

THE EFFECT OF SURFACE TERRACING AND CONFINED NANOPARTICLES ON CRAZING IN SYMMETRIC PS-B-P2VP THIN FILMS

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ABSTRACT

For many applications, like opto-electronic devices and templates for nanopattern fabrication, one or two dimensional arrays with long range order are needed. Block copolymer thin films offer a convenient route to make these arrays, but the growth of mechanically-imposed defects, such as crazes or cracks will limit their intended function. In this paper, we discuss the growth of crazes in nanocomposite thin films of polystyrene-b-poly-2-vinyl pyridine (PS-b-P2VP) with gold nanoparticles confined to the P2VP microphase. This material serves as a model system due to the similarity of physical properties (glass transition temperature, modulus, and onset of crazing stress) between the two polymer segments. To study the effects of a multivariable space on crazing phenomenon in symmetric diblock copolymers, we employ the use of combinatorial methods and the copper grid technique. We present results on the effect of surface defects (island/hole domains) on the initiation and propagation process of crazes in thin films, and we demonstrate how confined nanoparticles restrict the growth of crazes in these materials.

1 INTRODUCTION

Block copolymers are unique materials due to their inherent ability to self-assemble into nanoscale, periodic structures, such as spheres in BCC packing, cylinders in hexagonal packing, and stacked lamellae. These structures and their potential for long range order array are attractive for many applications, like opto-electronic devices and templates for nanopattern fabrication. (Morkved [1]) For some applications, such as photonic materials, a large difference in the dielectric constant between the two phases is also required. To meet this need, researchers, such as Thomas (Bockstaller [2]) and Sohn (Sohn [3]), have demonstrated several methods for embedding nanoparticles within one microphase to increase dielectric contrast. Although processing of these nanocomposite materials has been a focus over the last several years, the growth of mechanically-imposed defects, such as crazes or cracks, in these materials has not been investigated. These defects will alter the local dielectric constant and limit the material's proposed function.

In this paper, we investigate the growth of crazes in nanocomposite thin films of polystyrene-b-poly-2-vinyl pyridine (PS-b-P2VP). This material serves as a model system due to the similarity of physical properties (glass transition temperature, modulus, and onset of crazing stress) between the two polymer segments. P2VP also serves as a convenient template for *in situ* synthesis of gold nanoparticles. We present results on the effect of surface terracing and confined nanoparticles on craze initiation, craze topology, and path.

2 EXPERIMENT

2.1 Combinatorial method

To study the effect of a multivariable space on crazing phenomenon in symmetric diblock copolymers, we employ the use of combinatorial methods. Combinatorial methods are tools and

techniques that allow many experiments to be conducted in parallel by creating 1D or 2D variable gradients. These methods have been used in and validated for numerous experimental studies in polymer science (Meredith [4]). One example of a combinatorial approach in our research is the fabrication of thickness gradient libraries. As we discuss below, thickness alters the stress state in thin films and controls surface terracing in diblock copolymer films. By having one film with a large range of this critical variable, we can decouple competing effects.

2.2 Sample preparation and characterization

Polystyrene (PS) ($M_n=105,300$, $PI=1.05$) and PS-*b*-P2VP ($M_n=115,000$; $PI=1.08$; 50% PS) are purchased from Sigma-Aldrich and Polymer Source Inc. respectively. PS is dissolved in toluene (4.5 wt %), and PS-*b*-P2VP is dissolved in tetrahydrofuran (3.5 wt %). Polymer thin films with thickness gradients are prepared by flow coating on a clean silicon wafer with a thermally-grown silicon oxide layer (~350 nm). The PS-*b*-P2VP film is annealed under vacuum at 180°C for 72 h.

To quantify craze growth, we remove the annealed polymer film from the substrate by etching the silicon oxide layer with 10 vol % hydrofluoric acid (HF) to float the polymer film on the solution. The thin film is subsequently transferred onto a copper grid whose bars are pre-coated with PS or P2VP. To minimize the effect of HF on the P2VP, the HF solution is diluted before we transfer PS-*b*-P2VP film onto the copper grid. The film is dried, solvent annealed, and dried again prior to being strained by a tensile test instrument at a displacement rate of 1 mm/min. At a predetermined strain, the specimen is removed from the grip and characterized with optical microscopy (OM), atomic force microscopy (AFM) and transmission electron microscopy (TEM). (Lauterwasser [5]).

2.3 Fabrication of nanocomposites (based on Sohn et al (Sohn [3]))

To fabricate nanoparticle-filled block copolymers, after annealing, the block copolymer thin film on a silicon oxide wafer is immersed into 1 wt % HAuCl_4 /Ethanol solution for 30 sec, and rinsed with water to remove uncoordinated gold ions. The coordinated gold ions are reduced to gold by immersing the film into 1 wt % NaBH_4 solution for 20 sec, and rinsed with water again. The nanocomposite is then floated with 10 vol % hydrofluoric acid solution, and transferred to a copper grid.

3 RESULTS AND DISCUSSION

3.1 Effect of surface terracing on the initiation of crazes

Symmetric diblock copolymer thin films form lamellar structures parallel to the substrate when one component has a lower surface energy and the other component has an affinity to the substrate. In this asymmetric wetting situation, the surface will be flat if the thickness corresponds to $(n +$

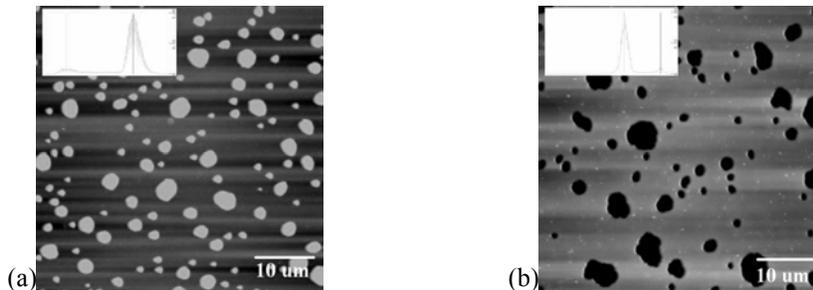


Figure 1: AFM images of (a) island and (b) hole domains on the surface of PS-*b*-P2VP (thin film is cast by flow coating). L_0 is 51.5 ± 1.5 nm.

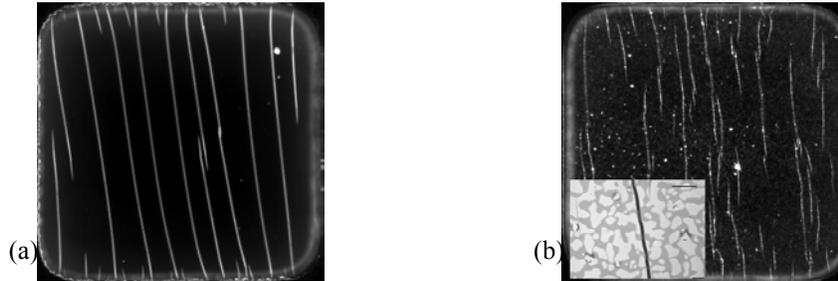


Figure 2: OM images of crazes on (a) PS and (b) PS-b-P2VP thin films (thickness is 130 nm). Grid dimension is 1mm \times 1mm. Inset shows surface morphology of block copolymers with crazes on copper grids.

$1/2) \times L_0$, where L_0 is the period of stacked lamellae in the bulk state and n is the number of lamellae. If the initial thickness (before annealing) is incommensurate with the above formula, surface terraces, commonly referred to as island, hole, or bicontinuous structures, will occur. The step height of an island and depth of the hole domains are equal to L_0 (Cai [6]). Figure 1 (a) and (b) show AFM images of island and hole domains on the surface of a PS-b-P2VP thin film. From these AFM images, we use the distribution of height values to measure L_0 statistically. We find that L_0 is $51.5 \text{ nm} \pm 1.5 \text{ nm}$.

It is known that crazes are initiated by defects, like dust or inclusions (Kramer [7]). In our thin films, the terrace on the block copolymer surface affects craze initiation. In PS (Figure 2 (a)), all crazes initiate near the edge of a grid square where the majority of defects exist. For PS-b-P2VP thin films with surface terraces, we find that most crazes initiate away from the edge (Figure 2 (b)). This suggests that surface defects (island/hole domains) serve to initiate crazes. Essentially, these surface domains are instant changes in film thickness. Depending on film thickness, the relative change in thickness can be $0.35 h$ to $0.60 h$ (h is post-annealing film thickness). This significant change in thickness alters the stress field sharply, thus causing a stress concentration to initiate crazes. Although the depth change is on the nanometer length scale, the lateral size of these domains are $0.2 \sim 10 \mu\text{m}$. This lateral size is consistent with the size of defects that affect crazing in filled polymer systems (Argon [8]). For PS-b-P2VP thin films with a flat surface, some crazes also initiate away from the edge. This behavior may indicate that defects in the lamellae are present, as suggested by Grim *et al* (Grim [9]).

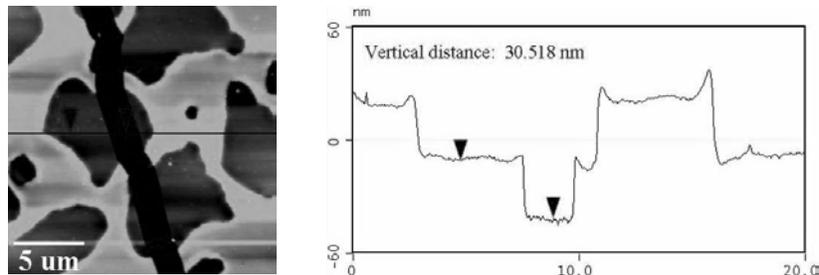


Figure 3: AFM image of the craze within the hole domain on PS-b-P2VP thin film. (thickness is 125 nm)

3.2 Effect of surface terracing on the path and topography of crazes

Crazes in glassy homopolymers are long, narrow regions with a straight path. In contrast, crazes in PS-b-P2VP thin films are deflected by the edges of surface terrace domains (Figure 3). We observe that the craze path is sinuous compared with crazes on PS-b-P2VP with flat surface and PS thin films. This deviation in the craze propagation is attributed to the stress field surrounding surface terraces.

Although surface terraces alter the path of crazes, they do not alter the “micro-necking” process of craze formation. Yang *et al* first reported that the ratio of craze depth to film thickness in a mature craze is constant for all film thicknesses. This ratio is 0.35 reported by Yang *et al*, (Yang [10]) and 0.37 by Crosby *et al*. (Crosby [11]) In PS thin films, we measure a ratio of 0.37. In block copolymer thin films, in regions surrounding a surface terrace (Figure 3), the craze depth to thickness ratio is 0.37, and within a surface terrace, the ratio is 0.38. Both values are close to 0.37, thus suggesting that crazes follow the same “micro-necking” mechanism as in homopolymers.

3.3 Effect of confined nanoparticles

In addition to the effect of block copolymer morphology and surface terracing on craze formation, the effect of confined nanoparticles is important to the development of future opto-electronic materials. To investigate this effect, we have fabricated a nanocomposite of gold nanoparticles confined to the P2VP phase of our block copolymer. (Figure 4)

As in the “neat” block copolymer case, we transfer the nanoparticle-filled film to a copper grid and apply a tensile strain. Using an *in situ* camera, we observe the growth of crazes and cracks as a function of strain. The nanoparticle-filled film fails at strains near 1.0% without significant craze growth. (Figure 5) This behavior is in contrast to “neat” PS and block copolymer films where crazes forms near 1% strain, and no failure is observed until higher strains.

4 SUMMARY

In summary, we find that surface terracing serves to initiate crazes in PS-b-P2VP thin films. For PS-b-P2VP thin films with flat surface, crazes are also initiated away from the grid edge, thus suggesting the existence of defects in the lamellae structure formed during thin film annealing

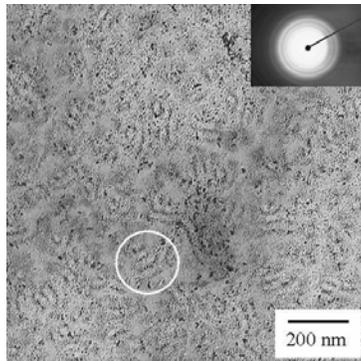


Figure 4: TEM image of PS-b-P2VP (MW=40K) with gold nanoparticles. Inset is electron diffraction pattern of gold. White circle shows lamellae standing normal to the substrate.

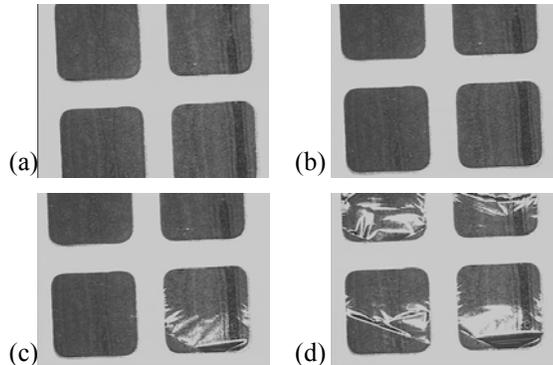


Figure 5: *In-situ* OM observation of PS-b-P2VP thin film (thickness is 125 nm) with nanoparticles under different strain. (a) 0% (b) 0.8% (c) 1.0% (d) 1.2%. During the test, the increment of strain is 0.2%, and the duration between different strains is 10 min. Grid dimension is 1mm × 1mm.

process. In addition to initiation, surface terracing alters the local vector of a craze, but does not modify the process of “micro-necking” in polymer thin film crazes. Finally, our preliminary results demonstrate that for PS-b-P2VP with a high density of confined gold nanoparticles, the film fails in a brittle manner, compared with PS and PS-b-P2VP without gold nanoparticles.

5 REFERENCES

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