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Investigations of Heterogeneous Ultrathin Blends Using Lateral Force Microscopy

Cynthia Buenviaje, Franco Dinelli, René M. Overney*

Department of Chemical Engineering, University of Washington,
Benson Hall, Box 351750; Seattle, WA 98195; USA

SUMMARY: In order to study the glass transition of thin film polymer blends, high spatial resolution and temperature sensitivity is needed. In this paper, we emphasize the importance of the calibration of scanning parameters such as load and speed when measuring the glass transition temperature of polymers using lateral force microscopy. Once calibrated, this method is ideal for investigations of heterogeneous samples such as blends and co-polymers. We present an analysis technique for lateral force imaging using a fast and stable cooling/heating stage. This approach involves mapping the friction forces over a certain area and identifying regions of different frictional properties. The difference in the average friction force can then be plotted as a function of temperature. The friction force is expected to vary around the glass transition. Therefore, the glass transition temperature can be defined as the temperature at which the difference in the average friction force undergoes a slope change. We present investigations of blends using polystyrene mixed with poly(butylmethacrylate). The transition temperatures obtained are in good agreement with the bulk values of corresponding homopolymeric films.

Introduction

Surface structure and properties of thin polymeric films are of interest for many technological applications. In particular, blends and copolymers have assumed a central role thanks to the possibility of tailoring surface properties.1) When cast in the shape of thin films, polymers present a wide spectrum of spinodal decomposition, from large tridimensional domains to lamellae, from micelles to cylindrical features.2-4) Therefore, high-resolution imaging is crucial to measure material properties of these thin film polymers.

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In recent years, thin homopolymeric films have been intensively investigated by scanning force microscopy (SFM). Since its inception, SFM has proved very successful in performing investigations on the nanoscale thanks to the size of the probing tip.[5,6] Using shear modulation SFM, the glass transition temperature can be accurately determined for thin film polymers.[7,8] In this technique, a lateral modulation is applied between the tip and sample and the amplitude of the response is measured as a function of temperature. Although this is a powerful technique for measuring temperature dependent transitions, the measurement is meaningful only if the surface is homogeneous. In the literature, there are few attempts to tackle the issue of heterogeneous samples One method is based on measuring the pull-off force as a function of the temperature. This method was proven useful in measuring the transition of pure polystyrene (PS) films of various molecular weights,[9] and can be extended to heterogeneous materials by mapping the topography and pull-off force over a defined area.[10]

In this paper, we will demonstrate that lateral force microscopy (LFM) can provide accurate measurements of the composition and material properties of phase separated components. Friction force measurements are performed via scanning the tip back and forth over long distances.[11-13] The friction force is obtained by subtraction of the lateral forces measured in the two directions. Therefore, it is an average measurement and unknown offsets and possible influences of topography are canceled out during subtraction. LFM will be used to measure changes in friction on heterogeneous samples as a function of temperature. Using a delta friction method, the transition temperatures obtained will be compared to the bulk values and to the values obtained for homopolymeric thin films. We will also discuss the influence of the scan conditions such as load and velocity on friction and pull - off force detection.

Experimental

Our SFM is a commercial system (Explorer, Thermomicroscopes, Inc.) where the cantilever position is controlled by linearized x, y, and z scanners. The sample holder was modified to house a cooling - heating stage (model R2700-2, MMR Technologies Inc.) The temperature can be varied in the range between 220 to 450 K with a precise control of ± 0.5 K. This cooling system is based on rapid gas expansion (Joule Thomson effect) and heating is controlled using an integrated thermoelectric device. The entire instrument is enclosed in a glove box that is flooded with dry nitrogen. Using this environmental chamber, a relative humidity less than 5% can be routinely achieved.

The samples were prepared by spin - casting polymer solutions from toluene onto silicon substrates treated in dilute hydrofluoric acid solution. The glass transition temperature, T_g, for the bulk polymer was determined by differential scanning calorimetry (DSC) and compared to shear modulation measurements on thick (>100 nm) homopolymeric films.7) For relatively thick films (> 100 nm), we found very good agreement between the shear modulation measurement and the bulk values obtained by DSC. Measurements of friction as a function of temperature were conducted on thin films of polystyrene (PS) (M_w 22.2 k, Polymer Source, Inc). Shear modulation measurements were taken on thick PS films (M_w 90 k, Polymer Source, Inc). Polymer blends of polystyrene (PS) and poly-butyl methacrylate (PBMA) were measured. PBMA (M_w 104k, Polymer Source, Inc) and PS (M_w 670k, Polymer Source, Inc) were mixed into a 50% : 50% film which was 200 nm thick. DSC measurements on the bulk homopolymers indicated the T_g of PBMA and PS to 305 K and 373 K, respectively.

Surface T_g values were obtained from homopolymer films using force modulation SFM. Once the surface T_g is known the friction force is measured at various loads and speeds, creating a T_g calibration curve.14) Scanning parameters were chosen in the load and speed regimes where the apparent T_g measured using LFM agreed to the T_g measured with force modulation SFM. Within these parameter ranges, forward and backward LFM images are taken on heterogenous films containing the homopolymer to determine transition temperatures. Then, a friction image is obtained by subtracting one image from another. This is made possible thanks to the high linearity of our scanning actuator. By analyzing histograms of the friction image, regions of different frictional properties can be identified and a value for the average friction force, the ‘delta friction force" (Δfriction), for each region obtained. LFM images are acquired at different temperatures and the Δfriction is plotted as a function of temperature. The glass transition temperature is defined as the temperature at which Δfriction changes in slope.

Results and Discussion

Critical Transitions Determined by Lateral Force Microscopy

Figure 1 shows a plot of the friction force as a function of temperature for three loads taken on a thick film of PS. It demonstrates the necessity of calibrating scanning parameters when using LFM. The scan length was 5 μm with a speed of 5 μm/s. At low loads, the friction force remains constant over a wide range of temperatures even above T_g. At high loads, a transition is observed at 373 K. As the load is decreased, the transition temperature is observed to increase. At low loads (12 nN), deformation of the sample was not observed on the investigated area. At high loads (250 nN), plastic deformation was observed, i.e., bundles were created and became more pronounced above T_g. At intermediate loads (80 nN), deformation was not observed below T_g but was apparent above the transition temperature. Similar shifts in the transition temperature have been also observed with scanning velocity.14) This measured transition temperature will be defined as T_C in order to differentiate it from the glass transition.

From Figure 1, it is evident that a T_C can be observed when working at high and intermediate loads. For high load, T_C corresponds well with the T_g taken on the bulk polymer. From shear modulation measurements taken on thick homopolymer films, the glass transition temperature corresponds to bulk T_g measurements on the polymer.7) The shift T_C for lower loads is controlled by the relaxation time of the sample. For example, at low loads or high scanning velocities, the cantilever tip is no longer sensitive to variations at the surface.14) A similar effect is observed when a magician pulls a tablecloth from underneath a setting of plates and cups; at the right speed, the magician can exert a force on the tablecloth such that its movement does not effect the cups and plates. At low loads, although the polymer goes through a glass transition, due to the speed of the tip over the surface and the load applied, the force on the tip is not affected by the transition.

Many have attributed changes in the transition temperature due to pressure exerted by the tip acting as hydrostatic pressure.15) However, this is in contradiction to what is observed in our measurement. Since the effect of a hydrostatic pressure would lead to an increase the transition temperature with increasing load, we can exclude contributions due to pressure exerted by the tip. In fact, since the contact area is small compared to the scan length, the dwell time over a specific area is short and lasts only a few milliseconds per cycle. Thus for the remaining scan cycle, the molecules are unconstrained and can relax. In addition, due to creep and thermal drift, it is quite unlikely that the tip ever passes the same molecules twice.[14] Therefore, it is more likely that the observed shift in transition temperature is due to the time dependence of the viscoelastic contact between tip and sample.

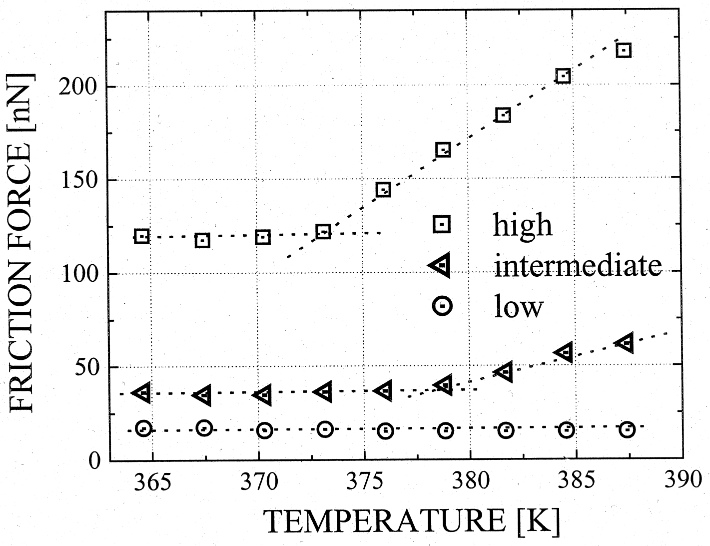

Figure 1: Friction force vs. temperature for three loads. The scan distance is 5 μm and the scan speed is 5 μm/s. At low loads, no apparent transition is observed. For high loads, a transition is observed at 374 K, which corresponds to the bulk T_g of the polymer. For intermediate loads, the transition temperature is shifted to increasing temperatures due to effect of the relaxation time of the polymer. At high loads, the polymer responds quickly to the load applied by the tip, however at low loads, the scan speed is fast enough that the tip does not sense the changes in the polymer.

Based on the viscoelastic contact and a step loading variation, we can describe the contact area as:[16]

$$a^3(t) = \frac{3RL_0}{8}\Phi(t), \qquad (1)$$

where L_0 is the load at time zero, R is the radius of the tip, and $\Phi(t)$ is the creep function derived by assuming an appropriate viscoelastic model. Using this equation, we can describe the system with a delayed elastic model below T_g and a steady creep model for the rubbery state above T_g.

delayed elastic
$$a^3(t) = \frac{3RL_0}{8}\left(\frac{1}{E_1} + \frac{1}{E_2}(1 - e^{-t/t_C})\right), \qquad (2)$$

steady creep
$$a^3(t) = \frac{3RL_0}{8}\left(\frac{1}{E_1} + \frac{1}{\eta_r}t\right), \qquad (3)$$

where η_g and η_r are the viscosity constants below and above T_g, E_1 and E_2 are two constants characteristic of the material, and t_C is equal to η_g/E_2. We will take $E_1 = E_2 = 3$ GPa and assume that E_1 does not change at T_g. In the range of temperature we explored, the main difference is represented by a large change in viscosity, as it emerges from macroscopic measurements.17)

Calibration of Lateral Force Microscopy Measurements With Shear Modulation

As discussed above, LFM-intrinsic parameters demand sample and probe specific calibration in order to determine actual glass transition temperatures. Such an in situ calibration method has been found with shear modulation microscopy. This stationary (non scanning) technique allows the determination of T_g at any location of the sample surface.7,18) Once the surface T_g is determined, it can be used as a "control" value, on homopolymer films, to determine the correct scanning parameters for LFM. Combination of LFM and shear modulation SFM offers a very powerful tool to measure phase transitions of heterogeneous surfaces such as blends. The shear modulation technique is briefly described here.

Figure 2 shows a typical example of a shear modulation measurement as a function of temperature. An increase in the response occurs at 373 K. The intersection of the linear fits is defined as T_g and corresponds well with the bulk T_g of the polymer taken using DSC. The basic principle of this technique uses a sinusoidal signal applied to the lateral motion of the piezo (x-direction). This induces an oscillatory local perturbation of the sample surface. The amplitude of modulation is chosen below the stick-slip threshold, therefore there is no sliding between the cantilever tip and sample. The tip is kept in contact with the sample surface using a force feedback loop. The amplitude shift of the modulation response is acquired as a function of temperature.

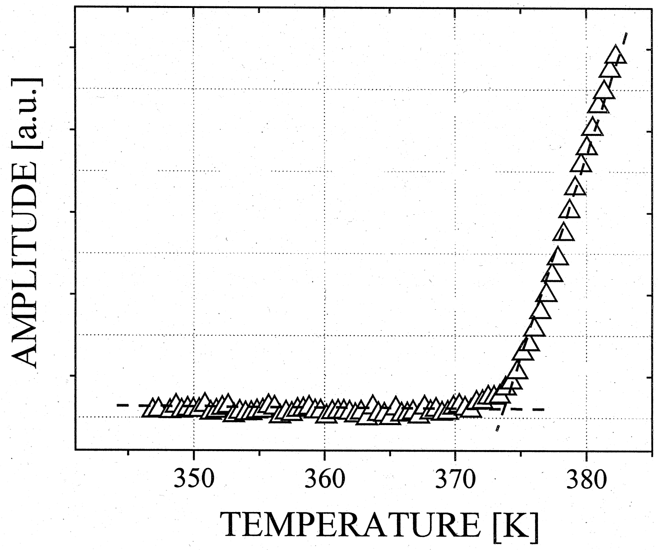

Figure 2: Shear modulation amplitude vs. temperature. A typical shear modulation curve taken on a thick film (475 nm) of polystyrene (M_w 90k). Increase in the amplitude response is seen at 373 K, which corresponds with the bulk transition taken with differential scanning calorimetry. Shear modulation measurements provide accurate determination of the local surface glass transition temperature of thin film polymers.7) Shear modulation results on thin film homopolymers were used to calibrate lateral force measurements on the polymer films.

Let us assume the shear modulation experiment can be modeled as two springs set in series with spring constants, k_s and k_L, representing the stiffness of the sample and the cantilever, respectively. The one-dimensional spring constant of the sample, k_s, is proportional to the shear modulus. Assuming fully elastic deformation during the shear process, Hooke's law applies, i.e.,

$$k_s \Delta x_s = k_L \Delta x_L = k^* (\Delta x_s + \Delta x_L); \; k^* = \left(\frac{1}{k_s} + \frac{1}{k_L} \right)^{-1}, \tag{4}$$

where k^* is the overall spring constant of the system, and Δx_s is the sample deformation. In contact mechanics, the quality of the contact, i.e., the contact stiffness, k_s, is crucial, Eq. (4). The contact stiffness is responsible for the energy transport between cantilever and sample.[19,20] The contact stiffness can be expressed for an adhesive elastic sphere-plane contact as[16,21]

$$k_c = 8Ga; \quad a^3 = \frac{3R}{4E}\left(L + 6\pi R\gamma + \sqrt{12\pi R\gamma L + (6\pi R\gamma)^2}\right), \tag{5}$$

with the contact radius, a, the radius of the spherical tip, R, the Young's and shear moduli of the sample, E and G, respectively, the externally applied load, L, and the interfacial energy per unit area, γ. To simplify the discussion, let us set L=0, which will not affect the following qualitative conclusions. We introduce the Poisson's ratio, ν, as

$$G = \frac{E}{2(1+\nu)}. \tag{6}$$

Combining equation (5) and (6), the contact stiffness is rewritten as

$$k_c = 8\left(\frac{9}{2}\pi\frac{\gamma}{(1+\nu)}(RG(\omega))^2\right)^{1/3}, \tag{7}$$

where $G(\omega)$ represents the frequency dependent shear modulus. Although the shear modulus changes significantly at T_g, what we find is that the contact area is the dominating influence in our contact stiffness measurement. From friction and adhesion measurements, we have found that the contact area increases significantly at T_g thereby explaining the increase in the response amplitude. From equation (5), we find that the elastic modulus and interfacial interaction govern contact area. Hence, we can infer that changes in the interfacial interaction strength, radius of curvature, and Poisson's ratio affect the contact stiffness.

Transition Temperature Measurements of Polymer Blends

Figure 3 shows lateral force images of a 50/50 blend of PBMA (104k) and PS (670k) at various temperatures. DSC measurements indicate the T_g of PBMA and PS as 305K and 373K, respectively. Clear phase separations are apparent from the frictional images. Topographical images, not shown here, are similar to the frictional images and show a flat background with circular depressions. The temperature was increased from 300 to 340K in 20 degree increments (Fig. 3a-3c), the sample was then cooled to 300K (Fig. 3d). Initially frictional contrast is negligible. However, once the temperature is increased above the T_g of PBMA, the frictional contrast between valleys and the background also increases. As the temperature is increased further, the contrast between the depression and its background is greatly enhanced. Once the sample is cooled to room temperature, the initial contrast was restored.

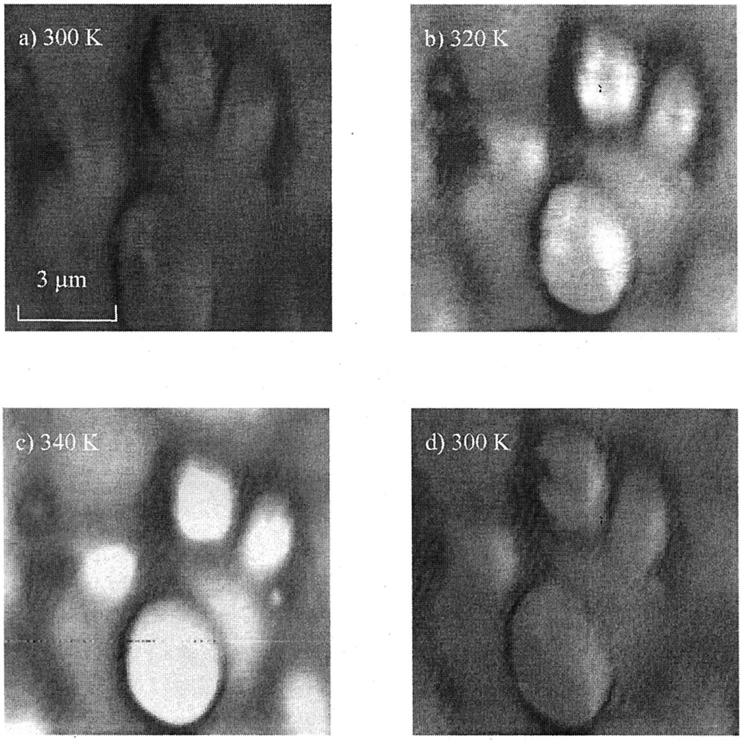

Figure 3: The first sample is a blend made of 50% PBMA and 50% PS. Friction images are reported for increasing temperatures. The round features, which change in contrast with increasing temperature, are shown as shallow depressions on topography images. The friction forces in these depressions increase as the temperature is increased above the T_g of PBMA. Figure 3d was acquired at 300K after the sample was cooled from 340K. The initial frictional contrast, as well as the friction value, is restored at room temperature, proving the reproducibility of this technique.

In Figure 4, the Δfriction force, as described in the experimental section, is plotted. A clear transition occurs at 305K, corresponding to the T_g of PBMA. As the temperature increased, Δfriction also increases. Once the sample is cooled to room temperature, the original friction value is measured on the sample as shown in Figure 4 with filled circles. From our results, we find that the depressions in the sample consist of PBMA while the background is made of PS.

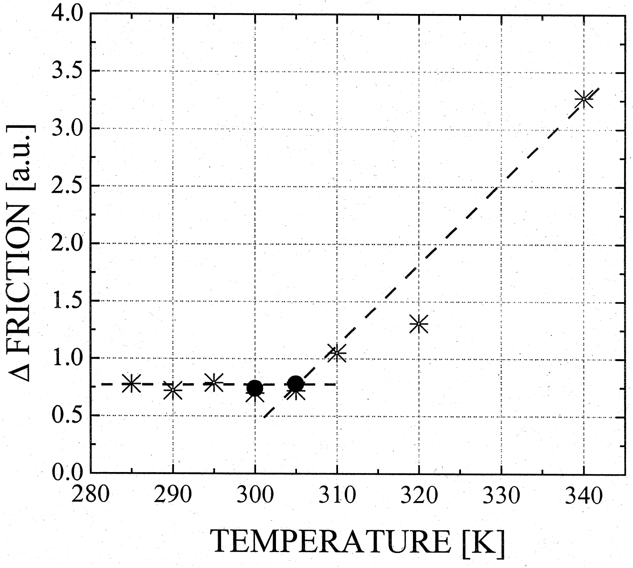

Figure 4: Δfriction as a function of temperature. An increase in the Δfriction value is observed at 305 K, which corresponds to the bulk T_g of PBMA. The change in the friction value in the round depressions is determined to be a response to changes in the PBMA phase. The reproducibility of the results is shown by the restoration of Δfriction near room temperature taken after the sample had been cooled.

This blend is an excellent test of our technique. The domains of the two phases were sufficiently large so that possible lateral confinement effects could be excluded, and we were able to easily distinguish one phase from the other by simply measuring the friction force at a certain temperatures. By using our Δfriction approach, we were able to identify the exact regions undergoing the phase transition and utilized this information to characterize the composition of different phases. In addition, the observed transitions in Δfriction are in good agreement with the values obtained for the bulk polymers. Furthermore, the measurements are reproducible as shown by the restoration of the initial friction contrast and Δfriction values. Further outlook for this technique is in the application of heterogeneous samples to study the effects of lateral confinement through phase separation such as in emulsions.

Conclusions

In this paper, we report that calibration of scanning parameters, such as load and velocity, are crucial for lateral force microscopy measurements. For example, at low loads or high scanning velocities, the cantilever tip is no longer sensitive to variations at the surface. Without proper calibration of the scanning parameters, artifacts in the transition temperature are observed,14) however with proper calibration, lateral force microscopy is a successful tool for studying heterogeneous surfaces.

It was demonstrated that different polymer phases are distinguishable by frictional imaging at various temperatures. In addition, with the application of our Δfriction method, it was possible to identify the composition of each phase. We conclude that lateral force microscopy is useful in studying simple systems such as homogeneous films once calibration of load and velocity parameters are made.

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