Cratering and plastic deformation in polystyrene induced by MeV heavy ions: Dependence on the molecular weight

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Cratering and plastic deformation induced by individual MeV ions on the surface of polystyrene thin films of different molecular weights (M_w) (from 3250 to 2 \times 10^7 u) are investigated using scanning force microscopy. 20 MeV, 85 MeV and 197 MeV gold ions are used to bombard the targets at grazing incidence (79° to the surface normal). Induced surface tracks consist of an elliptical crater followed by a hillock elongated in the direction of the ion incidence. For a given ion energy, the crater size is largest on the lowest M_w film. Crater dimensions are systematically reduced on films of heavier macro-molecules, up to a molecular weight of about 1.6 \times 10^7 u. For M_w > 1.6 \times 10^7 u, the crater size remains approximately constant. The difference observed for the lateral dimensions of the craters are about 50% when comparing the lowest and the highest M_w films at a fixed energy. The observed saturation of the crater size for high M_w values coincides with the onset of entanglement effects in the polymer, which influences the viscosity and the compliance of the material. Moreover, the curve of the crater size versus M_w follows the same trend as the reciprocal viscosity (\eta^{-1}) versus M_w, indicating that the viscosity is governing the final lateral dimensions of the craters. The hillock dimensions present a weak dependence on M_w, above a threshold at 3250u. The different behavior observed for craters and hillocks is discussed based on the viscoelastic properties of the polymer at different M_w and on the transient heating occurring close to the ion impact site.

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I. INTRODUCTION

When fast ions interact with thin solids the energy is deposited mostly in the form of electronic excitations, through the nearly straight path of the ion into the target. In insulators, such electronic energy can be rapidly converted into atomic motion, creating defects along a cylindrical region, called latent track.1–3 Near the vacuum/solid interface, deformation of the surface and ejection of material occurs, resulting in the formation of a crater and/or a raised rim or tail (hillock).4 These surface features are often referred to as surface tracks. For polymers, the ejected material can be very diverse, including intact molecules, molecular fragments, and highly reorganized species (e.g., carbon clusters).5,6 The remaining material in the bulk can be strongly modified near the ion path,7–10 but few tens of nanometers from the impact center, the deposited energy density is too low to induce significant chemical rearrangements.10,6

In recent years, the size and shape of the surface tracks, mostly produced at grazing incidence angles,11–15,46–19 have been investigated with scanning force microscopy (SFM). The use of this technique allows evaluation of the total sputtering yield in single ion events16,11 and the study of basic ion-solid interactions.12,20 An inherent limitation of measuring sputtering yields from crater volumes is the dependence of the measured dimensions on the SFM tip shape and on tip-surface interaction forces. However, tip convolution effects are not relevant whenever relative changes in the measured dimensions are involved. This was the case in many important experiments reported in the literature, such as the scalings of surface track dimensions with the stopping power,21 ion velocity,11 incidence angle,20,13 and target temperature.22 Eriksson et al.12 studied surface tracks of MeV ions on organic materials with different molecular weights, but distinct chemical structures. In this work a systematic study of surface tracks in an organic polymer [polystyrene (PS)] is performed for a wide range of molecular weights, keeping the chemical structure fixed. The crater and hillock formation processes are discussed, and correlated with the viscoelastic properties of the polymer.

II. EXPERIMENT

PS powder of different molecular weights, from 3250 to 2 \times 10^7 u, nearly monodisperse, were used to prepare the targets. Average molecular weights M_w and polydispersity given by the manufacturer (Polymer Standards Service, USA) and the glass transition temperatures (T_g), measured...
for some $M_w$, are shown in Table I. Thin films were prepared by spin coating, using Si substrates and a PS/xylene or toluene solution. The concentration of the solution and the spinner velocity were slightly different for different molecular weights in order to obtain a flat surface and thickness around 150 nm. The roughness of the surfaces, in a 500-nm² scan area, was around 0.3 nm. The thicknesses of the films were determined by two different means: (a) non-Rutherford elastic scattering, using 3.5-MeV $^3$He particles and measuring the carbon signal depth profile (the beam was aligned at 45° to the normal in order to improve the depth resolution) and (b) by imaging by SFM the film surface containing a previously made scratch and measuring the step between the silicon substrate and the polymer film. The scratches were made using a stainless-steel surgical blade and the width of the scratches varied from 10 to 30 µm. The thicknesses measured via the two methods agree within 10%. The glass transition temperature ($T_g$) of the polymers was determined by differential scanning calorimetry (Polymer Laboratories) at a heating rate of 20 °C/min.

Bombardments were performed at the Porto Alegre HVEE 3 MV Tandetron accelerator (20-MeV $^{197}$Au$^{7+}$) and at the Buenos Aires 20 MV Tandar accelerator (85-MeV $^{197}$Au$^{9+}$ and 197-MeV $^{197}$Au$^{20+}$) at a fixed impact angle (79° to the surface normal) and with an irradiation fluence around $3 \times 10^9$ cm⁻² and vacuum around 10⁻⁶ Torr.

Irradiated targets were analyzed by SFM using a Nanoscope IIIa equipment (Digital Instruments) in air (humidity ≈60–70 %) in the intermittent contact mode [Tapping Mode™ (TM-SFM)] with Nanoprobe™ Si tips (with nominal radius of curvature 10 nm and cone angle 36°) and Nanosensors SuperSharpSilicon tips (with nominal radius of curvature 2 nm and cone angle 20°). Further details on microscope operation and imaging quality are presented later in the text.

### III. RESULTS AND DISCUSSION

#### A. Image analysis

Figure 1 shows surface tracks in PS ($M_w = 160 000 u$) due to a bombardment with 197-MeV $^{197}$Au$^{20+}$. Figure 1(a) is a SFM topographic image where five induced surface tracks can be seen. Each one consists of a crater followed by a hillock elongated in the direction of the ion incidence. Sections of a surface track along the incidence direction (1-1') and perpendicular to the ion direction (2-2') are given in Figs. 1(c) and 1(e), respectively. The dimensions of the in-

<table>
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<th>$M_w$ (u)</th>
<th>$M_w/M_n$</th>
<th>$T_g$ (°C)</th>
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</tr>
<tr>
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<td></td>
</tr>
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</tr>
<tr>
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<tr>
<td>20 000 000</td>
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</table>

FIG. 1. TM-SFM images of surface tracks in PS targets ($M_w = 160 000 u$) bombarded with 197 MeV $^{197}$Au$^{20+}$, incident along the 1-1’ line at 79° to the surface normal. (a) Topography of the sample showing five induced surface tracks, (b) phase contrast image relative to the same region showed in (a), (c) section on the topographic image along a surface track (1-1' line), (d) section on the phase image over the same region showed in (c) (3-3' line), and (e) section perpendicular to a crater (2-2').
The reduced curvature radius can be altered via the topography of the sample, being presumably, responsible for the contrast in phase images observed in the boundaries of the hillocks and can also contribute to the phase shift observed in the region inside the crater. On the top of the hillock, however, no changes in the phase were observed, indicating that the material that composes the hillock is similar to the pristine polymer. This indicates that the formation of the hillock results basically from a physical reorganization of the molecules and does not involve significant chemical degradation. Similar results were found by Daya et al.\textsuperscript{21} for TM-SFM topography images of MeV-ion-bombarded mica surfaces. It was shown that the structural arrangement on the hillock tail is similar to that found on the undamaged mica surface. Energy transport models like the pressure pulse,\textsuperscript{26} that involve a correlated momentum transfer arising from the energy density gradient in the track, seem to be suitable to explain the observed phenomena.

TM-SFM images of PS targets of different molecular weights bombarded with 20-MeV $^{197}$Au$^{+}$ and 85-MeV $^{197}$Au$^{9+}$ are shown in Fig. 2. Most defects present a crater followed by a hillock elongated in the direction of the ion incidence and raised regions on the crater sides (rims). The dimensions of the defects induced by the 197-MeV $^{197}$Au$^{20+}$ ions are similar to the ones observed for the 85-MeV $^{197}$Au$^{9+}$ bombardment. It can be clearly seen in Fig. 2 the different morphologies of the impact features for the various molecular weights. For a given ion energy, at low $M_w$, the craters are large and the hillocks are tiny or absent. With increasing $M_w$, the craters become smaller and the deformed regions show up.

The crater length and width, $c_l$ and $c_w$, respectively, for the three bombardment energies are plotted as a function of $M_w$ in Fig. 3. A fast decrease of the crater lateral dimensions for low $M_w$ (<4 × 10$^7$u) is observed in Figs. 3(a) and 3(b). In this regime, the width of the craters is almost inversely proportional to $M_w$, e.g., $c_w \approx M_w^{-0.8}$ for 85-MeV ions. For higher $M_w$, the scaling of the surface track dimensions with $M_w$ is less steep. The crater size remains approximately constant for $M_w>1.6 \times 10^8$u up to the highest $M_w$ tested (2 × 10$^8$u), not shown in Fig. 3. A similar trend was observed by Eriksson et al.\textsuperscript{16} in their study of MeV-ion-induced cratering on several different bio-organic films, but the saturation of the crater size occurred at lower $M_w$ values, around 6 × 10$^7$u.

All the craters have an approximately elliptical shape, but are more rounded in low $M_w$ samples. The length/width ratio of craters produced by the 20-MeV Au bombardment varies from 1.6 (for low $M_w$) to about 2 (for high $M_w$), while for 85-MeV and 197-MeV Au bombardsments, the difference in this ratio for low and high molecular weights is even larger varying from 1.7 to about 3.

Figure 4 shows the mean hillock length (hl) and mean hillock height (hh) as a function of $M_w$. The lowest dimensions for hl and hh were found on the film with $M_w=3250u$. At this $M_w$, some defects present a hillock, but not all of them. In Fig. 4, the average values for $M_w=3250u$ are calculated only with the defects presenting a hillock. This
is considered a threshold for the observation of a permanent deformation. An increase of \( h_l \) and \( h_h \) is observed as \( M_w \) increases and, similar to those observed for the craters, the values are approximately constant for high \( M_w \) samples.

B. Dependence on viscoelastic parameters

In order to interpret the dependence of surface track dimensions on the polymer \( M_w \), an analysis of the dynamics of polymeric material at molecular level must be carried out. For this purpose, some well-known results from viscoelastic theory for undiluted and nearly monodisperse linear polymers in the melt are introduced below.\(^ {27,28} \)

For low \( M_w \) samples, the chain movement is governed by frictional forces between the monomeric units. Above a given molecular weight \( M_c \), besides the frictional force, the entanglement of the chains, or more precisely, the entanglement coupling, must be considered. This coupling between the entanglements is caused by topological restraints that are not spatially fixed, but can be treated as a set of obstacles or a sequence of slip links.\(^ {29,30} \) \( M_c \) is a critical molecular weight that influences steady-flow viscosity by entanglement coupling, being related with the entanglement molecular weight \( M_e \) (the average molecular weight between coupling loci), but not in a simple manner.\(^ {57} \) For PS, \( M_e (= 34000 u) \) is about two times \( M_c (= 17700 u) \).

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We argue that the viscosity of the films (or the frictional force plus the entanglement coupling at the molecular level) is a key parameter to understand the behavior of the crater lateral dimensions as a function of \( M_w \). Figure 3(a) shows also the reciprocal viscosity \( (1/\eta) \) as a function of \( M_w \). These data were extracted from viscosity measurements of PS fractions at 217 °C, taken from Ref. 27. The viscosity presents a linear dependence on \( M_w \), below \( M_c \), and a \( M_w^{3.4} \) dependence above \( M_c \). The change of the scaling of the viscosity with \( M_w \) above \( M_c \), results from the presence of entanglements between the chains, as stated before. There is a good correlation between the reciprocal viscosity curve and the observed crater size.

Besides the parameters \( M_e \) and \( M_c \), there is also a critical molecular weight that influences the steady-state recovery compliance, called \( M_c' (= 130000 u) \). \( M_c' \) concerns to the average distortion of the polymer coils during flow, being an estimate of the capacity to recover from an induced deformation after the stress is ceased. For \( M_w < M_c' \), the compliance is a linear function on \( M_w \); the lower the \( M_w \), the smaller the recovery capacity and the higher the permanent deformation (the crater) is expected to be. For \( M_w > M_c' \), the compliance becomes constant (independent of \( M_w \)). This behavior of the compliance with \( M_w \) is consistent with the results in Fig. 3.

In summary, the changes in the viscosity and in the compliance with \( M_w \) favor the formation of larger craters in the...
The presence of the hillocks behind the craters is an indication of the crater sizes on the different films. In samples with high $M_w$, the ejection is made difficult by the presence of entanglements or enhancement of the viscosity, resulting in smaller craters (as seen before) and larger hillocks, when compared to samples of low $M_w$.

However, the actual scenario may be more complex. The presence of the hillocks behind the craters is an indication that the local temperature at the hillock regions is below $T_g$, at least for time intervals not higher than about few minutes. Otherwise, the hillocks would not be observed because the chains would quickly relax, as has been recently demonstrated by Papaleo et al. Simple estimations of the temperature rise at a point corresponding to the hillock position using a thermal spike model indicate that the temperatures may be higher than the polymer $T_g$, but for time intervals smaller than few nanoseconds. This time is much smaller than the time necessary for a large-scale chain movement for a PS sample of 200,000 $u$. The decrease in hillock height can be associated to a deformation due to the high pressure exerted by the tip (compression) that acted equally in the two samples.

The differences between the crater depth for the low- and the high-$M_w$ samples can possibly be understood by the facility to drag low molecular weight molecules from the surface into the crater, resulting in a shallower hole. The crater width behaves in a similar manner in the two cases suggesting that the material drag is not important in the variation of this dimension. The decrease in hillock height can be associated to a deformation due to the high pressure exerted by the tip (compression) that acted equally in the two samples. We found that the induced changes of the crater depth and width and the hillock height with the increase of tip-sample interaction are not recoverable, i.e., when the tip-sample interaction is decreased to lower levels, the initial values of the measured dimensions are not restored.

Permanent deformations induced by the tip on surface tracks in biomolecular samples were also detected. On the
other hand, induced surface tracks in mica,\textsuperscript{20,34} a much stronger material, were stable over a large amplitude attenuation range.

In this work the images were taken with amplitude attenuation in the 0.15–0.28 range. Under such conditions, the interaction was high enough for a stable imaging and the tip-induced deformations were relatively small, \(<3\%\) for the crater width and \(<15\%\) for the hillock height; for example, and imaging was stable during a complete scan.

IV. CONCLUSIONS

PS thin films with different molecular weights (3250 to \(2 \times 10^7\)) were bombarded at a grazing angle by MeV ions, and characterized by scanning force microscopy in the intermittent contact mode. Phase mode imaging shows that the material that forms the hillock has similar elastic response as the pristine polymer, suggesting that a “gentle” energy deposition process is related to hillock formation, without a large chemical degradation. Craters’ lateral dimensions are systematically reduced on films of heavier macromolecules. A fast decrease in crater area is observed in the region of low \(M_w\) (<4 \(\times 10^4\)). In this region the crater width scales with \(M_w^{0.8}\) for 85-MeV Au ions. For higher \(M_w\), the scaling is less steep and the craters’ size remain approximately constant for \(M_w > 1.6 \times 10^5\). The observed saturation of the crater size for high \(M_w\) values, coincides with the onset of entanglement effects in the polymer. Moreover, the lateral dimensions of the craters follow the same trend as the reciprocal viscosity (1/\(\eta\)) when plotted against \(M_w\), indicating that the viscosity is governing the final lateral dimensions of the craters. Hillock dimensions are roughly independent of \(M_w\) above the threshold \(M_w\), around 3250\(\mu\) and the total length of the defects (crater plus hillock lengths) is approximately constant. The survival of the plastically deformed regions, originating in the hillocks, is an indication that the local temperature rises, due to the ion impact at these regions is insufficient to induce large-scale movements of the chains, and the polymer response is of a glass. In this case, the viscoelastic properties are dominated by short range configurational rearrangements, which are not much affected by differences in \(M_w\).

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