978-1-605-11278-7 - Materials Research Society Symposium Proceedings Volume 1301: Soft Matter, Biological Materials and Biomedical Materials – Synthesis, Characterization and Applications

Editors Adam J. Nolte, Christopher M. Stafford, Teng Li, Pil J. Yoo, John Harding, Sheng Lin-Gibson, John Spencer Evans, Kiyotaka Shiba, Christian Hellmich, Ulrike G.K. Wegst, Markus J. Buehler, Roger Narayan, Peter Kiesel, David Nolte, Xudong (Sherman) Fan and Martin Zillmann

Excerpt More information

Harnessing Instabilities in Soft Material Films and Interfaces

978-1-605-11278-7 - Materials Research Society Symposium Proceedings Volume 1301: Soft Matter, Biological Materials and Biomedical Materials – Synthesis, Characterization and Applications

Editors Adam J. Nolte, Christopher M. Stafford, Teng Li, Pil J. Yoo, John Harding, Sheng Lin-Gibson, John Spencer Evans, Kiyotaka Shiba, Christian Hellmich, Ulrike G.K. Wegst, Markus J. Buehler, Roger Narayan, Peter Kiesel, David Nolte, Xudong (Sherman) Fan and Martin Zillmann

Excerpt More information

978-1-605-11278-7 - Materials Research Society Symposium Proceedings Volume 1301: Soft Matter, Biological Materials and Biomedical Materials – Synthesis, Characterization and Applications

Editors Adam J. Nolte, Christopher M. Stafford, Teng Li, Pil J. Yoo, John Harding, Sheng Lin-Gibson, John Spencer Evans, Kiyotaka Shiba, Christian Hellmich, Ulrike G.K. Wegst, Markus J. Buehler, Roger Narayan, Peter Kiesel, David Nolte, Xudong (Sherman) Fan and Martin Zillmann

Excerpt More information

Mater. Res. Soc. Symp. Proc. Vol. 1301@2011 Materials Research Society DOI: 10.1557/opl.2011.537

Anomalous Behavior of Polystyrene Blends Using Thermally Induced Surface Wrinkling

Jessica M. Torres¹ and Bryan D. Vogt¹ ¹Department of Chemical Engineering, Arizona State University, Tempe, AZ 85284

ABSTRACT

The wrinkling of a 50:50 blend of a high molecular mass (M_n = 990 kg/mol) and low molecular mass (M_n = 1.3 kg/mol) polystyrene (PS) film is studied as a function of annealing temperature and film thickness. Both thermal and mechanical wrinkling are utilized to elucidate the apparent modulus of these PS blend films. The PS blend shows a modulus comparable to the high molecular weight PS, ≈ 3.2 GPa for mechanical wrinkling at ambient and thermal wrinkling for T \leq 50 °C. A sharp decrease in the apparent modulus of the film occurs when thermal wrinkling occurs at 60 °C or higher. The calculated modulus in this case is 0.5 GPa, which is significantly below the modulus determined the neat PS for either Mn when thermally wrinkled at T > 60 °C. This behavior is attributed to a combination of surface segregation of the low molecular weight PS as well as the large difference in bulk glass transition temperature (Tg) of each component. During thermal wrinkling, the high Mn PS vitrifies first, while the surface containing primarily low M_n PS is rubbery; this leads to only the underlayer of PS wrinkling initially and selection of a shorter wavelength due to the effective thickness. The increased thermally induced stresses during cooling when the low Mn PS is vitrified do not change the selected wavelength and instead only leads to an increase in the wrinkle amplitude. These results illustrate a potential method to modulate the wrinkle wavelength without changing the overlayer, which could be useful for patterning applications.

INTRODUCTION

Polymer blends are an effective way to develop commercial materials with a variety of desired properties without the need for synthesis of new polymers [1]. The morphology of the blend that develops during processing is critical to its ultimate properties. As such there has been considerable efforts in understanding the bulk properties of polymer blends [2]. More recently, there have been significant efforts in extending thin film studies to polymers blends [3], but the mechanical properties of these materials have not been investigated. Understanding the modulus of these thin films could be important to understanding how morphology impacts mechanics and could have implications in applications such as flexible polymer solar cells where a blend is utilized as the active layer [4]. In order to study the modulus of soft polymer films, a surface wrinkling technique can been utilized [5] to elucidate the elastic modulus of the film from the wavelength of the wrinkles by using linear elastic mechanics. However, recent work on examining the modulus of monodisperse polystyrene (PS) films illustrated that low molecular mass (Mn) PS behaves significantly different from high Mn PS [6]. As commercial polymers typically contain a broad distribution of M_n , it is important to first understand how a blend of different molecular mass of the same polymer impacts the wrinkling and the apparent elastic modulus of the polymer film. In this work, both thermal and mechanical wrinkling techniques are employed using a symmetric (50:50) blend of 990 kg/mol and 1.3 kg/mol PS. These results illustrate anomalous behavior in the wrinkle wavelength for thermal wrinkling as a result of

978-1-605-11278-7 - Materials Research Society Symposium Proceedings Volume 1301: Soft Matter, Biological Materials and Biomedical Materials – Synthesis, Characterization and Applications Editors Adam J. Nolte, Christopher M. Stafford, Teng Li, Pil J. Yoo, John Harding, Sheng Lin-Cibson, John Spencer Evans, Kiyotaka Shiba, Christian Hellmich, Ulrike G.K. Wegst

Lin-Gibson, John Spencer Evans, Kiyotaka Shiba, Christian Hellmich, Ulrike G.K. Wegst, Markus J. Buehler, Roger Narayan, Peter Kiesel, David Nolte, Xudong (Sherman) Fan and Martin Zillmann

Excerpt More information

surface segregation and the disparity in the glass transition temperature (T_g) between the different components.

EXPERIMENT

PS was purchased from Polymer Laboratories ($M_n = 1.3 \text{ kg/mol}$, $M_w/M_n = 1.13$, $T_g = 29.9 \,^{\circ}\text{C}$, and $M_n = 990 \text{ kg/mol}$, $M_w/M_n = 1.05$, $T_g = 106.3 \,^{\circ}\text{C}$). This dependence of T_g on molecular mass for PS has been previously reported [7]. A 50:50 mixture by mass of 1.3 kg/mol and 990 kg/mol PS was dissolved in toluene. Polymer films were spin-cast from toluene solutions on 2.5 cm × 1 cm pieces of UVO cleaned (model 42, Jelight) silicon wafers (450 µm thick). The thickness of the spin cast polymer film was determined using a Variable Angle Spectroscopic Ellipsometer (VASE M-2000, J.A. Woollam Co., Inc.) over a wavelength range from 250 nm to 1700 nm using four incident angles, 60° , 65° , 70° , and 75° . The data were modeled using the optical properties of the wafer substrate and a Cauchy layer to describe the polymer film.

PDMS (Sylgard 184, Dow Corning) was prepared at a ratio of 20:1 by mass of base to curing agent, cast into 1.5 mm thick sheets, and allowed to gel at room temperature for 3 h before curing at 100 °C for 2 h. After cooling to ambient, the PDMS was cut into approximately 2.5 cm \times 7.5 cm strips. The modulus of the PDMS was determined using a Texture Analyzer (TA-TX Plus) at a strain rate of 0.01 mm/s and found to be 0.6 MPa \pm 0.2 MPa. Surface wrinkling at ambient conditions was induced via a 4 % uniaxial compressive force as described previously [8]. The PS films were also thermally wrinkled at temperatures of 40 °C, 50 °C, 55 °C, 60 °C, 70 °C, 100 °C, and 120 °C by annealing in vacuum for 60 minutes at the temperature of interest and then cooling to ambient. The difference in the coefficient of thermal expansion (CTE) between the PS and PDMS results in a stress in the film that is relieved by isotropic wrinkling [5]. The wavelength of the wrinkles (λ) is dependent upon the modulus of the PS (\overline{E}_f) and PDMS (\overline{E}_s) as well as the thickness of the PS film (h_f) as:

$$\lambda = 2\pi h_f \left(\frac{\overline{E}_f}{3\overline{E}_s}\right)^{1/3}$$

This expression can be re-arranged to provide a route to determine E_f for thin soft films [5], where $\overline{E} = E/(1-\nu)^2$ is the plane strain modulus, E is the Young's modulus and ν is Poisson's ratio.

Characterization of the wrinkled surfaces was performed using atomic force microscopy (AFM) and optical microscopy. AFM images were acquired at ambient temperature on an Agilent Technologies 5500 system in tapping mode using a constant scan size of 7.5 μ m × 7.5 μ m at a scan rate of 1 Hz. AFM images were analyzed using 1D Fast Fourier Transform (FFT) to obtain the wavelength of the wrinkles. Optical images were acquired using a Mititoyo Ultraplan FS-110 and analyzed using a 1D Fast Fourier Transform (FFT) to determine the wrinkle wavelength.

978-1-605-11278-7 - Materials Research Society Symposium Proceedings Volume 1301: Soft Matter, Biological Materials and Biomedical Materials – Synthesis, Characterization and Applications

Editors Adam J. Nolte, Christopher M. Stafford, Teng Li, Pil J. Yoo, John Harding, Sheng Lin-Gibson, John Spencer Evans, Kiyotaka Shiba, Christian Hellmich, Ulrike G.K. Wegst, Markus J. Buehler, Roger Narayan, Peter Kiesel, David Nolte, Xudong (Sherman) Fan and Martin Zillmann

Excerpt More information

DISCUSSION

Figure 1 show optical micrographs for the 50:50 PS blend films that are approximately 100 nm thick wrinkled after heating to 40 °C and 100 °C. An isotropic wrinkling morphology of uniform wavelength is observed as expected [5], but there is a dramatic difference in the wrinkle wavelength depending upon the initial condition despite the films containing the same material with the same thickness. For the film wrinkled upon cooling from 40 °C, the wavelength is approximately 7.25 \pm 0.19 µm, while the film wrinkled using 100 °C anneal exhibits a wavelength of approximately 4.46 \pm 0.17 µm. This strong temperature dependence on wavelength is unexpected as the wrinkle wavelength is independent of initial temperature for a monodisperse PS film.



Figure 1. Optical micrographs of the PS blend [a] thermally wrinkled at 40 °C with a $\lambda \approx 7.2 \,\mu$ m and [b] 100 °C thermally wrinkled with a $\lambda \approx 4.4 \,\mu$ m, both films are approximately 100 nm thick.

Similarly, Figure 2a shows the wavelength as a function of film thickness for films wrinkled via mechanical compression, and by thermal wrinkling after heating to 40 °C, 70 °C and 100 °C. Films of the PS blend wrinkled via mechanical compression and thermally at 40 °C collapse onto a single curve with behavior comparable to that of the neat 990 kg/mol PS previously reported [6]. Interestingly, the wavelength for the PS blends wrinkled at both 70 °C and 100 °C collapse onto a single curve. This wavelength is significantly decreased for all film thicknesses and is less than expected for the neat 1.3 kg/mol PS as well. By using a 70 nm thick PS blend film, the temperature dependence of the wrinkle wavelength can be assessed as shown in Figure 2b. The wavelength remains statistically invariant at $\approx 4.8 \ \mu m$ for treatment temperatures below 50 °C followed by an abrupt decrease to $\approx 2.2 \ \mu m$ for higher temperatures (55 °C to 120 °C). This behavior is unusual due to the abrupt nature of the 'transition' and the large difference in wavelength. To interpret these data, it is important to consider the possible origins of the behavior. It is well known that low Mn polymers preferentially wet the surface of polydisperse polymer films [9] and can significantly alter the thin film behavior [10]. Although full phase separation of these components would not be expected, these data could be explained by a bilayer [11] in which the low M_n component is segregated to the surface. Thermal wrinkling is induced by the difference in CTE between PS and PDMS, however there is a minimum change in temperature to allow the strain to exceed the critical strain at which

978-1-605-11278-7 - Materials Research Society Symposium Proceedings Volume 1301: Soft Matter, Biological Materials and Biomedical Materials – Synthesis, Characterization and Applications

Editors Adam J. Nolte, Christopher M. Stafford, Teng Li, Pil J. Yoo, John Harding, Sheng Lin-Gibson, John Spencer Evans, Kiyotaka Shiba, Christian Hellmich, Ulrike G.K. Wegst, Markus J. Buehler, Roger Narayan, Peter Kiesel, David Nolte, Xudong (Sherman) Fan and Martin Zillmann

Excerpt More information

wrinkling occurs. Upon heating to 40 °C and cooling, the critical strain is not exceeded until cooled below the T_g of the 1.3 kg/mol PS. Thus, the entire thickness of the film is felt during the wavelength selection from wrinkling. Conversely after heating to much higher temperatures, the critical strain is exceeded while the low M_n component is still rubbery; in this case, only the glassy fraction provides mechanical resistance to the substrate contraction and hence the wavelength would be decreased by a factor of approximately 2 as one half of the film is glassy, so the effective thickness is 1/2 of the actual thickness. This interpretation suggests that low M_n PS phase separates from high M_n PS in thin films, which is unexpected. Additional experiments that examine the distribution of components are required to confirm this hypothesized mechanism for the temperature dependence of the wrinkle wavelength for the PS blends.



Figure 2. [a] The wavelength as a function of film thickness for the PS blend that is wrinkled mechanically (\Box , blue) or thermally by heating at 40 °C (∇ , green), 70 °C (\blacktriangle , yellow), and 100 °C (\bullet , red). The neat 990 kg/mol PS (dashed black line) is shown for reference. [b] The impact of temperature on the observed wavelength for PS blend films that are nominally 70 nm thick. The error bars represent one standard deviation.

One additional implication from these data is that the apparent moduli of the films determined from thermal wrinkling can be altered significantly. The data in Figure 2 have converted to the modulus as a function of film thickness using well reported buckling mechanics [8]. As shown in Figure 3, the modulus as a function of film thickness for the PS blend mechanically wrinkled and wrinkled at 40°C have a bulk modulus of approximately 3.2 GPa and deviate from thickness independent behavior at a length scale of 50 nm similar to previously reported data for the high molecular weight PS [6, 12]. However, the apparent modulus of the films wrinkled at 70 °C and 100 °C is decreased to approximately 0.5GPa which remains statistically invariant from 180 nm down to 40 nm. Data below 40 nm could not be obtained for due to dewetting of the films. Interestingly, the calculated moduli for these films are less than for either pure component, which is consistent with the prior hypothesis for the wavelength dependent origins. As the surface in this case would be covered with a liquid PS, this blend technique could be useful for separating free surface effects from physical confinement effects

978-1-605-11278-7 - Materials Research Society Symposium Proceedings Volume 1301: Soft Matter, Biological Materials and Biomedical Materials – Synthesis, Characterization and Applications

Editors Adam J. Nolte, Christopher M. Stafford, Teng Li, Pil J. Yoo, John Harding, Sheng Lin-Gibson, John Spencer Evans, Kiyotaka Shiba, Christian Hellmich, Ulrike G.K. Wegst, Markus J. Buehler, Roger Narayan, Peter Kiesel, David Nolte, Xudong (Sherman) Fan and Martin Zillmann

Excerpt More information

for polymer thin films. The apparent modulus at sub-50 nm length scales seems to be independent of film thickness as perhaps the free surface, the source of the sub-50 nm modulus reduction [6], is eliminated due to the remaining liquid layer of the 1.3 kg/mol PS.



Figure 3. Apparent modulus as a function of film thickness for neat PS of 990 kg/mol (•,black) and 1.3 kg/mol (\circ , black). Interestingly the apparent modulus for the blend is dependent upon the temperature at which the wrinkles are induced: mechanically wrinkled at ambient (\Box , blue), thermally wrinkled at 40 °C (∇ , green), at 70 °C (\blacktriangle , yellow), and at 100 °C (\blacklozenge , red). The error bars represent one standard deviation.

The significant reduction in apparent modulus at temperatures above 40 °C can be attributed to a combination of surface segregation and the bulk glass transition temperature of the individual PS components. The low molecular weight PS begins to preferentially segregates to the free surface due to an entropic driving force [13]. Surface segregation of the low molecular weight PS has been studied via surface tension of a 1.9 kg/mol: 9 kg/mol blend system [14]. At compositions > 50 wt% of the low M_n PS component, the surface tension of the blend approaches that of the pure 1.9 kg/mol PS. This phase separation combined with the large difference in bulk Tg of the $M_n = 1.3$ kg/mol PS, 29.9 °C, and $M_n = 990$ kg/mol PS, 106.3 °C, could lead to wavelengths representing only a fraction of the film thickness.

CONCLUSIONS

This work illustrates that the wrinkle wavelength for PS films with a bimodal distribution of molecular mass (PS blend) can be significantly altered by the temperature at which thermal wrinkling occurs. The modulus of a blend at room temperature exhibits a bulk modulus and thickness dependent modulus similar to that of the pure high molecular weight PS. However, thermal wrinkling after annealing at temperatures greater than 55 °C leads to an overall decrease in the equilibrium wavelength and hence the apparent modulus of the blend. These results are

978-1-605-11278-7 - Materials Research Society Symposium Proceedings Volume 1301: Soft Matter, Biological Materials and Biomedical Materials – Synthesis, Characterization and Applications

Editors Adam J. Nolte, Christopher M. Stafford, Teng Li, Pil J. Yoo, John Harding, Sheng Lin-Gibson, John Spencer Evans, Kiyotaka Shiba, Christian Hellmich, Ulrike G.K. Wegst, Markus J. Buehler, Roger Narayan, Peter Kiesel, David Nolte, Xudong (Sherman) Fan and Martin Zillmann

Excerpt More information

interpreted in terms of a surface induced phase separation of the different M_n PS which could yield a liquid-like layer of low M_n PS on top of the glassy high M_n PS when wrinkling is induced.

ACKNOWLEDGMENTS

This work was financially supported by the National Science Foundation under grant #0653989-CMMI. We gratefully acknowledge the use of facilities within the LeRoy Eyring Center for Solid State Science and Arizona State University. The authors thank Christopher M. Stafford at NIST for helpful discussion.

REFERENCES

- 1. P. H. P. Macaubas, N. R. Demarquette, Polymer 42, 2543-2554 (2001).
- 2. Z. M. Xie, J. Sheng, Z. M. Wan, J. Macromol. Sci., Phys. 40, 251-261 (2001).
- 3. H. Wang, R.J. Composto, J. Chem. Phys. 113, 10386-10397 (2000)
- 4. G. Yu, J. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger, Science 270, 1789-1791 (1995).
- C. M. Stafford, C. Harrison, K. L. Beers, A. Karim, E. J. Amis, M. R. Vanlandingham, H. C. Kim, W. Volksen, R. D. Miller, E. E. Simonyi, *Nat. Mater.* 3, 545-550 (2004).
- 6. J. M. Torres, C.M. Stafford, B.D. Vogt, Polymer 51, 4211-4217 (2010).
- 7. Y.F. Ding, A. Kisliuk, A.P Sokolov, Macromolecules 37, 161-166 (2004).
- C. M. Stafford, S. Guo, C. Harrison, M. Y. M. Chiang, *Rev. of Sci. Instrum.* 76, 062207 (2005).
- C. Jalbert, J.T. Koberstein, I. Yilgo, P. Gallagher, V. Krukonis, *Macromolecules* 26, 3039-3074 (1993).
- 10. M. Dion, A.B. Larson, B.D. Vogt, J. Polym. Sci B 48, 2366-2370 (2010).
- 11. R. Huang, C. M. Stafford, B. D. Vogt, J. Aerosp. Eng. 20, 38-44 (2007).
- C. M. Stafford, B. D. Vogt, C. Harrison, D. Julthongpiput, R. Huang, *Macromolecules* 39, 5095-5099 (2006).
- 13.V. S. Minnikanti, Z. Qian, L. A. Archer, J. Chem. Phys. 126, 144905-144907 (2007).
- 14. Z. Qian, V. S. Minnikanti, B. B. Sauer, G. T. Dee, W. G. Kampert, L. A. Archer, J. Polym. Sci., Part B: Polym. Phys. 47, 1666-1685 (2009).

978-1-605-11278-7 - Materials Research Society Symposium Proceedings Volume 1301: Soft Matter, Biological Materials and Biomedical Materials – Synthesis, Characterization and Applications

Editors Adam J. Nolte, Christopher M. Stafford, Teng Li, Pil J. Yoo, John Harding, Sheng Lin-Gibson, John Spencer Evans, Kiyotaka Shiba, Christian Hellmich, Ulrike G.K. Wegst, Markus J. Buehler, Roger Narayan, Peter Kiesel, David Nolte, Xudong (Sherman) Fan and Martin Zillmann

Excerpt More information

Mater. Res. Soc. Symp. Proc. Vol. 1301 $\ensuremath{\mathbb C}$ 2011 Materials Research Society DOI: 10.1557/opl.2011.538

Sharp Tips from Crumples and Capillary Bridges

Sanjiv Sambandan^{1,2}

¹Xerox Palo Alto Research Center, 3333 Coyote Hill Road, California, USA 94304 ²Division of Mathematical and Physical Sciences, Indian Institute of Science, India

ABSTRACT

We describe two techniques to create sharp tips. The first involves the buckling of thin metal films deposited on soft, stretchable substrates. The second involves the formation of narrow necked capillary bridges.

INTRODUCTION

Sharp tips for field emission are currently manufactured by either photo lithography or molding techniques with low work function materials, or using vertically structured nanopillars made from carbon nanotubes or other metallic or semiconducting nanowires [1], [2].

In this paper we consider two approaches to achieve the low temperature self organization of sharp tips. The first method takes advantage of the sharp features formed of crumples of metal films. The ridges and tips seen in a crumple have an elemental geometric entity - the developable cone (d-cone). We self assemble d-cones using two-dimensional buckling of thin metal films deposited on flexible substrates.

The second approach is to use low melting point metals (such as Tin/Lead or Gallium) and create a capillary bridge between the molten metal 'droplet' and a foreign micro-tip. The metal is frozen as the bridge is drawn. If the bridge is thin enough, we are left with the formation of a sharp tip.

MICRO CRUMPLES FOR SHARP TIPS

Theory

Crumpling is ubiquitous in nature and occurs due to a combination of bending and stretching, with more bending than stretching [3]. When a foil is crumpled, the energy is focused at vertices and ridges with the focus points providing the reaction to the applied force. These focus points in a crumple lead to the formation of sharp features.



Figure 1: The geometry of a d-cone.

978-1-605-11278-7 - Materials Research Society Symposium Proceedings Volume 1301: Soft Matter, Biological Materials and Biomedical Materials – Synthesis, Characterization and Applications

Editors Adam J. Nolte, Christopher M. Stafford, Teng Li, Pil J. Yoo, John Harding, Sheng Lin-Gibson, John Spencer Evans, Kiyotaka Shiba, Christian Hellmich, Ulrike G.K. Wegst, Markus J. Buehler, Roger Narayan, Peter Kiesel, David Nolte, Xudong (Sherman) Fan and Martin Zillmann

Excerpt More information

The developable cone (d-cone) has been identified as a possible building block for the geometry of a crumple [4],[5]. A d-cone can be constructed by taking a circular foil forcing its face into a cylinder of smaller radius via a point force applied at its center. The surface area of the foil is conserved in the confinement by taking the shape of a d-cone as shown in Figure 1. Strong crumpling forces cause folding and creasing creating the main ridge, and left and right flap creases with the top being a sharp crescent. The upper part of the main ridge appears like an inverted elliptic cone with the crescent as its base since it is energetically cheaper to bend the main ridge far away from crescent. The creased left and right flaps appear like upright elliptic cones. The flap cones, unlike the main ridge cone, are wider at the bottom since any folding force results in the flaps moving towards each other without much creasing and at the expense of creasing the main ridge. The minimization of the bending and stretching energies of the main ridge define the radius of the crescent to be proportional to $t^{1/3}$, where t is the thickness of the foil [6]. Thus crumples on thinner foils have sharper features.

Figure 2a shows the theoretical model (left) and physics based simulations (right) of the vertical electric filed strength of the d-cone. The d-cone is h units tall (with respect to the origin), and the electric field is measured at a point d units above the origin. There is a good comparison between the theoretical model and simulation (Figure 2b).



Figure 2: Expected vertical electric field from the d-cone. (a) left-simulations based on