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Process comparison for fracture-induced formation of surface structures on polymer films

Yueh-Ying Lee [a], Fuqian Yang [b], Chia-Chieh Chen [c], Sanboh Lee [a,*]

[a] Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan
[b] Department of Chemical and Materials Engineering, University of Kentucky, Lexington, KY 40506, USA
[c] Institute of Nuclear Energy Research, Longtan, Taoyuan 32546, Taiwan

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ABSTRACT

Using three different splitting approaches such as point-load splitting, tension-splitting and peeling–splitting, different surface ripples were produced on poly(methyl methacrylate) (PMMA)-based polymer films. Independent of the splitting approaches, the spatial wavelength of the surface structures is a linear function of the film thickness with the approximately same differential ratio of the spatial wavelength to the film thickness. The apparent surface residual stress was calculated from the thickness dependence of the spatial frequency, and the magnitude of the apparent surface stress increased with the increase of the film thickness. After exposing the aged PMMA-based photoresist at liquid state to gamma-irradiation, the effects of aging and the gamma-irradiation were investigated on the splitting-induced formation of surface structures. For the peeling–splitting process, the differential ratio of the spatial wavelength to the film thickness for the aged samples is larger than that for non-aged samples. The point-load splitting could not produce any surface pattern on the gamma-irradiated films. None of the splitting approaches could form surface structures for polymer films exposed to irradiation of high dose. Both the spatial wavelength and the apparent surface stress increased with the film thickness for the irradiated polymer films.

1. Introduction

Polymeric thin films have been extensively applied to a variety of technological applications, such as organic electronics [1–3], optics [4], and biomedical devices [5]. Recently, various processing techniques have been developed to produce controllable nano/microscale structures on the surface of materials. Applying electric field between two electrodes, Schäffer et al. [6] demonstrated that electric field can induce surface instability of liquid-like polymer and form ordered surface pattern on polymeric films. Ghatak et al. [7] reported the fingering instability of polydimethylsiloxane films confined between two glass plates, which might be used to construct surface structure on the glass surface. Chung et al. [8] observed the formation of surface patterns on polystyrene (PS) films after exposing the PS films to toluene vapor. They suggested that the formation of surface patterns was due to the internal compressive stress created by the swelling of the unmodified PS.

To produce controllable structures on the surface of polymer films, Pease III et al. [9] used the peeling-induced splitting of a polymer thin film sandwiched between two relatively rigid flat plates to produce sub-60-nm half-pitch highly ordered gratings over large surface area, which was termed as fracture-induced structuring (FIS). They examined the effect of molecular weight, bonding strength between the polymer film and the plates, and temperature on the formation of surface structures. To extend this method to cross-linked elastomers, Cai and Newby [10] used ultraviolet/ozone to form a silica layer on the surface of a silicone sheet and applied the fracture-based peeling technique to create parallel silicone strips of spatial wavelength larger than 10 μm on silicon substrate. In contrast to the fracture-based peeling approach, Lin et al. [11] and Liang et al. [12] used a fracture-based tension approach to form sub-micron grating structures and semi-circular surface patterns on poly(methyl methacrylate) (PMMA)-based polymeric films. They suggested that the residual surface stress created during the separation caused the formation of surface patterns and derived the relationship between the spatial frequency and the film thickness.

Considering the importance of surface modulation in the applications of flexible electronics and biomedical devices, we compare the surface patterns formed on PMMA-based photoresists by using three different FIS processes, i.e. 1) the peeling-induced splitting, 2) the tension-induced splitting, and 3) the point-load-induced splitting. Also, we examine the effects of aging and gamma-irradiation on the pattern formation and the residual surface stress.

* Corresponding author. Tel./fax: +886 3 571 9677.
E-mail address: sblee@mx.nthu.edu.tw (S. Lee).

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2. Experimental details

2.1. Sample preparation

For the point-load-induced splitting of polymer films, 4-inch silicon wafers (Summit-Tech Resource Corp., Hsinchu, Taiwan) and the mr-I8030E PMMA-based photoresist (Micro Resist Technology GmbH, Berlin, Germany) were used. The silicon wafers were etched by reactive ion etching to improve the adhesion between photoresist and silicon substrate, which were then cut into $2 \times 2\ cm^2$ plates. The silicon plates were cleaned by using acetone and deionized water in an ultrasonic bath for 15 min and then baked. The PMMA-based photoresist was spin-coated on the silicon plates at 25 °C. Polymer thin films of different thicknesses were obtained by controlling the concentration of photoresist and the spin speed in the range of 700 to 6000 rpm. After the prebake at 150 °C for 5 min to ensure full evaporation of solvent, another silicon plate was placed on top of the polymer thin film to make sandwiched structure.

For the tension-induced splitting of polymer films, O_2-plasma surface modification was used to change the surface structure of silicon wafers. After spin-coating and baking processes as stated above, the photoresist was patterned into 10:1 long-rectangles on the silicon wafer. Following the prebake at 150 °C for 5 min, a clean silicon plate of same size was placed on the patterned-rectangular plate to form a sandwiched structure.

For the peeling-induced splitting of polymer films, no surface modification was made on the silicon wafers. Sandwiched structures of $2 \times 2\ cm^2$ were prepared by following the procedure as stated above.

To examine the effect of irradiation on the formation of surface structures, gamma-irradiation was performed at Radiation Application Technology Center in the Institute of Nuclear Energy Research (Longtan, Taiwan) on the mr-I8030 resist at liquid-state, which was contained in a glass container. The irradiation used Co-60 gamma-ray source at 25 °C in air, and the dose rate was 5 kGy/h. The irradiated resists were used to prepare sandwiched structures for studying the effect of gamma-irradiation on the FIS-induced surface patterns.

All of the sandwiched specimens were pressed and heated above the glass transition temperature of the polymer thin films ($T_g = 115$ °C for non-irradiated polymer). During the hot-pressing, temperature was held at 170 °C for 5 min to ensure strong bonding between the polymer thin film and the top/bottom plates. After the hot press, the specimens were air-cooled to room temperature.

2.2. Splitting of the sandwiched structures

Both the point-load-induced splitting process and the tension-induced splitting process have been described in detail in recent publications [11–13]. For the peeling-induced splitting process, a razor blade was pushed into the middle of the sandwiched structure to initiate a crack. Further pushing the razor caused the separating of the polymer film. All of the separations were performed at 25 °C.

3. Results and discussion

3.1. Non-irradiated polymer films

Fig. 1 shows optical images of the surface structures created by the three different splitting processes, respectively. The point-load splitting created semi-circular surface ripples, similar to the results given by Liang et al. [12] for the splitting of a polymer film sandwiched between two glass plates. Both the tension-splitting and the peeling–splitting created parallel surface gratings while the tension-splitting produced surface gratings with the orientation about 45° to the long edge of the long-rectangular polymer thin films and the peeling–splitting produced surface gratings with the orientation perpendicular or parallel to the peeling direction. Obviously, depending on the loading condition and the geometrical configuration, one can control the morphology of the surface structures formed on polymer films. Compared to the results given by Liang et al. [12] and Lin et al. [11,13] for the polymer films coated on glass plate, the substrate has no significant effect on the formation of surface structures during the FIS processing. These results demonstrate that surface structures of various geometrical configurations can be produced through the FIS processing by controlling the loading condition and the film geometry.

Note that local non-uniformity can be observed through the surface of the polymer films near the edges for both the point-load splitting and tension-splitting processes. To reduce the effect of the non-uniformity, the characterization of the surface structures was performed away from the edges of the films.

Using an atomic force microscope (Dimension 3100, Veeco Instruments Inc., Santa Barbara, CA), the topology of the surface structures was determined. Fig. 2(a) shows the variation of the spatial wavelength of the surface structures with the film thickness for all the three splitting techniques. The spatial wavelength is a linear function of the film thickness for the experimental conditions. Using curve fitting to fit the experimental data, one obtains

$$\lambda = \begin{cases} (4.20 \pm 0.11)h & \text{point-load} \\ (3.87 \pm 0.05)h + 333 & \text{tension} \\ (3.86 \pm 0.11)h & \text{peeling} \end{cases} \quad (1)$$

where λ is the spatial wavelength in the unit of nm and h is the film thickness in the unit of nm. Please note that Eq. (1) cannot be used to describe the dependence of the spatial wavelength on the film thickness as h approaches zero. The value of 333 nm in Eq. (1) for the tension-splitting implies that the spatial wavelength of the surface gratings created by the tension-splitting is always larger than 333 nm for the experimental conditions. The mechanism is unclear, which might involve

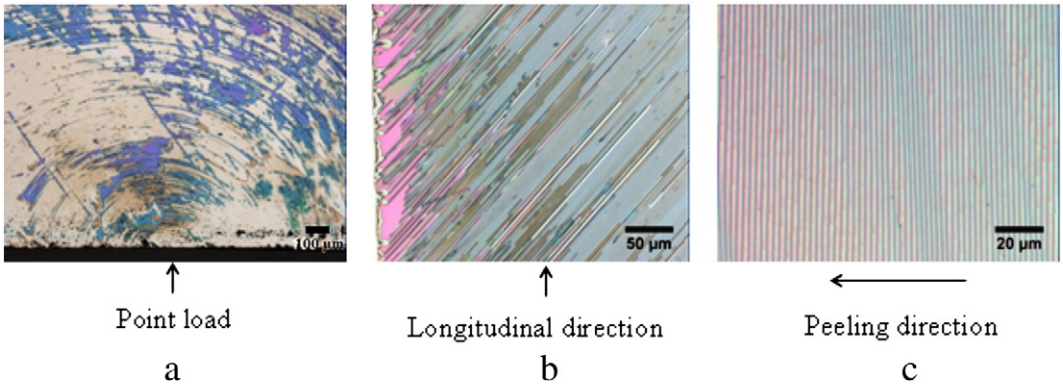

Fig. 1. Surface structures created by the fracture-induced splitting of non-aged and non-irradiated polymer films: a) point load, b) uniform tension of rectangular specimen, and c) peeling.