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Influence of Octacyclopentylsilsesquioxane Nanofiller on the Dewetting Behavior of Polymer Thin Film

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In this study, the strategy to suppress the dewetting of polystyrene (PS) thin films by the addition of octacyclopentylsilsesquioxane (cPOSS) as a nanofiller was proposed. PS thin films by cPOSS were prepared by spin-coating. The bulk glass transition temperature of PS was not changed with an addition of the nanofiller up to 10 wt%. On the other hand, the addition of cPOSS to the PS thin films led to a great inhibition of dewetting. After annealing for 3 h at 373 K, no appreciable dewetting was observed by optical microscopy in the PS film with 15 wt% cPOSS, in contrast, the PS film without cPOSS was completely dewetted. Holes formed on the PS films with 10 wt% cPOSS. However, in that case, the growth of the holes stopped before reaching the final stage of the dewetting. This suggests that the increase of the cPOSS concentration per unit area at the rim of the holes prevents further growth of the holes, and this inhibition effect can be attributed to the interaction between cPOSS and the substrate accompanying modification of the PS-substrate interface.

Key words: Dewetting, Silsesquioxane, Polymer thin film, Nanofiller

1. INTRODUCTION

Miniature devices and various applications like coatings, lubrication, or electronic packing demand progressively thinner polymer films. However, producing stable and defect-free films is particularly problematic in very thin films where thermally induced fluctuations of the polymer-air boundary tend to cause film rupture and dewetting of the films from the substrates.[1] Dewetting can often compromise the effectiveness of the coatings, and this fundamental problem motivates the development of strategies for stabilizing polymer thin films against dewetting.

Surface energetics is an important factor causing the film rupture. The key to whether a film is stable or not on a certain substrate is given by Young's equation for the spreading coefficient,[2]

$$S = \gamma_B - (\gamma_A + \gamma_{AB}) \qquad (1)$$

where γ_A, γ_B and γ_{AB} are the surface energies of the polymer film, substrate and polymer-substrate interface, respectively. If the spreading coefficient is negative, then the film is unstable.

The usual approaches to stabilize films naturally involve a modification of the polymer-surface interaction to promote wetting through grafting chains onto the surface,[3] the introduction of specialized end groups onto the polymer with a high affinity for the inorganic substrate,[4] or modification of the substrate roughness or chemistry by irradiation.[5] Dewetting can be greatly suppressed in very high molecular mass, glassy or entangled, polymer films spin-coated from solution. It is difficult for these films to equilibrate so that surface energetics is less of a factor governing surface wetting. A shortcoming of this approach is that dewetting still tends to occur, albeit on long time scales. Recently, Barnes et. al. discovered a novel stabilizing method through addition of nanoparticles to the matrix polymer.[6] The addition of a small amount of fullerene nanoparticles to the spin-coating polymer solution led to an inhibition of dewetting in polymer thin films. This stabilization is contrary to the usual experience where film inhomogeneities (particles and air bubbles) often lead to the hole formation,[7] and thus, the nanosize of the particles seems to be essential to the nature of this inhibited dewetting phenomenon.

The present work shows the addition of polyhedral oligomeric silsesquioxane (POSS) also rises to dewetitng inhibition. POSS, of which the most common octameric structure is characterized by the formula $R_8Si_8O_{12}$, is one of nanosized materials with a silica core and organic groups on the surface providing a high compatibility with organic polymers. Currently, POSS derivatives meet increasing interest as building units for inorganic-organic hybrid materials, and the addition of POSS to the bulk polymers is proved to improve mechanical properties such as tensile strength and flexural modulus.[8] In this paper, POSS is introduced to polymer thin films as a nanofiller, and its influence on the dewetting behavior of the film is investigated.

2. EXPERIMENTAL

2.1 Materials

To observe the film dewetting in the experimental time scale, low molecular weight (below the critical entanglement molecular weight) polymer was used in this study. Low molecular weight polystyrene (PS2k) was purchased from Polymer Source, Inc. with reported average molecular mass and polydispersity value of M_n = 2100, M_w/M_n = 1.06, respectively. 1,3,5,7,9,11,13,15-octacyclopentylpentacyclo-[9.5.1.$1^{3,9}$.$1^{5,15}$.$1^{7,3}$]octasiloxane (cPOSS, Figure 1) was purchased from Aldrich Chem. Co.. The silicon wafer substrates were purchased from Sumitomo Mitsubishi Silicon Co., and cleaned in a 70/30 volume ratio solution of concentrated H_2SO_4 (97 wt%) and H_2O_2 (34.5 wt%) for 1 h at 353 K, rinsed in deionized water and dried under vacuum before spin-coating.

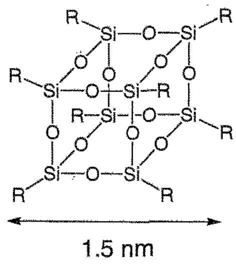

Figure 1 Chemical structure of cPOSS.

2.2 Thermal Properties

Thermal stability of cPOSS powder and the glass transition temperatures (T_g) of pure PS2k and PS2k with 10 wt% cPOSS bulk films were determined by differential scanning calorimetry (DSC) using DSC 8230 (Rigaku) in nitrogen atmosphere from 303 K to 413 K at heating rate of 10 K min^{-1}.

2.3 Sample Preparation

Mixtures of cPOSS and PS2k with specific compositions were dissolved in toluene. A total solid (PS2k and cPOSS) mass fraction of a solution was 2 wt%, and the relative cPOSS mass fractions to polymer were in the range 0-15 wt%. Solutions were filtered using 0.2 μm poly(tetrafluoroethylene) (PTFE) filters, and spin-coated onto the treated silicon substrates at various speeds ranging 1500-5000 rotations per minute (rpm) for 30 s to obtain films ranging 40-100 nm in thickness. The thicknesses of the films were calculated by ellipsometry using Imaging Ellipsometer (Nippon Laser & Electronics Lab. Inc.) with the refractive index of the films to be 1.58. Optical microscopy indicated that the films were smooth and uniform when inspected immediately after spin-coating.

2.4 Morphological Observation

The films were annealed at various temperatures above T_g of pure PS2k with a hot stage directly under the microscope. The dewetting process was observed in real time by OLYMPAS BX51 (Olympas Optical Co., Ltd.) optical microscopy under reflection mode. The sample was then quenched down to room temperature and observed with atomic force microscopy (AFM) using SPA-400 (Seiko Instruments Inc.).

3. RESULTS AND DISCUSSION

3.1 Thermal Properties

Figure 2 shows DSC results of cPOSS powder, pure PS2k and PS2k with 10 wt% cPOSS bulk films. As for curve (1) in Figure 2, cPOSS did not show significant thermal transitions at this temperature range, confirming the thermal stability of cPOSS. T_g of pure PS2k was evaluated from curve (2) in Figure 2 to be 331 K. T_g of PS2k with 10 wt% cPOSS was evaluated from curve (3) in Figure 2 to be 333 K, almost same value as that of pure PS2k. It can be concluded that the addition of cPOSS does not change T_g of PS2k bulk film up to 10 wt%.

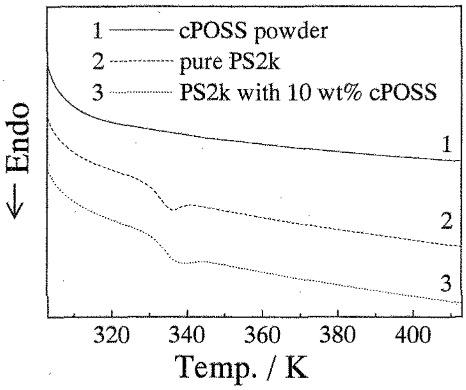

Figure 2 DSC curves of (1) cPOSS powder, (2) pure PS2k bulk film, and (3) PS2k with 10 wt% cPOSS bulk film.

3.2 Dewetting of the Pure PS2k thin film

The dewetting pattern of a 53 nm thick PS2k thin film after annealing at 373 K for 3 h is shown in Figure 3a. The film was uniform and smooth before annealing. When annealed at 373 K, the film broke up by the creation of cylindrical holes. The holes then grew and formed rims ahead of them, which finally contacted each other creating cellular structures. The rims were unstable and decayed into droplets at the final stage of the dewetting as shown Figure 3a.

To understand these dewetting observations of PS2k film, preliminary measurements of the surface energy of the treated silicon substrates were done by the static contact angle measurement of pure water and diiodomethane. The surface energy of the substrate (γ_B) was approximately 72.7 mN m^{-1}, and its dispersive ($\gamma_B{}^d$) and polar ($\gamma_B{}^h$) components were 29.9 mN m^{-1} and 42.8

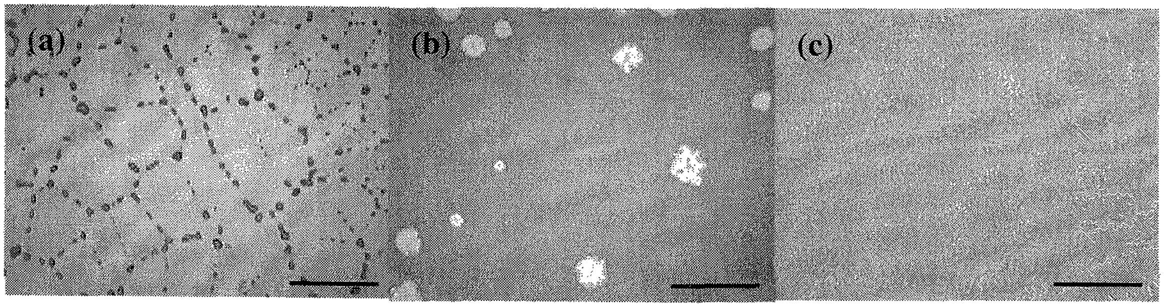

Figure 3 Optical micrographs of (a) 53 nm thick pure PS2k film, (b) 52 nm thick PS2k film with 10 wt% cPOSS, and (c) 56 nm thick PS2k with 15 wt% cPOSS film after annealing at 373 K for 3 h. The length of the bar is 300 μm.

mN m^{-1}, respectively. The surface energy of PS (γ_A), dispersive (γ_A^d), and polar (γ_A^h) components are known as 42.0 mN m^{-1}, 41.4 mN m^{-1}, and 0.6 mN m^{-1}, respectively.[9] The polymer-substrate interfacial energy is then evaluated by using the following equation.

$$\gamma_{AB} = \gamma_A + \gamma_B - 2\sqrt{\gamma_A^d \gamma_B^d} - 2\sqrt{\gamma_A^h \gamma_B^h} \qquad (2)$$

From the surface energies mentioned above, the interfacial energy between A and B was evaluated to be 34.1 mN m^{-1}. On the basis of these values of surface and interfacial energies, the observed dewetting of the PS2k film can be explained by the negative spreading coefficient, $S = -3.4$ mN m^{-1}.

3.3 Dewetting of the cPOSS-filled PS2k films

Figures 3b and 3c show the dewetting patterns of the cPOSS-filled films at various cPOSS concentrations. The film thicknesses were approximately 50 nm. After annealing at 373 K for 3 h, no appreciable dewetting was observed by optical microscopy in the PS2k film with 15 wt% cPOSS (Figure 3c), in contrast, the PS2k film without cPOSS was completely dewetted (Figure 3a). The holes were observed for the PS2k films at lower cPOSS concentrations. Figure 3b shows the hole morphology of the PS2k film with 10 wt% cPOSS. The rim of the holes was distorted. Dewetting was suppressed in these films compared with PS2k film. These findings show that the addition of cPOSS has a tendency to inhibit the film from dewetting, and the degree of the inhibition depends on the cPOSS concentrations.

To obtain a more detailed view, the samples were also observed with AFM in the contact mode. Figure 4 shows the AFM image of PS2k film with 10 wt% cPOSS along with the line profile after annealing at 373 K for 3 h. The inset shows the AFM image of the film before annealing. The line profile revealed that the initially smooth film was roughened through annealing process on the scale of scores nm in height and several μm in width. These structures are occasionally observed in pure PS films as a result of the capillary instability,[10] however, there is a possibility that the aggregation of cPOSS in the films plays a role in the formation of such structure.

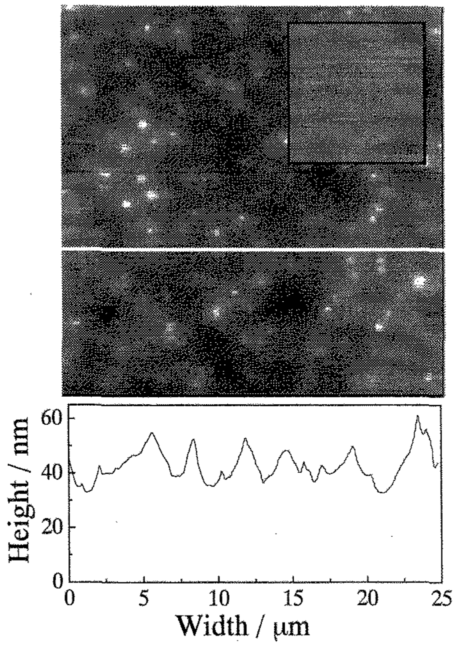

Figure 4 AFM image and line profile of 52 nm thick PS2k film with 10 wt% cPOSS after annealing at 373 K for 3 h. The scale of the image is 25 μm × 25 μm. The inset shows the AFM image of the film before annealing.

3.4 Influence of the Film Thickness

To investigate the influence of the film thickness on the dewetting behavior, PS2k films and PS2k films with 10 wt% cPOSS ranging 40-100 nm in thickness were annealed at 373 K for 1 h. The dewetting process was observed in real time by reflective optical microscopy, and the dewetting area (a percentage of the hole area) and the average diameter of the holes was calculated from the optical micrographs.

Figure 5 shows the dewetting area as a function of the annealing time for each film. The addition of 10 wt% cPOSS brought a great suppression of the film dewetting in this range of film thickness. Figure 6 shows the diameter of the holes as a function of the annealing time for the same films as Figure 5. The rates of hole growth were independent on the film thickness, and reduced through the addition of cPOSS.

3.5 Influence of the Annealing Temperature

The PS2k films and PS2k films with 10 wt% cPOSS were annealed at several temperatures above T_g of pure PS2k. The film thicknesses were approximately 50 nm. Figure 7 shows that the increase of the annealing temperature induces dewetting both for the PS2k films and PS2k films with 10 wt% cPOSS, however, the dewetting behavior of these two films were completely different. As for Figure 7b, the growth of the holes of PS2k films with 10 wt% cPOSS was arrested before reaching the final stage of the dewetting when they were annealed at 393 K and 413 K. The dewetting areas of the films annealed for 1 h at 393 K and 413 K were different, however, the magnitudes of the hole area per rim length result in the almost same value for these films. This suggests that the increase of the cPOSS concentration per unit area at the rim of the holes prevents further growth of the holes, and this inhibition effect can be attributed to the interaction between cPOSS and the substrate accompanying modification of the PS-substrate interface.

4. CONCLUSION

The present paper demonstrated that the addition of cPOSS to a spin-coated polymer thin film can actually stabilize the film against dewetting. Even though the bulk glass transition temperature of PS2k was not changed with an addition of cPOSS, the addition of cPOSS to the PS2k thin films resulted in the decrease of the rates of hole growth. The evidence available implies that the cPOSS concentration per unit area played an important role in the inhibition of dewetting. These results suggest that the inhibition of dewetting can be attributed to the interaction between cPOSS and the substrate accompanying modification of the PS-substrate interface.

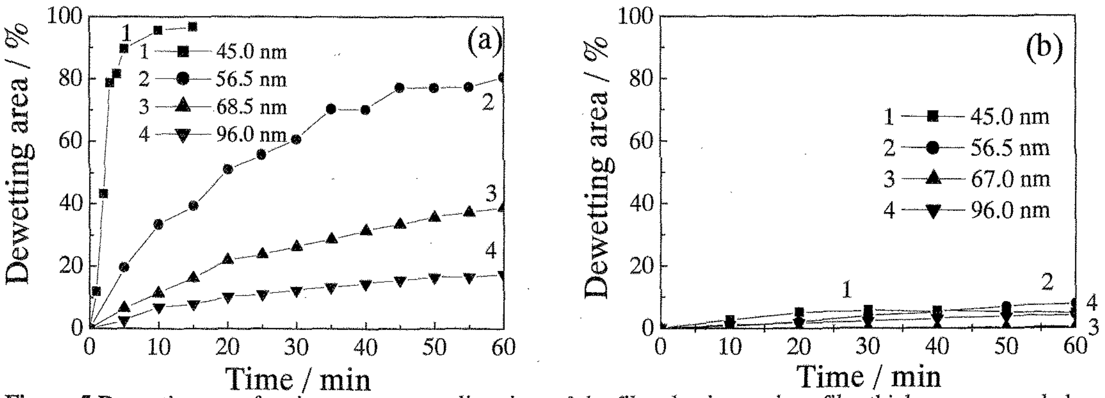

Figure 5 Dewetting area fraction versus annealing time of the films having various film thicknesses annealed at 373 K (a) PS2k films (b) PS2k films with 10 wt%cPOSS.

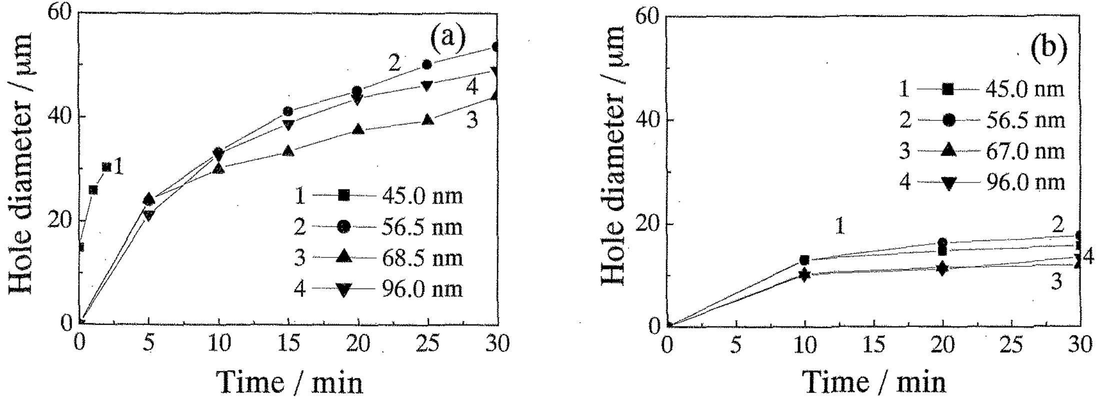

Figure 6 Hole diameter versus annealing time of the films having various film thicknesses annealed at 373 K (a) PS2k films (b) PS2k films with 10 wt%cPOSS.

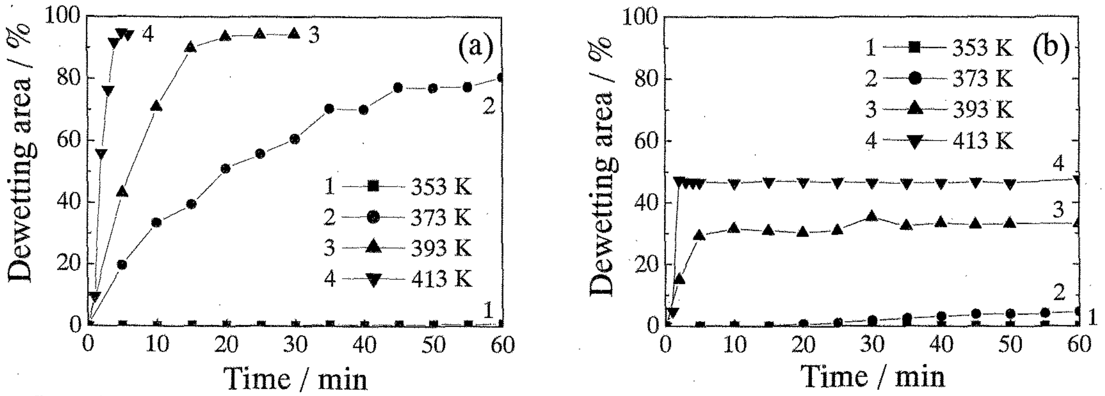

Figure 7 Dewetting area fraction versus annealing time at various annealing temperature (a) PS2k films (b) PS2k films with 10 wt%cPOSS.

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