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Nanomechanical Thermal Analysis with Silicon Cantilevers of the Mechanical Properties of Poly(vinyl acetate) near the Glass Transition Temperature

Namchul Jung and Sangmin Jeon*

Department of Chemical Engineering, Pohang University of Science and Technology, Pohang, Korea

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ABSTRACT: Poly(vinyl acetate) (PVAc) was coated onto one side of a silicon cantilever, and the variations with temperature in the deflection, resonance frequency, and Q factor of the PVAc-coated silicon cantilever were measured simultaneously. The changes in the resonance frequency and the inverse of the Q factor of the cantilever are related to the variations in the elastic modulus and the loss tangent of PVAc, respectively. The loss modulus of PVAc was calculated from the resonance frequency and Q factor and used to determine the glass transition temperature (T_g) of PVAc (66 °C), which was found to be higher than that obtained from the cantilever deflection (43 °C); this difference is attributed to the high resonance frequency of the cantilever (or the fast rate of the applied stress). A series of measurements at various frequencies were carried out to obtain the accurate T_g and apparent activation energy for the glass transition.

1. Introduction

A nanomechanical thermal analysis method that uses cantilever sensors has recently been developed for investigating the glass transition phenomena of amorphous polymers.[1] When a silicon cantilever coated with a polymer is heated or cooled, the difference between the volume expansion coefficients of the silicon and the polymer induces the cantilever to bend, which can be related to volume changes in the coated polymer. Compared to conventional methods for investigating the glass transition phenomena of polymers such as differential scanning calorimetry (DSC),[2−4] dilatometry,[5,6] and dynamic mechanical spectroscopy (DMS),[7,8] cantilever sensors need samples of only a few nanograms for measurements. In addition, fast thermal equilibrium and multiple sample measurements can be achieved due to their miniaturized array structure. Despite the advantages of cantilever sensors for investigating polymer properties, most studies using cantilever sensors have so far focused on the detection of gases, ions, and biomolecules,[9−11] and only a few studies in polymer research have used cantilever sensors.[12−15]

Berger et al. and Nakagawa et al. monitored the melting of paraffin by using a paraffin-coated cantilever.[12,13] Wen et al. investigated the polymerization kinetics of acrylate by measuring the variations in the stress of an acrylate-coated cantilever during UV curing.[14] However, they only carried out deflection measurements and did not utilize the potential of cantilever sensors to relate the resonance frequency of the cantilever to the mechanical properties of the polymer. Thundat et al. measured the variations with UV exposure time in the deflection and resonance frequency of UV-curable polymer-coated cantilevers and determined the variation in the stiffness of the polymer.[15] However, their study focused on the cross-linking of the polymers rather than on their glass transitions.

In a previous publication, we measured the variations with temperature in the resonance frequency and the deflection of a polystyrene-coated cantilever near the glass transition temperature (T_g) and found that the deflection measurements could be used to investigate not only T_g but also the in situ changes in the volume of the polymer induced by physical aging or stress relaxation.[1] However, very little information on the mechanical properties of the coated polymer was obtained from the resonance frequency measurements.

In this study, we coated rectangular silicon cantilevers with poly(vinyl acetate) (PVAc) and measured the variations with temperature in their deflections, resonance frequencies, and Q factors. The resonance frequency and Q factor of the PVAc-coated cantilevers are related to the elastic modulus and loss tangent of PVAc, respectively. The loss modulus of PVAc was calculated from the elastic modulus and the loss tangent and used to determine T_g of PVAc.

2. Experimental Section

2.1. Materials. PVAc was purchased from Polymer Source (Quebec, Canada). The weight-average molecular weight and polydispersity were specified by the manufacturer as 62 000 g/mol and 1.5, respectively. Anhydrous toluene was purchased from Aldrich (Saint Louis, MO) and used without further purification to prepare a 0.5 wt % PVAc solution. Rectangular silicon cantilevers with a triangular free end (cantilever A) were obtained from Nanoworld (Neuchatel, Switzerland). Each cantilever is 500 μm long, 100 μm wide, and 1 μm thick, with a spring constant of ~0.03 N/m. One side of each cantilever was coated with a 0.5 wt % PVAc solution in toluene by using an inkjet printing method (Cantion, Denmark). The average film thickness was measured to be ~0.8 μm with atomic force microscopy (Veeco, Santa Barbara, CA). To investigate the influence of the resonance frequency of the cantilever on T_g, longer rectangular silicon cantilevers (cantilever B) were obtained from Concentris (Basel, Switzerland). These cantilevers are 750 μm long, 100 μm wide, and 1 μm thick, with a spring constant of ~0.01 N/m.

2.2. Instruments. Each PVAc-coated cantilever was mounted onto a thin aluminum holder, and its temperature was controlled by using a resistance heater with a programmable temperature controller (Hanyoung, Inchon, Korea). After the temperature had been increased from 25 to 95 °C at a rate of 5 °C/min, the heater was switched off, and the cantilever was cooled to 25 °C. The typical cooling time was about 80 min. The heating and cooling cycles were repeated several times to relieve the stress developed during polymer coating. The microcantilever's motion was tracked with a laser beam reflected from the cantilever surface onto a duolateral position-sensitive detector (SiTek Electro Optics, Partille, Sweden). The resonance frequency and Q factor of the self-thermally vibrating cantilever were calculated using a fast Fourier transform (FFT) algorithm.

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* To whom correspondence should be addressed. E-mail: jeons@postech.ac.kr.

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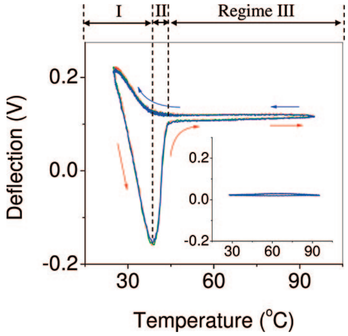

Figure 1. Variation in the deflection of a PVAc-coated cantilever during three thermal cycles (red, first; green, second; blue, third). The inset shows the variation with temperature in the deflection of an uncoated silicon cantilever.

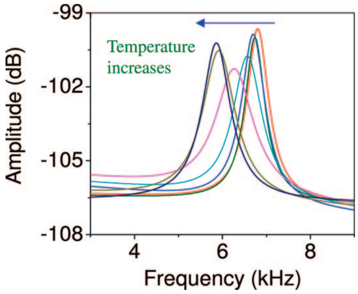

Figure 2. Variations in the resonance peak of a PVAc-coated cantilever at 30 °C (red), 40 °C (green), 50 °C (blue), 60 °C (sky blue), 70 °C (pink), 80 °C (dark yellow), and 90 °C (dark blue). The graphs shown here are Lorentzian curves fitted to the raw data.

3. Results and Discussion

Figure 1 shows the variation with temperature in the deflection of a PVAc-coated cantilever A. The measurements were conducted three times, and identical responses were found, indicating that these measurements are reproducible and reversible. As for polystyrene-coated cantilevers,[1] three characteristic regimes are present in the variation in the deflection of the PVAc-coated cantilever during heating. The deflection of the cantilever decreases in regime I, indicating that the PVAc volume increases upon heating. The decrease in the volume of PVAc with temperature in regime II is due to the physical aging of PVAc in the glassy state. Further heating to 95 °C results in almost constant deflection (regime III) due to the decreases in the modulus of PVAc during the glass transition; the Young's modulus of the polymer is known to decrease by a factor of 1000 in this temperature range,[16] and above T_g PVAc is too soft to deflect the silicon cantilever.

The glass transition temperature was determined to be 43 °C from the intersection of the tangents to the curves in regimes II and III, which is identical with the value obtained from DSC measurements. Once the temperature reached 95 °C, the heater was switched off, and the cantilever was cooled to 25 °C. A hysteresis was observed in the deflection during heating and cooling due to the physical aging of PVAc.[1] The inset in Figure 1 shows the results of a control experiment: the deflection of an uncoated silicon cantilever is almost constant with temperature, which indicates that the changes with temperature in the deflection of the PVAc-coated cantilever are induced by the different thermal expansion/contraction behaviors of PVAc and the silicon cantilever.

To investigate the mechanical properties of PVAc, the resonant responses of the PVAc-coated cantilever A were measured. Figure 2 shows the variations in the resonance peak for various temperatures, which were obtained at the same time as the deflection measurements. The thermal vibrations of the cantilever were transformed into resonance peaks using an FFT algorithm. The peak frequency monotonously decreases with temperature, and the minimum amplitude of the peak is at 70 °C, at which temperature the width of the peak is at its maximum. The resonance frequency and the Q factor of the cantilever were obtained by fitting the peaks with Lorentzian curves.

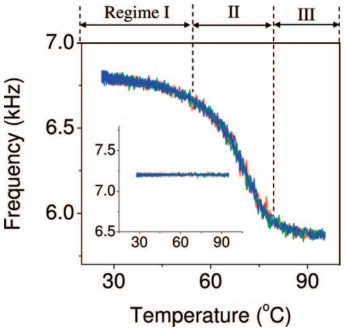

Figure 3. Variation with temperature in the resonance frequency of a PVAc-coated cantilever (obtained at the same time as the cantilever bending results shown in Figure 1). The inset shows the variation with temperature in the resonance frequency of an uncoated silicon cantilever.

Figure 3 shows the variation with temperature in the resonance frequency of a PVAc-coated cantilever A. A typical viscoelastic response for amorphous polymers was observed: a glass region (~50 °C), a glass transition region (~80 °C), and a rubbery plateau region (>80 °C). However, these regimes are different from the deflection regimes shown in Figure 1. The inset shows the variation with temperature in the resonance frequency of an uncoated silicon cantilever, which is almost constant, indicating that the changes in the modulus of PVAc are responsible for the changes in the resonance frequency of the PVAc-coated cantilever.

The cantilever thermally vibrates with a resonance frequency (f) that is a function of its effective mass (m) and spring constant (k):

$$f = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \qquad (1)$$

Since the mass of the PVAc-coated cantilever is constant during the measurements, the change in the resonance frequency is proportional to the square root of the spring constant, which is related to the effective Young's modulus of the cantilever (E):[17]

$$k = \frac{Ewt^3}{4l^3} \qquad (2)$$

where l, w, and t are the length, width, and thickness of the cantilever, respectively. Since the changes in the Young's modulus of the silicon cantilever are much smaller than those of PVAc,[18] the variation in the resonance frequency with temperature can be related to the changes in the Young's modulus of the coated polymer.

Since the PVAc-coated cantilever is a bilayer beam rather than a homogeneous beam, the effective Young's modulus of the PVAc (E_f) can be calculated from the frequencies of the uncoated (f) and the coated cantilever (f_f):[19]

$$E_f = \frac{E}{3}\left(\frac{\rho_f}{\rho} + \frac{2t_f}{t}\right)\left(\frac{1 - \nu_f^2}{1 + \nu_f^2 - 2\nu_f\nu}\right)\left(\frac{f_f - f}{f}\right) \qquad (3)$$

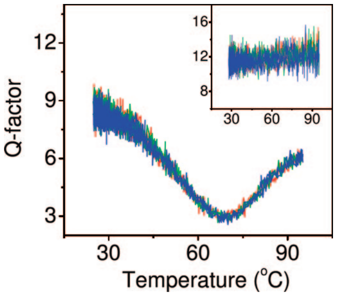

Figure 4. Variation with temperature in the Q factor of a PVAc-coated cantilever (obtained at the same time as the cantilever bending results shown in Figure 1). The inset shows the variation with temperature in the Q factor of an uncoated silicon cantilever.

where ρ and ν are the density and Poisson ratio of the silicon cantilever, respectively. The subscript f denotes the PVAc film. The modulus of the PVAc is calculated using eq 3 to be 28 GPa, which is far higher than the typical value for poly(vinyl acetate) at room temperature (~1 GPa) because the coated film using an inkjet printing method is not uniform. In addition, changes in the PVAc thickness with temperature can lead to errors in estimating the modulus of PVAc. However, it is possible to estimate the qualitative variations in the Young's modulus of the PVAc with temperature from the changes in the frequency because almost no change was observed for the uncoated silicon cantilever. Note that the absolute resonance frequency of the cantilever can be affected by surface stress effects due to the PVAc coating.[20−22] However, the changes with temperature in the frequency are caused by variations in the Young's modulus of the PVAc.

Figure 4 shows the variation with temperature in the Q factor of the PVAc-coated cantilever A. The Q factor of a resonator is defined as the ratio of energy stored to energy dissipated per cycle and can be calculated as follows:

$$Q \text{ factor} = \frac{\text{resonance frequency}}{\text{fwhm}} \tag{4}$$

where fwhm is the full width at half-maximum, which in this case was obtained from Figure 2. A lower Q factor implies a higher rate of energy dissipation relative to the oscillation frequency. The minimum Q factor is at ~70 °C, indicating that the maximum dissipation occurs at that temperature. The Q factor can be related to the loss tangent (tan δ) of PVAc because tan δ is the ratio of the loss modulus (E'') to the elastic modulus (E'), i.e., tan δ where E' and E'' are the energy stored elastically and the energy converted to heat during deformation, respectively. Therefore, tan δ is inversely proportional to the Q factor.

The temperature at the maximum in E'' can be used as the definition of T_g.[16] Since the effective E' of PVAc is proportional to the square of the resonance frequency, the effective E'' can be calculated by multiplying the square of the resonance frequency by the inverse of Q factor. Figure 5 shows the variations in E', E'', and tan δ with temperature. The glass transition temperature was determined from the maximum in E'' to be 66 °C, which is higher than that obtained from Figure 1. This difference arises because T_g is not a thermodynamic value but depends on the heating rate and the rate of applied stress. The well-known time−temperature superposition principle indicates that time (the heating rate or the rate of applied stress) is equivalent to temperature because molecular motion is faster at higher temperatures (or time moves faster for chains at higher temperatures).[16]

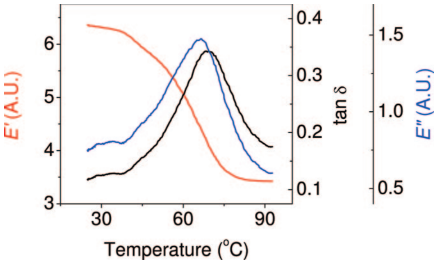

Figure 5. Variations with temperature in the effective E' (red), E'' (blue), and tan δ (black) of a PVAc-coated cantilever. All the data were fitted with smooth curves to remove the excessive noise that results from the multiplication of fluctuating signals.

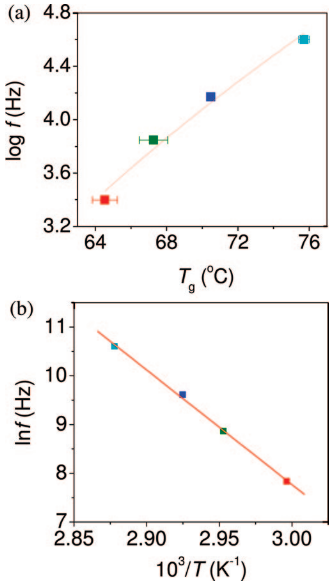

Figure 6. (a) Variation in the glass transition temperature of PVAc as a function of the resonance frequency of the PVAc-coated cantilever. (b) Natural logarithmic resonance frequency is plotted against inverse absolute temperature. Symbols: green, first mode of cantilever A; sky blue, second mode of cantilever A; red, first mode of cantilever B; blue, second mode of cantilever B.

When an amorphous polymer is heated above T_g over a period that is shorter than the time required for molecular rearrangements to accommodate the changes, the polymer chains maintain their glass state, which results in an increase in T_g. Similarly, if the rate of applied stress is very fast, PVAc remains in the glass state because there is insufficient time for the chains to rearrange, which also results in an increase in T_g. In contrast, T_g decreases for a very low rate of applied stress because the PVAc chains can always move past each other, and so PVAc behaves as a viscous liquid. Since the thermal vibration of the PVAc-coated cantilever is the source of the stress applied to the PVAc, a high resonance frequency of the PVAc-coated cantilever results in a high T_g.

To investigate the influence of the resonance frequency of the cantilever on T_g, a series of measurements were carried out at various frequencies. The fundamental and second harmonic resonance peaks of the cantilever A and cantilever B were obtained from their thermal vibrations. Figure 6a shows that T_g increases with the logarithm of the resonance frequency of the cantilevers, as predicted by time−temperature superposition principle.[16] This indicates that T_g is a kinetic parameter rather than a thermodynamic value. For linear amorphous polymers, independent of chemical structure, the measured T_g can be best fitted with the modified WLF equation:[16]

$$\log\left(\frac{f_g}{f}\right) = -\frac{17.44(T - T_g)}{51.6 + T - T_g} \tag{5}$$

where f_g and T_g are calculated to be 0.027 Hz and 29.2 °C, respectively, indicating that the glass transition temperature of PVAc may decrease to 29.2 °C when measured at very low frequency of 0.027 Hz. However, it is almost impossible to measure T_g at 0.027 Hz because of the insufficient sensitivity of the cantilever at such a low frequency. Figure 6b shows the variations in natural logarithmic resonance frequency with inverse absolute temperature. Assuming Arrhenius-type relationship between the frequency and temperature, the apparent activation energy for the glass transition was calculated from the slope to be 195 kJ/mol, which is close to the value obtained from DMS measurements (180 kJ/mol).[23]

4. Conclusion

We have used PVAc-coated silicon cantilevers to investigate the mechanical properties of PVAc samples in the vicinity of the glass transition temperature. By measuring the variations with temperature in the resonance frequency and Q factor of the cantilever, we obtained the temperature dependence of the effective complex modulus of the PVAc sample. Further, we found that T_g and apparent activation energy for the glass transition relaxation can be determined by carrying out a series of measurements at various frequencies. These results indicate that nanomechanical thermal analysis with polymer-coated silicon cantilevers is a useful method for probing the thermomechanical properties of amorphous polymers. We plan to fabricate an array of piezoelectric cantilevers with various resonance frequencies. The electrical detection of the resonance frequency is expected to make such measurements easier and more convenient.

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Supporting Information Available: A total heat flow DSC trace and the influence of heating rate on the glass transition temperature of PVAc. This material is available free of charge via the Internet at http://pubs.acs.org.

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