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Thermal Probe Surface Treatment of a Bulk Polymer: Does a Surface Layer with a Lower Glass Transition Than the Bulk Exist?

Hartmut Fischer

Department of Innovative Materials, Materials Division, TNO-TPD, and Dutch Polymer Institute, P.O. Box 595, 5600 AN Eindhoven, The Netherlands

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ABSTRACT: The surface of a bulk polystyrene has been scanned using a AFM equipped with a thermal probe at different temperatures. Scanning at room temperature reveals a real picture of the surface roughness, while scanning 40 and 20 K below the glass transition of the bulk PS results in a very flat smooth surface. Scans at the T_g show a deformation pattern corresponding to a rubbery substance. Finally, scanning 10 K above the glass transition temperature shows a surface with intense "droplet" formation. It is concluded that a thin surface layer (a few nanometers) exists, which shows a significantly lower glass transition. This effect can be used to manufacture supersmooth surface areas.

Introduction

The recently introduced combination of thermal analysis and scanning force microscopy (scanning thermal microscopy, SThM) has so far been used to inspect surfaces with respect to their thermal properties by using a scanner with a thermal sensor as probe (tip). This principle has been explored and tested on many different materials and surfaces. Furthermore, the option to perform a local thermomechanical analysis of discrete areas of a few square micrometerss (L-TMA and L-CA) has gained a broad interest.[1] A recent publication describes an alternative determination of glass transition temperatures in thin polymer films using local thermal analysis experiments on thin films of polystyrene (PS) and of poly(methyl methacrylate) (PMMA).[2] Those experiments confirmed the earlier ones by means of ellipsometry,[3,4] Brillouin light scattering,[5−8] positron annihilation spectroscopy,[9] and lateral force microscopy[10,11] but also by simulations[12] and molecular dynamics calculations[13] found a decrease in T_g for PS with decreasing thickness of thin free-standing and/or supported films. Also, DSC experiments on bulk samples of diblock copolymers reveal a decrease of the T_g of the confined blocks by up to 33 K compared to homoblock copolymers with the same molecular weight.[14] Another paper reports describes the determination of T_g's also in thin films of diblock copolymers using X-ray photoelectron spectroscopy.[15] Also there a much lower T_g compared to the bulk phase was found, dependent on the film thickness. There are several other papers which report an independence,[16,17] or even an increase, in T_g with decreasing film thickness.[2,18] Obviously, the type and energy of interaction of the thin polymer film with the surface of the supporting substrate influences the sign of chances on the T_g significantly.

Comparatively few experiments have been carried out so far for a determination of the T_g of near surface areas of *bulky polymer samples*. One recent study reports about nanoindentation experiments using indenters with different diameters on bulk PS samples.[19] There it was found that an indentation using indentor spheres with a diameter of 2.5 μm instead of 150 μm resulted in an extended plastic flow zone at the surface of the sample. The depth of this zone of extended plastic flow is clearly related to the size of indenter and hence to the depth of indentation.

In this paper, we try to evaluate the method of scanning themal microscopy with respect to its use as a processing tool for a controlled surface treatment/pattering but also for a special analytical question, the determination of the T_g in thin surface layers of bulky polymer materials.

Experimental Section

The PS sample (M_n = 276 kg/mol, polydispersity D = 3.6, Shell) was prepared by compression molding of 4 mm thick plates under nitrogen at 120 °C against freshly cleaned float glass surfaces. The scanning thermal microscope (SThM) used in this study was a Micro-Thermal analyzer (mTA 2990) from TA-Instruments. The microscope was operated after calibration of the probe using $C_{32}H_{66}$ (T_m = 70 °C), LDPE (T_m = 105 °C), PS (T_g = 105 °C), HDPE (T_m = 128 °C), iPP (T_m = 163 °C), PA 6 (T_m = 205 °C), and PETP (T_m = 263 °C). Local thermal analysis was performed using heating and cooling speeds of 5 K/s; 20 data points were collected per second. The probes have a spring constant of about 10 N/m. The contact surface area between probe and substrate (ca. 6 μm^2) was determined by inspection of the mark of the probe left on the substrate after a short contact (1−2 s) at 100 °C. All experiments have been carried out in contact mode with a contact force of about 10 nN resulting in a contact pressure of about 1.7 kPa, the contact force was regulated to be constant by addressing the z-piezo. The final indentation depth is dependent on the final temperature in the thermal analysis program; it is usually 2 μm for a upper temperature limit 100 K above T_g. The scans at elevated temperatures were performed in the following way: after choosing the area to be scanned, the probe was placed and heated to the scanning temperature simultaneously while the scanning started. After the scans were complete, the tip was removed immediately to minimize a static thermal contact between probe and substrate. The scanning speed used was 20 μm/s for a scan size of 20 × 20 μm.

The thermally scanned areas were subsequently inspected using AFM-probes (Si_3N_4, probe radius ca. 20 nm) using the same scanning speed and a contact force of between 1 and 3 nN, resulting in a much higher contact pressures of about 20−60 MPa.

Results and Discussion

The nature of polymers changes rigorously while crossing the T_g. Polymers are hard and glassy at

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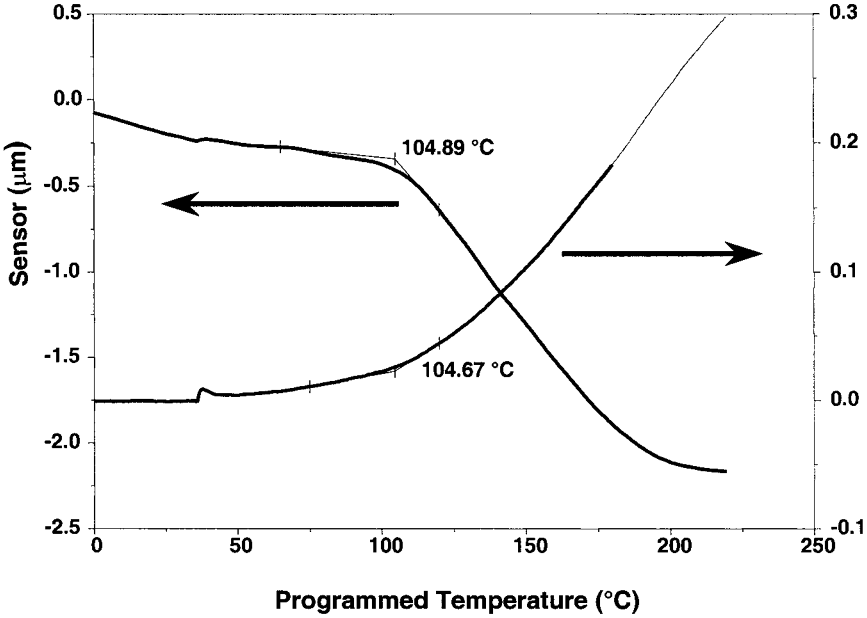

Figure 1. Localized thermal analysis of the PS sample under investigation, using a heating scan with a scan rate of 5 K/s. Both signals, the sensor location as well as the power supply to the probe, indicate a "bulk" T_g of about 105 °C.

temperatures below the T_g, and for temperatures above the T_g, they are soft and rubbery. The T_g, however, is a function of the molecular weight of polymers and can be described with a simple equation:

$$T_g = T_{g\infty} - \frac{K}{M_n} \qquad (1)$$

The asymptotic part of this equation is reached when entanglements of random coils are observable and is therefore dependent on the flexibility of the polymer chain. The T_g of polystyrene of a molecular weight higher than the critical value of $M_n = 30$ kg/mol is about 102−105 °C. The molecular weight dependency of the T_g is well-known and is reported elsewhere.[20,21,16] However, since the molecular weight of the PS sample used in this investigation is far above the critical value, a depression in T_g due to this effect could not be expected. Indeed, a local thermal analysis[1] performed on the surface of the inspected sample confirmed the bulk T_g of about 105 °C (see Figure 1). Here, both signals of the thermomechanical sensor show the existence of the glass transition independently. Figure 2 shows an AFM image of a rather large area of the surface of the PS sample after performing several experiments. Distinct areas, labeled with the tip temperature during the scanning operation using the thermal probe, are visible and marked due to the scanning.

The area scanned at 50 °C shows nearly no change of the surface structure respectively roughness compared to the nontreated, surrounding surface indicating almost no interaction of the hot probe with the surface. Grooves from scratches on the surface of the sample remain unchanged and clearly visible also in the scanned area. However the other areas (70, 90, and 100 °C) show rather distinct changes. The two scans at 70 and 90 °C display a much smoother surface than the original surrounding area. Grooves, especially while scanning at 90 °C, are erased substantially. The scan taken at 100 °C shows a completely changed picture. Here, deep indentations due to the contact of the tip at a temperature close to the T_g can be seen. Obviously is the surface already in the rubbery state and allows deep indentations. Scratches are completely removed or better erased. While scanning, a partially wavy pattern has been produced. Such a pattern is typically for a abrasion/sliding on/over a rubbery surface.[22−24] The appearance of a wavy surface after scanning could be a result of the reduced yield stress at higher temperatures. Finally, at the center of Figure 2, the mark left behind from the hot tip after a contact of a few seconds can be seen. This mark has been used to determine the maximal contact area between the hot probe tip and the PS surface. Interestingly, but not surprisingly, such a mark cannot be seen at the scans at 50 and 70 °C and

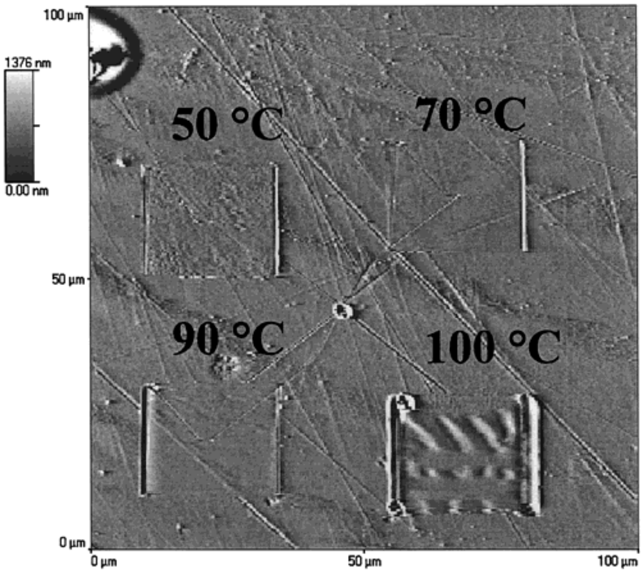

Figure 2. Images of areas of 20 × 20 μm after scanning at 50, 70, 90 °C and 100 °C taken with an AFM probe. Note the central mark left behind from the hot tip after the scans were performed. The image of the area scanned at 50 °C shows almost no change compared to the surrounding surface. The images of the areas scanned at 70 and at 90 °C show a much flatter surface than before. Finally the image of the area scanned at 100 °C shows a wavy pattern typically for the deformation of a rubbery material.

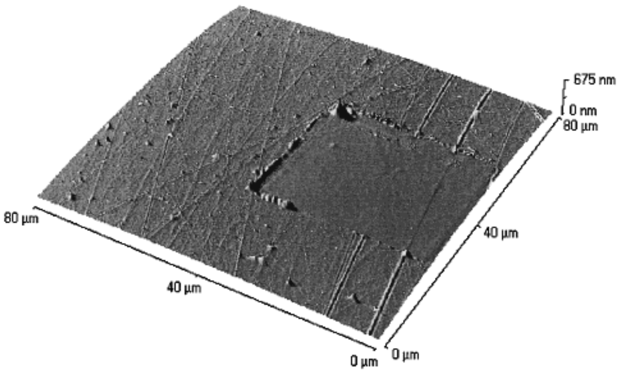

Figure 3. 3D-plot of an images of an area of 20 × 20 μm after scanning at 90 °C. Note the flattened surface of the scanned area and the erased grooves crossing over the scanned area.

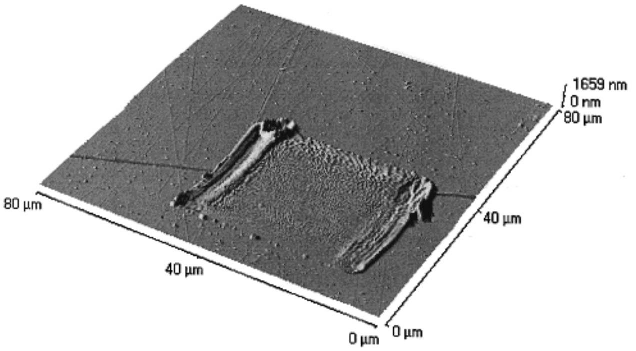

Figure 4. 3D-plot of an images of an area of 20 × 20 μm after scanning at 110 °C. Note the roughened surface of the scanned area and the clear marks of the hot tip at the positioning left behind.

only a very small mark is observable at the upper left corner of the scan taken at 90 °C. However, a rather clear mark is visible at the scan area taken at 100 °C.

Figure 3 shows a 3-D plot of the surface of a new scan again performed with a probe temperature of about 90 °C. The surface of the scan is completely flat, and the rms roughness is 0.5 nm compared to 2−3 nm, the value of the untreated and already very flat substrate. The remaining roughness of the thermally treated and flattened surface is defined by the spectrum of capillary waves of the surface fluctuations in the rubbery state. At least three grooves of a depth of 5 nm are completely erased/have disappeared within the scanned area due to the action of the heated tip.

Figure 4 shows on the other hand a 3-D plot of the surface of yet another scan now performed with a probe temperature of 110 °C and thus *above* the T_g of PS. First of all, a mark from the hot tip can be seen at the upper left corner of the scanned area. This is the spot where the probe made contact with the substrate. In contrast to the other scans at low temperatures, the mark here is rather deep and pronounced. This is due to the increased temperature and the change of the viscoelastical properties of the bulk material while crossing over the T_g. The whole material becomes rubbery with a much lower elastic modulus and yield stress compared to the glassy state. The interaction with the tip during approaching is therefore less intense, which causes the tip to sink deeper into the material before the mechanical resistance required for the feedback loop for a contact mode of operation can be found. During scanning, the material becomes liquidlike. The result can be seen in Figure 4. Not only did the groove crossing through the scanned area disappear completely beneath the surface, but also small droplets are observable now. The average size of these droplets is about 300 nm. The formation of droplets can be caused by several means. One possible reason is a changing penetration depth during the scanning experiments due to the low heat transfer coefficient of PS causing a constant change between the viscoelasticity of a glass and a rubber at the surface. Another reason could be the coalescence of the fluid surface into droplets after the very short contact with a subject (tip) at temperatures above T_g, whereas the complete bulky mass stays at room temperature or only little above. The existence of such island droplets with a characteristically size has, however, been described earlier as a consequence of dewetting of surfaces.

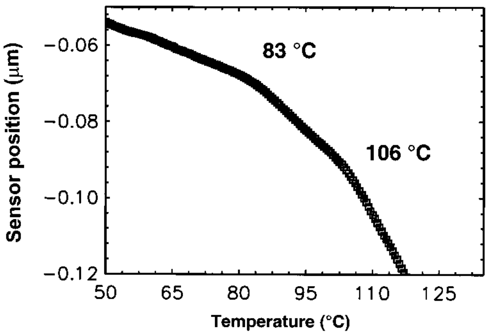

Figure 5. Details of the localized thermal analysis of the PS sample, heating scan with a scan rate of 5 K/s. All data points are printed. Note the first change of the slope of the signal of the sensor location at 83 °C indicating a lower T_g at a surface layer of about 14 nm (traveling distance of the sensor until the second change of slope) and the second change of slope at 106 °C indicating the T_g of the bulk PS material.

The last experimental result gave enough reason to return to the local thermal analysis experiment (Figure 1) in more detail (see Figure 5). A closer inspection of the sensor signal, obtained during the experiment reveals that the sensor signal has two points of change of slope. The first point is recorded at a temperature of 83 °C. Staring from this temperature the probe moves into the sample for approximately 14 nm after subtraction of a linear expansion of the materials in contact in this temperature range of 1 nm assuming a linear thermal extension of the probe as recorded below this temperature. A second, much steeper change in slope is recorded starting at a temperature of about 105 °C, the bulk glass transition of PS. The height difference between the two points of change in slope can be addressed to the thickness of a surface layer with a different, lower T_g (83 °C).

The layered model for the description of near surface layers with a lower T_g than the bulk polymer described by Mattson et al.[8] and in general for materials by van der Veen[25] can be applied very easily for the interpretation of the obtained experimental results. Only the surface layer with a lower glass transition temperature than the bulk material has been penetrated during the scans at temperatures of 70 and 90 °C. The tip slides in a fluidlike layer on top of a solid glassy material. At lower temperatures (50 °C) even this surface layer is in the glassy state. At higher temperatures (100 °C), the contact pressure of the thermal probe is high enough to exceed the yield stress of the material resulting in the typical wavy pattern of an abraded rubbery phase. At even higher temperatures, temperatures above the bulk glass transition temperature (110 °C), the obtained picture represents a surface of separated droplets after the scanning experiment. The experiments described demonstrate a possibility to obtain ultrasmooth flat surfaces by treatment with a probe at temperatures below the glass transition temperature of the bulk material. This may have implications for the process of welding of polymers and of adhesion onto polymer surfaces.

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