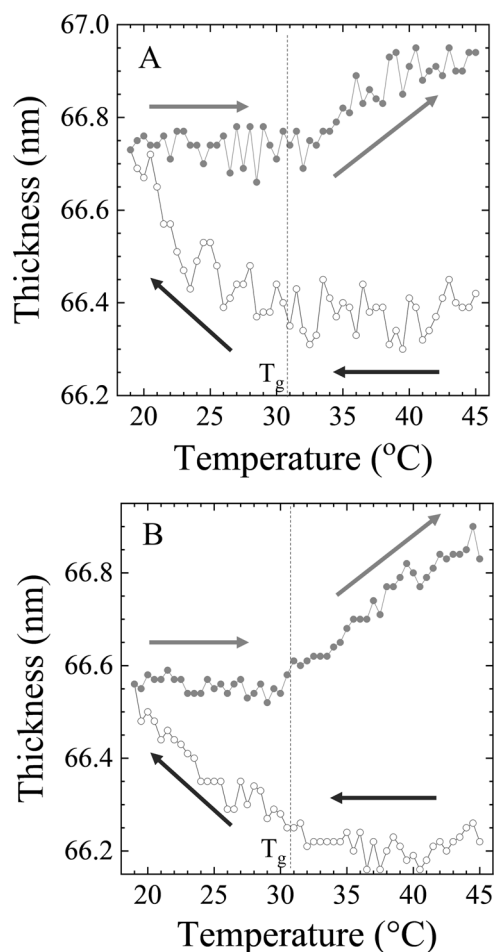


Fig. 2 **a** Thickness change (calculated by FT) of a PVAc thin film during the first temperature cycle between 45 and 19 °C and **b** after heating at 45 °C for 4 days: the thickness change (calculated by FT) of the PVAc thin film in the second temperature cycle between 45 and 19 °C

Table 1 Experimentally obtained thermal expansion coefficients of the PVAc film at each stage of the temperature cycles

Sample	Process	Coefficient of thermal expansion (ppm K^{-1})			
		Cooling		Heating	
		Rubbery state	Glassy state	Glassy state	Rubbery state
PVAc	1st cycle	24	−417	13	232
(60 nm)	2nd cycle	−11	−334	−11	311

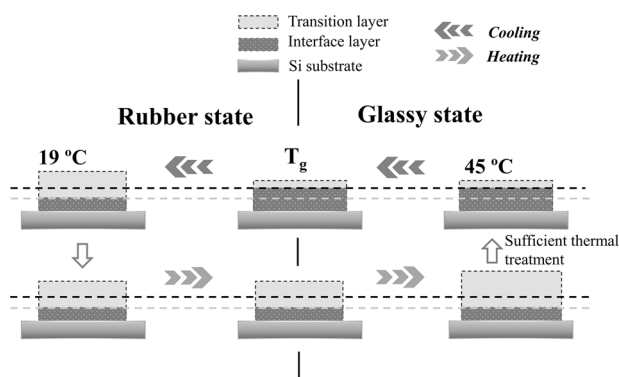


Fig. 3 Conceptual sketch of the unusual thickness change in a PVAc thin-film system with sufficient thermal treatment; the interface layer can gradually grow and dominate the thickness change of the PVAc thin film during the cooling when the temperature is above T_g . When the temperature is below T_g , an NTE can occur with the additional deformation of the transition layer. Some part of the interface layer transforms into the transition layer. When the cooling ends and heating begins, the transition layer dominates the thickness change of the PVAc thin film. As the temperature returns to a value above T_g , the interface layer gradually grows again

could produce an additional internal stress by normal thermal expansion with temperature. Therefore, the transition layer would be forced by the interface layer, causing an additional deformation in the vertical direction, and the NTE would occur. Meanwhile, the interface layer could also be influenced by the stress, causing the 2D to 3D changes in the polymer chains. During the NTE with cooling, the influence of the interface layer on the CTE of the PVAc ultrathin film could gradually decline with the loosening of the interface layer. In the heating process, because of the transformation from the interface layer to the transition layer, the difference in CTEs between the interface layer and the transition layer become small, and the thickness change of the PVAc thin film is dominated by the performance of the transition layer, the CTE of which would be close to that of the bulk. Considering the remaining interface layer, the observed CTE must be lower than that in the bulk system. Therefore, suppressed thermal expansion of the PVAc thin film is observed in the heating process. However, this new state of the PVAc thin film would be unstable in its rubbery state, and the slow formation of an interface layer would occur again with heating to more than T_g . Finally, a slightly decrease in the thickness of the PVAc thin film is observed at the initial state of the second temperature cycle, together with the similar thickness change with the temperature cycle. Obviously, the interface layer state should vary in the different cases. Because the interface can gradually grow with time in the rubbery state and transform to a transition layer with an NTE in the glassy state, the interface layer state greatly depends on the interface interaction, mobility of polymer chains, thermal

treatment, and initial state of the polymer thin film itself. In this study, the NTE of the PVAc ultrathin film is observed exclusively with cooling, but this result does not imply that the NTE can only occur with cooling. In the proposed model, the NTE of the polymer ultrathin film can occur with different CTEs between the interface layer and transition layer, while the difference in CTEs can also gradually decline with the NTE process, causing the disappearance of the NTE with the temperature change in the glassy state.

Finally, some researchers may suspect that the free surface layer in the polymer ultrathin film affects the NTE behaviors. In related reports [1, 25, 38–40], it was confirmed that the existence of a free end chain can cause the high mobility of a surface layer and decrease T_g . However, even in the studies for a free-standing PS thin film, which has two free surface layers [1], there is no report on NTE, which indicates that enthalpic terms at the free surface layer cannot be the main factor behind the NTE observed in the experiments reported here. Therefore, it is proposed that even though the free surface layer is crucial in the polymer ultrathin-film system, the effect of the free surface layer on the NTE is not significant.

Conclusion

With years of research, our understanding of the NTE in polymer thin films has become more comprehensive; even so, there are still many unknown details. In this study, we focused on the relationship between the NTE of the polymer thin film and its interface layer. An asymmetric and reproducible thickness change of the PVAc thin film was observed by an X-ray reflectivity technique in a temperature cycle across the T_g , and it is proposed that the interface layer might exist and contribute to the unusual thickness change in the polymer thin film with temperature: (i) in the rubbery state, the interface layer can gradually grow with the thermodynamic equilibrium process and dominate the thermally responsive behaviors of the polymer thin film as a stable layer, (ii) in the glassy state, the different CTEs of the interface layer and transition layer can contribute toward the internal stress with a normal thermal expansion resulting in the NTE, (iii) meanwhile, the interface layer can also transform toward the transition layer with this reaction force, and (iv) after the loss of the interface layer in the glassy state, the thermally responsive behaviors of the polymer thin film can recover to normal in the heating process. Noticeably, the interface layer is important and varies in polymer thin-film systems. Further investigations of the interface layer can help to develop a better understanding of the thermal expansion behavior of the polymer thin film.

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Compliance with ethical standards

Conflict of interest The author declares that he has no conflict of interest.

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