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Force Microscopy of Stretched Polymer Glasses

Introduction. When an amorphous glassy polymer, e.g., polystyrene, is stretched, the polymer deforms and crazes.[1,2] As suggested by the results of transmission electron microscopy,[1,2] the boundaries between a craze and the bulk polymer are very sharp, indicative of a very narrow transition region, the so-called "active zone".[2,3] Up to now, there has not been enough evidence to fully unveil the deformation mechanism of crazing on a molecular scale. Nevertheless, it is generally accepted that, once crazes are initiated, they become weak spots and absorb the subsequently applied deformation. The deformation in the uncrazed region is usually assumed to be viscoelastic, and the stress there is approximated by a sum of the craze initiation stress and local stress concentrations. If the elongation is held constant in polymer glasses, the stress will relax.

It has long been assumed that the relaxation takes place homogeneously throughout the entire glassy solid, and hence the surface topography after relaxation is expected to remain unchanged. Yet, the evolution of the topography during stress relaxation has rarely been studied. This lack of information is probably due to the absence of convenient tools capable of detecting small height variations over large areas. With the recent invention of high-resolution surface probes, such as the force microscope, it may now be possible to investigate the film topography as the polymer relaxes. Therefore, we have used a scanning force microscope (SFM) to study the polymer surface before and after deformation. In this paper, the results obtained from stretched polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) films are presented.

Experimental Procedures. Samples. The main polymer studied was a monodisperse polystyrene (M_w = 2 000 000; M_w/M_n = 1.06) from Pressure Chemical Co. A second polymer, poly(2,6-dimethyl-1,4-phenylene oxide), with M_w = 244 000 and M_n = 8000 (Aldrich Chemical Co.) was also investigated. The polymer films were spin cast from toluene and bonded onto supporting copper grids.[4] The polymer films were prepared in two thicknesses: 0.1 μm (thin) and 0.5 μm (thick). The specimens were then stretched to an elongation ϵ = 3–6%, at which point the films either crazed (PS) or formed shear deformation zones (PPO). After stretching, the films were held under constant strain by the copper grids and kept at ambient conditions. At various aging times (t_a), the deformed surfaces were imaged using the SFM.

Scanning Force Microscopy (SFM). The scanning force microscope used here is similar to that described previously[5] and operated in the attractive force regime.[6] The data are thus obtained by a noncontact measurement, and the possibility of tip-induced change to the polymer surface is minimal. Briefly, the microscope lever/tip is oscillated at a frequency slightly above its natural resonant frequency. The lever motion is detected with an optical fiber based interferometer.[7] The lever/tips were fabricated from etched tungsten wires, bent at a 90° angle, and had a tip radius of curvature of ca. 50 nm. Typical spring constants were 1 N/m and resonant frequencies were ca. 10 kHz. As the tip scans the surface, changes in the tip-to-sample force gradient will alter the effective spring constant of the lever, thereby changing the lever resonant frequency and oscillation amplitude. A feedback loop adjusts the tip–sample spacing so as to keep the oscillation amplitude, and hence force gradient, constant. This feedback signal is recorded, and the images obtained are maps of constant force gradient. In order to ensure stable operation of the microscope, it is often necessary to supplement the van der Waals tip–sample force with an additional force. This is done by applying a small voltage between the tip and an electrode on the back side of the sample. In the absence of any spatially varying forces, the images of constant force gradient will resemble the surface topography. It should be noted, however, that, due to a convolution of the comparable-sized tip and polymer topography and to the long-range nature of the electrostatic force, the size of the bumps may be overestimated here. The distance between bumps, however, should be influenced to a much lesser extent.

Results. The topography of the polymer film was studied using the SFM before and after the application of tensile elongation. It was found that, before the application of tensile strain, the surface was smooth and remained smooth even after long aging times, as shown in Figure 1a. The small height variation, ±2 nm, in Figure 1a is the noise level in the SFM measurements. When imaged immediately after deformation, the free surface of the stretched polymer films was still smooth. However, topographic bumps developed as the aging time increased.

In thin PS films, the bumps were detected as early as 20 h after deformation. At this time, the height of the bumps ranged between 5 and 15 nm. These bumps grew steadily to around 25–35 nm in height 18 days later, as shown in Figure 1b,c. Concurrently, as the aging time increased, new bumps continued to emerge. The bumps are approximately cone shaped, usually isolated, and present over much of the stretched polymer surface. Some bumps, however, are so close that they appear as ridges. In order to describe the bump growth more quantitatively, the total volume of bumps per unit surface area, υ_b, was estimated and plotted versus the aging time in Figure 2. To estimate υ_b, the bumps were assumed to be perfect cones, of which the height and base width were measured from the raw data. The bump volume υ_b increases monotonically with time. The rate of increase, however, decreases with aging time and approaches zero after very long aging times. The average bump size follows the same growth trend.

Although the bumps were generally distributed throughout the entire surface, they tended to populate more densely close to crazes. In fact, at short aging times, the bumps were found only in the areas near crazes. As the aging time increased, new bumps slowly emerged in the vicinity of crazes as well as in the regions farther away, spreading slowly over the entire film. More quantitatively, Figure 3 shows the bump distribution in an aged sample in a plot of υ_b versus the distance from the craze boundary. It should be noted that the size of the bumps near the crazes is far larger than the dimension, approximately 20 nm, proposed for the active zones.[2,3] In addition to the gradient perpendicular to the craze, there seemed to be a large υ_b at regions near the craze tip.

Figure 4 shows the topography of a section of an aged craze in a thin PS film (ϵ = 3.6%, t_a = 19 days). The bumps are clearly visible in both the crazed and bulk regions. However, the formation of the bumps in the crazed regions required a longer incubation period than that in the bulk. Once emerged, the bumps in the crazed regions grew and some became comparable in size to those in the vicinity of the crazes, as shown in Figures 3 and 4. Figure 4 also demonstrates that there is a remarkable depression in film thickness in the crazed region. If we assume a comparable surface depression on the other side of the film, the total depression reaches a value of more than 80% of the film thickness and indicates a very small

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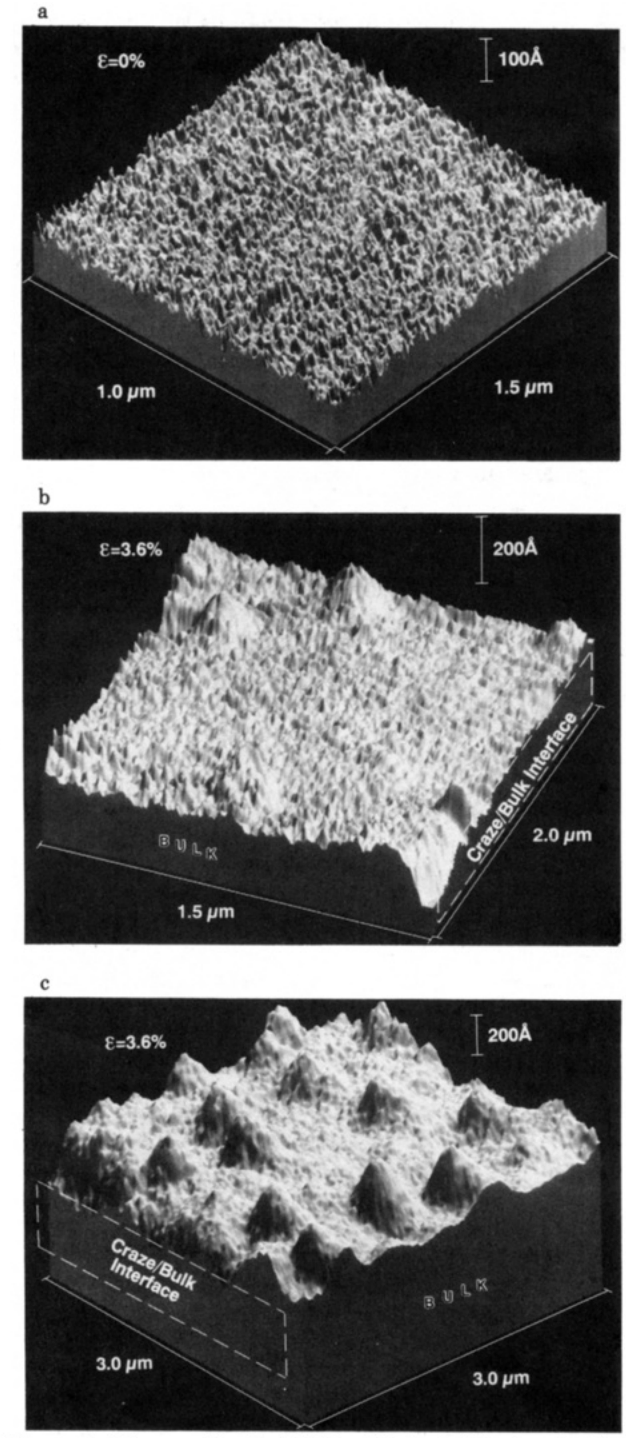

Figure 1. Topography of a PS film: (a) strain (ϵ) = 0, aging time (t_a) ~ 1 month, (b) ϵ = 3.6%, t_a = 20 h, and (c) ϵ = 3.6%, t_a = 19 days.

thickness for the aged crazed matter. The reason for the large depression is not clear yet, but it is possibly due to the coalescence of craze fibrils upon aging.[8]

In thick PS films, similar bumps were observed. The bump growth, however, was considerably slower than in thin films. The bumps were located mostly near the crazes, and the decay of the bump distribution perpendicular to the craze was much faster than for thin films. In contrast to the thin films, no bumps were ever observed in the crazed regions even for an aging time longer than 2 months.

Preliminary data on a 0.5-μm-thick PPO film, which was stretched to ϵ = 10% and aged 2 months, also showed the cone-shaped bumps. These bumps, however, were smaller, around 5 nm in height and 100 nm in lateral dimension, compared to 10 nm in height and around 250 nm in diameter for a thick PS film (ϵ = 6%). This suggests that the formation of bumps is typical for stretched glassy polymers. The difference in bump size between the two polymers may be due to the differences in chemical structure, physical properties, and possibly the different molecular weights of the polymers used.

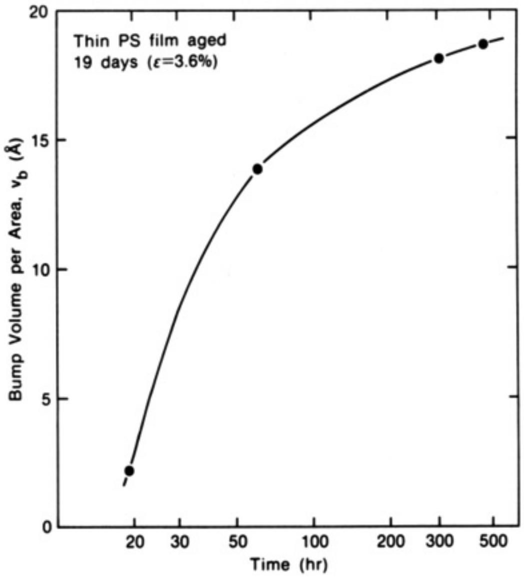

Figure 2. Bump volume v_b in the bulk versus the aging time t_a.

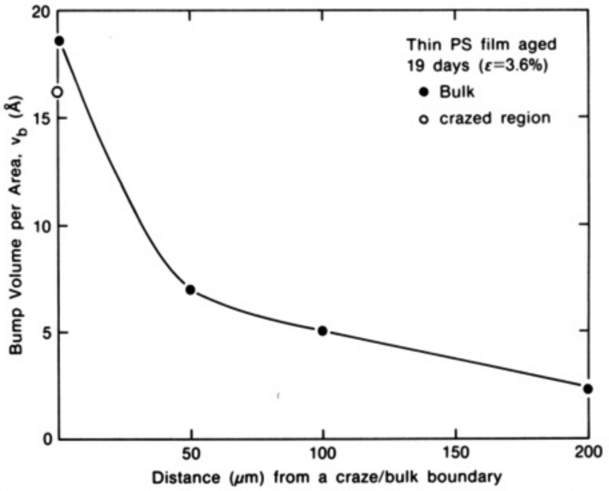

Figure 3. Bump volume v_b in the bulk versus the distance from the craze/bulk boundary.

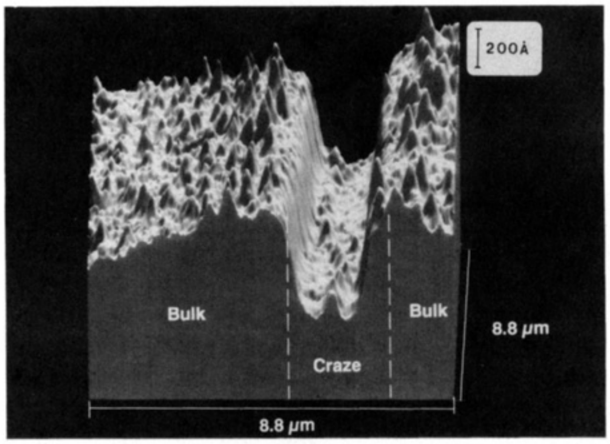

Figure 4. Topography of an aged craze in thin PS film held at strain (ϵ) = 3.6% (scan area: 8.8 μm × 8.8 μm).

The data shown here demonstrate that SFM enables us to study the topography of local deformation zones and the bulk with high accuracy and provides important structural information which may help to clarify the deformation mechanisms.

The driving force for the bumps to grow on the surface of glassy polymer films upon stress relaxation is intriguing and could be important for understanding the fundamentals of polymer chain behavior. Research work to examine the effects of entanglement network structure, e.g., molecular weight and diluent concentration, and the aging temperature on the formation of these bumps is underway.

Conclusions. The conclusions are as follows:

1. Scanning force microscope (SFM) can be used to study polymer deformation and small-scale relaxation at the surface.

2. The "elastically" deformed films relax considerably, at a temperature well below glass transition temperature, forming large surface fluctuations (bumps). This relaxation was observed in both PS and PPO, two thermoplastics of very different mechanical and fracture properties. The effect of film thickness on bump formation is consistent with a relaxation process.

3. At crazed regions in aged PS films, an unexpectedly large surface depression was found. The total depression from both sides accounts for more than 80% of the total film thickness.

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