Multi-modal characterization of nanogram amounts of a photosensitive polymer

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Here, we demonstrate multi-modal approach of simultaneous characterization of poly(vinyl cinnamate) (PVCN) using a microcantilever sensor. We integrate nanomechanical thermal analysis with photothermal cantilever deflection spectroscopy for discerning ultraviolet (UV) exposure-induced variations in the thermodynamic and thermomechanical properties of the PVCN as a function of temperature and UV irradiation time. UV radiation-induced photo-cross-linking processes in the PVCN are verified with the increase of the Young's modulus and cantilever deflection as well as the decrease in the hysteresis of deflection and the intensity of C=C peak in the nanomechanical infrared spectrum as a function of UV irradiation time. © 2013 American Institute of Physics.
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Generally, physical properties of materials are measured by using multiple techniques in a serial fashion. This approach, although widely practiced, is time consuming and not cost effective. Therefore, monitoring multiple physical properties of extremely small quantities of samples using a single platform is very attractive for rapid material characterization. Over the last couple of decades, micro and nanomechanical sensing systems have attracted much attention as ultrasensitive mechanical transducers for physical, chemical, and biological interactions.[1–4] However, the strength of microcantilever sensor platform lies in its ability to measure small displacements with very high precision. Microcantilevers, therefore, are excellent sensors for physical phenomena. Recently, the microcantilever platform has been demonstrated as sensitive tool for materials characterization. For example, mechanical spectroscopy of polymer thin films[5–7] and nanomechanical thermal analysis (NTA) of various polymers[8–12] in a few nanograms range have been reported using a microcantilever sensor platform. In addition, photothermal cantilever deflection spectroscopy (PCDS) of polymers has been presented with a polymer-coated cantilever to simultaneously characterize chemical as well as mechanical properties of a polymer.[13,14]

The NTA using a silicon microcantilever provides information on the thermodynamic as well as thermomechanical properties of a material coated on the cantilever. When an amorphous polymer is coated on the cantilever, solvent evaporation induces shrinkage of the polymer that results in the development of tensile stress.[15] Then, generally, a compressive stress develops upon heating of the cantilever due to larger thermal expansion of the polymer compared to that of silicon. A maximum compressive stress is reached near glass transition temperature (T_g) of the polymer just before the onset of the glass-to-rubber transition. Beyond T_g, the polymer is too soft to create thermal stress on the cantilever. This temperature-dependent thermal stress can be sensitively measured by monitoring the static deflection of the polymer-coated cantilever as a function of temperature. The T_g of the polymer is determined by careful analysis of this thermal stress on the cantilever.[8,10,11] In addition, the temperature-dependent change in the Young's modulus of the coated polymer simultaneously causes resonance frequency shift of the cantilever. By employing the differential Euler-Bernoulli beam equation, the Young's modulus of the coated polymer can be determined as a function of temperature. Moreover, unlike conventional PCDS, which employs a bimetallic cantilever to sensitively detect the minute temperature change in the cantilever with target molecules, the polymer-coated cantilever can directly transduce the minute temperature variation into nanomechanical motion of the cantilever. Therefore, nanomechanical infrared (IR) absorption spectrum of the coated polymer can be directly obtained with the same cantilever used for NTA.

Here, we demonstrate the capability of a microcantilever as a multi-modal device for simultaneous measurement of multiple physical and chemical properties by integrating cantilever-based NTA with the PCDS. We demonstrate the characterization of ultraviolet (UV) radiation-induced changes in the thermodynamic, thermomechanical, and chemical properties of nanogram amount of poly(vinyl cinnamate) (PVCN) on a cantilever substrate. The PVCN is a light-sensitive negative photoresist and widely investigated as a dielectric organic gate insulator for the fabrication of flexible electronic devices, such as organic thin film transistors or organic field-effect transistors.[16–18] Exposure to UV radiation results in photo-cross-linking of the PVCN polymer chain.[6,16] These photo-cross-linking processes affect the thermodynamic, thermomechanical, and chemical properties of PVCN and induce changes in the glass transition temperature,[6,11] surface stress,[11] and dielectric strength[18] of a PVCN film.

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The PVCN was purchased from Sigma Aldrich (Saint Louis, MO) and used without further purification. As indicated by the manufacturer, the weight-average molecular weight and polydispersity index of PVCN were 200 000 g/mol and 2.2, respectively. Anhydrous toluene was purchased from Sigma Aldrich (Saint Louis, MO) and used without further purification to prepare 0.8 wt. % PVCN solution. Commercially available arrays of eight rectangular silicon cantilevers with a triangular free end (Arrow[TM] TL8) were obtained from Nanoworld (Neuchatel, Switzerland). Each cantilever in the array was 500 μm in length, 100 μm in width, 1 μm in thickness, and had a nominal spring constant of ~0.03 N/m according to the manufacturer. The PVCN was coated on the clamping region of each cantilever, which is insensitive to mass change[19] using micro glass capillary then the PVCN-coated cantilever was dried in a vacuum oven at 80 °C for 15 h. Volume of the coated PVCN was measured using a MultiMode atomic force microscope (AFM) (Bruker, Santa Barbara, CA).

For our experiments, the PVCN-coated microcantilever array was mounted on a thin aluminum holder and its temperature was controlled using a micro ceramic heater with a programmable temperature controller (Hanyoung, Incheon, Korea). The temperature was cycled between 60 °C and 180 °C several times to relieve any stress developed during the coating process. The heating and cooling rates were maintained at 10 °C/min. The deflection and frequency response of the PVCN-coated cantilever were measured as a function of temperature using an optical lever method. The absolute deflection of the cantilever and the temperature of the aluminum holder were calibrated using a calibrated indium-coated microcantilever. Nanomechanical IR spectra from the same PVCN-coated silicon microcantilever were acquired as a function of UV irradiation time at room temperature with the current setup which employed a quantum cascade laser (QCL). Schematic illustration of our current experimental setup is shown in Figure 1. The 100 kHz pulsed IR radiation with 5% duty cycle from the QCL (Daylight Solutions, San Diego, CA) was electrically burst at 80 Hz using a function generator DS345 (Stanford Research Systems, Sunnyvale, CA) and directed to the cantilever. The IR wavelength was scanned from 5.835 μm to 6.4 μm (1714 cm^{-1} to 1562 cm^{-1}

in wavenumber) with a spectral resolution of 5 nm. The nanomechanical IR spectra were taken using a SR850 lock-in amplifier (Stanford Research Systems, Sunnyvale, CA) and a Fourier filter was applied. The power of a UV pencil lamp (254 nm) was measured to be 4.5 mW/cm^2 at a distance of 2.54 cm (1 in.).

Figure 2 shows the temperature-dependent variations in the resonance frequency of the PVCN-coated cantilever and the estimated Young's modulus of the coated PVCN as a function of UV irradiation time. The resonance frequency of a thermally vibrating cantilever depends on its dimensions, effective mass, and effective Young's modulus. Negligible changes in the dimensions and mass of the PVCN were confirmed in our previous study.[11] Thus, the resonance frequency of the PVCN-coated cantilever is related to the Young's modulus of the coated PVCN. In order to estimate the Young's modulus of the coated PVCN as a function of temperature and UV irradiation time, the differential Euler-Bernoulli beam equation modified to accommodate the partial PVCN coating was employed[20] and the PVCN was approximated as a rectangular patch on the cantilever and the effective thickness was deduced by equaling the volume of the PVCN on the cantilever from AFM measurements to the volume of a patch. Detailed calculation procedure can be found in our previous publications.[14,21] The determined Young's modulus of PVCN at room temperature (2.98 GPa) before UV irradiation is in excellent agreement with the previously reported value in the literature.[6] The increase of Young's modulus of PVCN upon UV radiation-induced photo-cross-linking processes was clearly observed. In addition, the glass transition region gradually disappeared as photo-cross-linking progressed, as typically observed in cross-linked polymers.[22]

Figure 3(a) shows the temperature-dependent variations in the deflection of the PVCN-coated cantilever as a function of UV irradiation time. Positive deflection means the PVCN-coated cantilever experiences a tensile stress and bends upward (toward the PVCN side). Initial tensile stress developed due to the polymer coating decreased upon heating of the cantilever due to larger thermal expansion of the polymer than that of silicon. Local minima near T_g of the coated PVCN were gradually shifted to higher temperature and
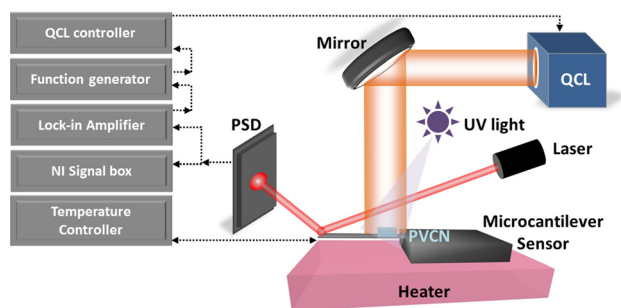

FIG. 1. Schematic drawing of the experimental setup used for NTA integrated with PCDS. The heater temperature is controlled using a micro ceramic heater with a programmable temperature controller. The 100 kHz pulsed IR light with 5% duty cycle from the QCL is electrically burst at 80 Hz, directed to the PVCN-coated microcantilever, and scanned from 5.835 μm to 6.4 μm (1714 cm^{-1} to 1562 cm^{-1} in wavenumber) with a spectral resolution of 5 nm. The NTA and PCDS signals are measured by optical beam deflection method.
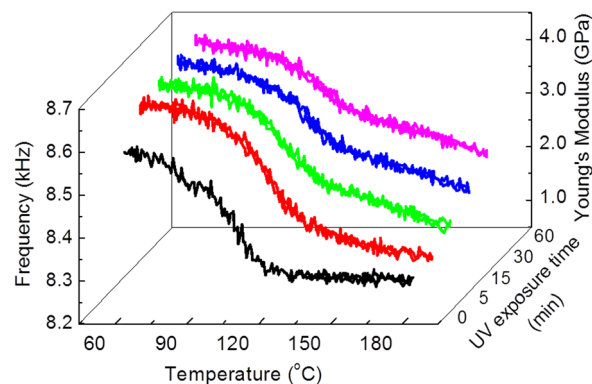

FIG. 2. Measured temperature-dependent shifts in the resonance frequency of the PVCN-coated cantilever and the estimated Young's modulus of the coated PVCN after various periods of UV irradiation time: 0 min (black), 5 min (red), 15 min (light green), 30 min (blue), and 60 min (magenta).
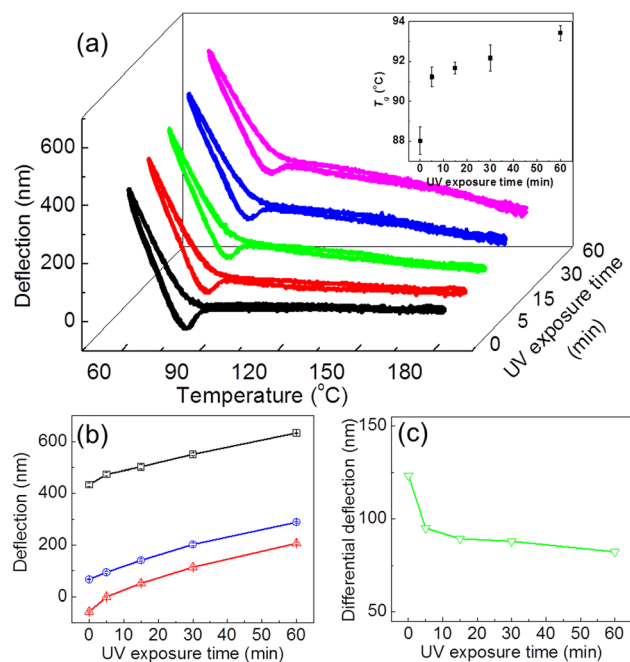
FIG. 3. (a) Measured temperature-dependent variations in the deflection of the PVCN-coated cantilever after various periods of UV irradiation time: 0 min (black), 5 min (red), 15 min (light green), 30 min (blue), and 60 min (magenta). The inset shows variations in the T_g of the coated PVCN as a function of UV irradiation time. (b) Measured deflection at 60 °C (black squares), the temperatures of local minima in heating cycle (red triangles) and in cooling cycle (blue circles) as a function of UV irradiation time. Error bars are too small compared to symbols. (c) Differential deflection at the temperatures of local minima between heating and cooling cycles as a function of UV irradiation time. The lines are drawn to guide the eyes.
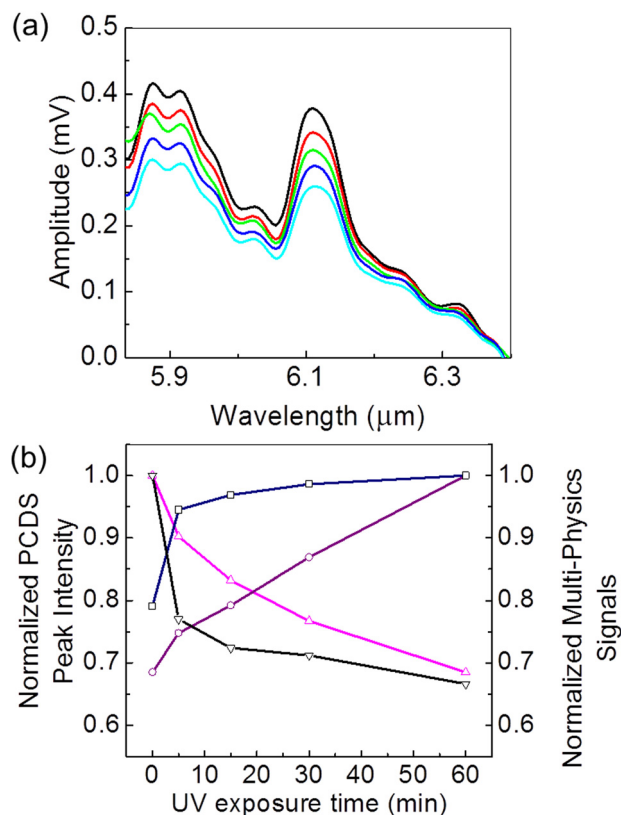

FIG. 4. (a) PCDS spectra of PVCN as a function of UV irradiation time: 0 min (black), 5 min (red), 15 min (light green), 30 min (blue), and 60 min (cyan). (b) Variations in the intensity of the normalized PCDS peak (magenta triangles) at 6.11 μm (1637 cm^{-1} in wavenumber) and the normalized multi-physics signals: Young's modulus (navy squares), static deflection (purple circles), and the differential deflection (black inverted triangles) as a function of UV irradiation time. The lines are drawn to guide the eyes.

substantial hysteresis in the deflection during heating and cooling was decreased as a function of UV irradiation time since photo-cross-linking restricted the physical aging of the PVCN chains.[23] Thus, the inset in Figure 3(a) only presents the variations in the T_g of un-cross-linked PVCN part as a function of UV irradiation time and the T_g of cross-linked PVCN part is hard to be determined.[11] Increasing tensile stress on the cantilever as a function of UV irradiation time can be deduced from the deflection measurement at 60 °C (black squares) and at the temperatures of local minima in heating cycle (red triangles) and in cooling cycle (blue circles) as shown in Figure 3(b). Decrease of the hysteresis as a function of UV irradiation time can be clearly observed from the differential deflection signal at the temperatures of local minima during heating and cooling as shown in Figure 3(c).

The PCDS spectra of PVCN in Figure 4(a) represent the absorbance of the C=C bonds in the cinnamate groups as a function of UV irradiation time. The major peak at 6.11 μm (1637 cm^{-1} in wavenumber) corresponds to aliphatic C=C stretching vibrations of PVCN and decreases over time due to photo-cross-linking processes, which involve the breakage of the π-π conjugation, consisting of C=O, aliphatic C=C, and aromatic C=C bonds and the formation of cyclobutane ring.[6,18,24,25] The rate of PVCN photo-cross-linking was related to the decrease in the normalized differential deflection signal at the temperatures of local minima during heating and cooling as well as the increase in the normalized Young's modulus at 60 °C in Figure 4(b). Rapid photo-cross-linking of PVCN within 15 min of UV irradiation is clearly

observed. The decrease in normalized PCDS peak intensity (the peak intensity divided by the maximum peak intensity) at 6.11 μm (1637 cm^{-1} in wavenumber) and the increase in the normalized deflection signal at 60 °C are also shown in Figure 4(b). Unlike conventional PCDS, the PVCN-coated cantilever without a metal layer directly transduces the thermal stress due to the minute temperature change caused by IR absorption into nanomechanical motion. The thermal stress, σ, induced by the coated PVCN is given by[26]

$$\sigma = \int \frac{E_{PVCN}(\alpha_{PVCN} - \alpha_{Si})}{1 - \nu_{PVCN}} dT, \quad (1)$$

where α_{Si}, α_{PVCN}, E_{PVCN}, and ν_{PVCN} are the thermal expansion coefficients of silicon and PVCN, the Young's modulus, and Poisson's ratio of PVCN, respectively. Thus, nanomechanical IR spectra shown in Figure 4(a) come from the changes in physical as well as chemical characteristics of PVCN during photo-cross-linking processes. Similarly, the surface stress which induces the deflection of PVCN-coated cantilever is closely related with the Young's modulus and Poisson's ratio of PVCN. Therefore, the trends of these normalized PCDS peak and static deflection signals confirm photo-cross-linking of PVCN but do not directly present the kinetics of photo-cross-linking processes.

In summary, we have integrated NTA with the PCDS to demonstrate the capability of a microcantilever as a

multi-modal device for the characterization of variations in the thermodynamic, thermomechanical, and chemical properties of a photosensitive polymer on a flexible substrate. By measuring the resonance frequency of the PVCN-coated microcantilever, we acquire the temperature-dependent thermomechanical information of the coated PVCN as a function of UV irradiation time. In addition, the measured deflection provides the information on the glass transition temperature of the coated PVCN as a function of UV irradiation time and the kinetics of photo-cross-linking processes of PVCN. Moreover, nanomechanical IR spectra provide the chemical information of the coated PVCN, which is the breakdown of the π-π conjugation in PVCN polymer chain under UV irradiation. The changes in Young's modulus and Poisson's ratio of PVCN after UV irradiation affect the thermal stress and surface stress on the microcantilever. Therefore, the rate of photo-cross-linking is related with the rate of decrease in the normalized differential deflection signal at the temperatures of local minima during heating and cooling as well as the increase in the normalized Young's modulus rather than to the intensity of the characteristic IR absorption peaks in PCDS spectra and the magnitude of the static deflection. These multi-modal signals confirm photo-cross-linking processes of PVCN and enable us to investigate the various properties of polymers, especially on flexible substrates.

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