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Probing thermomechanical behavior of polymers at the nanometer scale with single-ion bombardment and scanning force microscopy

R. M. Papaléo* and L. D. de Oliveira
Faculty of Physics, Catholic University of Rio Grande do Sul, Av. Ipiranga 6681, C.P. 1429, 90619-900, Porto Alegre, RS, Brazil

L. S. Farenzena, M. A. de Araújo, and R. P. Livi
Institute of Physics, Institute of Chemistry, Federal University of Rio Grande do Sul, C.P. 15051, 91501-970 Porto Alegre, RS, Brazil

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Features produced by swift heavy ions on polymer thin films at different temperatures are used to identify the transition between vitreous and viscoelastic behaviors (the glass transition temperature) and to probe the relaxation of nanodeformations in the material. Scanning force microscopy images reveal nanometer-sized craters and raised regions around the point of ion impact. The size of such defects is independent of temperature for $-196\,^{\circ}\mathrm{C} < T < 80\,^{\circ}\mathrm{C}$, but above a critical temperature crater dimensions increase steeply and *no* plastic deformation is observed. This critical temperature is sensitive to the cooling rate, and for rapidly cooled targets it is close to the glass transition temperature of the polymer.

Tracks produced by individual energetic ions impacting a solid have been used for many years to modify materials in a controlled manner.[1,2] The present technological challenge to develop tools for nanometer-scale engineering and characterization of surfaces and devices has rekindled interest in the field of MeV-GeV ion track production. When a fast particle penetrates a solid a large amount of energy is rapidly pumped into the material (in a time scale of 10^{-15}–10^{-12} s) in a small (nanometer) region around the ion path.[1–3] The localized nature of the energy deposited by a fast ion is what makes ion tracks technologically useful, e.g., for selective molecule adsorption,[4] and hole engineering[1,2] for template synthesis of nanomaterials[5] such as magnetic nanowires[6] or thermally responsive membranes.[7] Here, features created by MeV heavy ions bombarding the surfaces of polymer films at various temperatures are used to characterize the transition between vitreous and viscoelastic behaviors and to probe the relaxation of nanodeformations on such films.

Single-ion impact features (also referred to as surface tracks) were studied by scanning force microscopy (SFM) in various materials.[8] The surface tracks observed by SFM are either holes (craters) due to material ejection and/or raised regions attributed to local plastic deformation (Fig. 1). The initial stages of ion track formation are complex and dynamic, involving fast conversion of the electronic excitation energy into atomic motion. In spite of this complexity, the main features of surface track formation in molecular solids have been described[9–12] relatively well by simple hydrodynamic mechanisms.[13] Due to the large energy gradient built up in the region of the impact, a pressure pulse emanates from the ion track, transferring, coherently, enough momentum for molecules close to the surface to be displaced and ejected.[13] Even thermally labile biomolecules are observed to be ejected intact into the gas phase, presumably due to this process, but fragmentation and reconstruction of bonds is extensive in the track core where the energy density is highest.[14] Note that the texture of the raised region behind the crater in Fig. 1 is the same as that of the unaffected neighborhoods of the polymer film. This provides evidence for the existence of a collective movement of molecules due to a mechanical pressure wave, as already pointed out by various authors,[9–12] instead of a pure melt flow from the impact center. Further evidence for this interpretation is also given by SFM phase imaging, discussed later in the text.

Poly(methyl metacrylate) (PMMA) thin films (around 1000 Å thick, $M_W \sim 500\,000$ u) prepared by spin coating

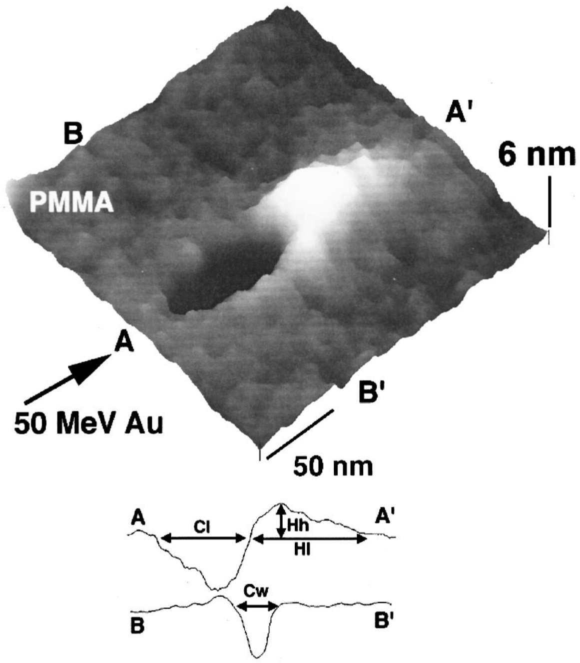

FIG. 1. Crater and plastic deformation induced by a single 55 MeV I ion impact on a PMMA film. Note the similarities in surface texture between the pristine regions and the raised region behind the crater. The image was generated by an exceptionally good SSS tip. The impact feature dimensions are defined in the cross sections *AA′* and *BB′*:*Hl* and *Hh* are the hillock length and height; *Cl* and *Cw* are the crater length and width. This irradiation was performed at the 6 MV Tandem accelerator at Uppsala University, Sweden.

were bombarded at various temperatures between −196 and 150 °C. The bombardments were performed at a HVEE 3 MV Tandetron ion implanter, using 20 MeV $^{197}\mathrm{Au}^{7+}$ projectiles, impacting the target at 79° to the surface normal in vacuum better than 10^{-6} torr. The ion fluence was around 10^9 ions/cm^2, reached in about 3 s with a scanned beam of $\approx$1 nA/cm^2. The temperature T of the targets was monitored with a chromel-alumel thermocouple (precision 0.75%) installed in a copper sample holder. Before each irradiation the targets were maintained at the desired temperature for a period of about 15 min to allow thermal equilibration of the system. The overall uncertainty in T at 100 °C is estimated to be around 5 °C, as the polymer surface may be a few degrees colder than the target holder. Immediately after the bombardment, the sample holder was left to cool down in vacuum without any external cooling (slow cooling rate), or was quenched by circulating water through it (fast cooling). The temperature of water-cooled targets decreased from $\approx$100 to 50 °C in a few minutes. The cooling timescale rises to hours without external cooling.

The surfaces of the targets were analyzed by scanning force microscopy (SFM) using a Nanoscope IIIa equipment (Digital Instruments). Images were collected in air in the intermittent contact mode (Tapping Mode™, TM-SFM) with Nanoprobe™ Si tips and nanosensors SuperSharpSilicon (SSS) tips. The damping of the free oscillation of the cantilever was kept to a minimum value ($\approx$20%) compatible with stable imaging of the surface. The dimensions of the impact features (length, width and depth) are defined in Fig. 1 and were calculated from cross-sectional profiles using the microscope software. The influence of the microscope operating conditions on the size of the imaged defects was previously investigated and is presented elsewhere.[15]

Craters produced by molecular ejection were observed on the bombarded surfaces at a surface density in accordance with the irradiation fluence. The total mass of PMMA ejected per 20 MeV Au ion impact can be obtained from the crater volume, and is estimated to be $(3\pm1)\times10^5$ u (at 20 °C). This is expected to be a lower limit for the sputtering yield mainly because of the finite size of the SFM tip, although crater relaxation may also be substantial at high T, as discussed later in the text. Figure 2 illustrates the effect of temperature on the morphology of the impact features and Fig. 3 shows their average dimensions as a function of the target temperature and cooling rate.

Images of PMMA bombarded at temperatures from −196 up to 80 °C show craters always accompanied by hillocks, independent of the cooling rate. In this regime, the sizes of the ion impact features are independent of temperature: typical craters are 35 nm long and 20 nm wide; the length and height of the hillocks are around 35 and 2.5 nm, respectively (Fig. 3). However, the morphology of the impact features changes markedly when T is close to 100 °C, i.e., the glass transition temperature, T_g (Fig. 2). In this case (and for higher temperatures) hillocks are absent and the horizontal dimensions of the craters increase abruptly by up to a factor of three [Fig. 3(c)]. Since chain mobility is increased at T_g, this behavior is attributed to a fast relaxation of the mechanical deformation induced by the ion impact and to an enhanced sputtering yield. The results suggest that we have found an alternative method for determination of T_g in a polymer film.

The critical temperature above which the hillocks relax and vanish is sensitive to the cooling rate, as would be expected if the critical temperature corresponds to the glass transition temperature.[16] Here, the cooling rate governs the time available for the chains to relax before significant chain movement is quenched.[17] If targets are allowed to cool down slowly, bumps are not seen even at $T=85\,^\circ\mathrm{C}$. However, rapidly cooled targets show a transition between the two mechanical responses at $T\approx100\,^\circ\mathrm{C}$. This value is still a few degrees lower than the bulk T_g of PMMA ($\approx$105 °C), but the temperature difference is within the experimental uncertainty. Note that at 90 °C the relaxation time of the bumps is larger than about one minute [the cooling time in Fig. 2(e)], but smaller than about 1 h [Fig. 2(f)]. For $T>100\,^\circ\mathrm{C}$ [Figs. 2(g) and 2(h)], the relaxation is much faster: even water-cooling is too slow to prevent the disappearance of the hillocks. Ongoing experiments are now being conducted in order to improve the accuracy of evaluation of the temperature at the surface and to produce better controlled cooling rates. When targets are bombarded at room temperature, the hillocks do not relax upon post-irradiation annealing at 100 °C for 30 min. That is, relaxation is fast only if the polymer is in the viscoelastic state *during* the arrival of the ion.

TM-phase images of PMMA bombarded in the vitreous state [Fig. 2(d)] revealed negative phase shifts in the crater region. Phase shifts of the cantilever oscillation are caused by variations in the sample mechanical properties or composition across the scanned region,[18] which are expected to occur in the core of the impact. Note that at the hillock there

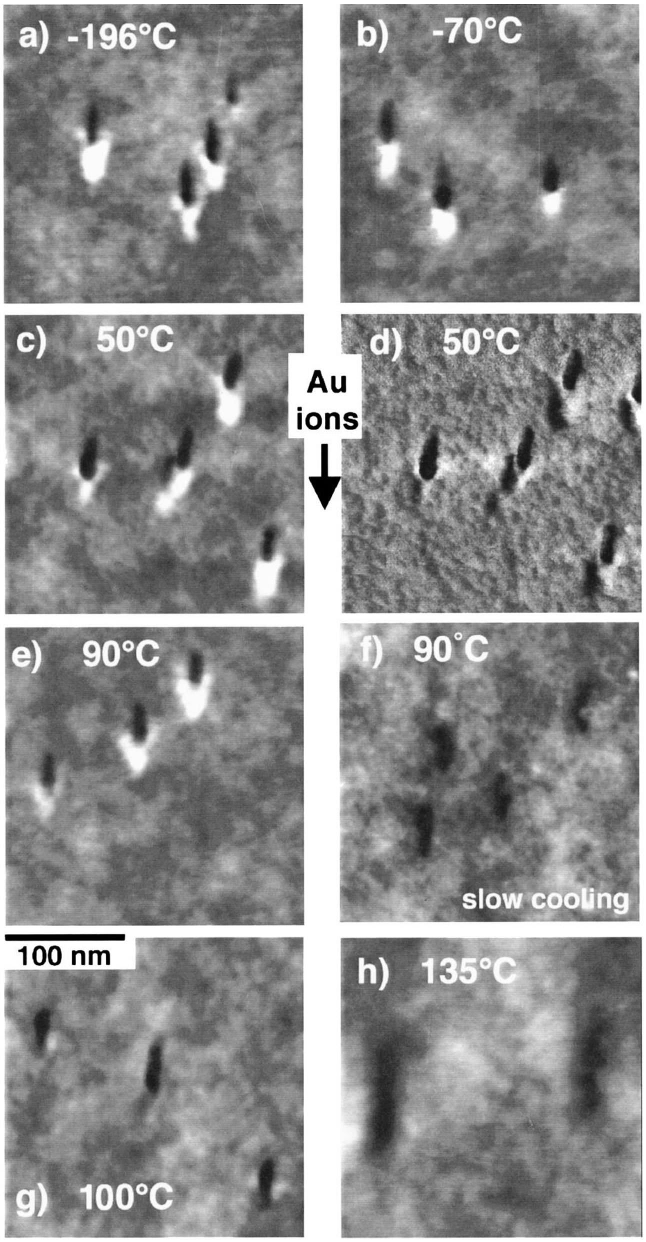

FIG. 2. TM-SFM images of PMMA targets bombarded by 20 MeV Au ions at temperatures between −196 and 135 °C. Targets were water-cooled immediately after the ≈3 s irradiation time, except on (f) where a slow cooling rate was used. Note the remarkable change in the rate of relaxation of the hillocks between (e) 90 °C and (g) 100 °C. (d) shows the phase image corresponding to the height image given in (c). The contrast covers height variations in the 8 nm range in (a)–(c), (e)–(h) and phase angle variations in the 30° range in (d). The impact angle is 79° to the surface normal. The arrow indicates the ion penetration direction and the slow scanning axis of the microscope.

is *no* phase shift, consistent with there being no significant change in the material properties. Using elevated temperatures and slow cooling rates, phase shifts in the crater region are no longer seen. This suggests that pristine polymer flows into the hole. Shallower craters are in fact observed for T appreciably higher than T_g [Fig. 2(h)].

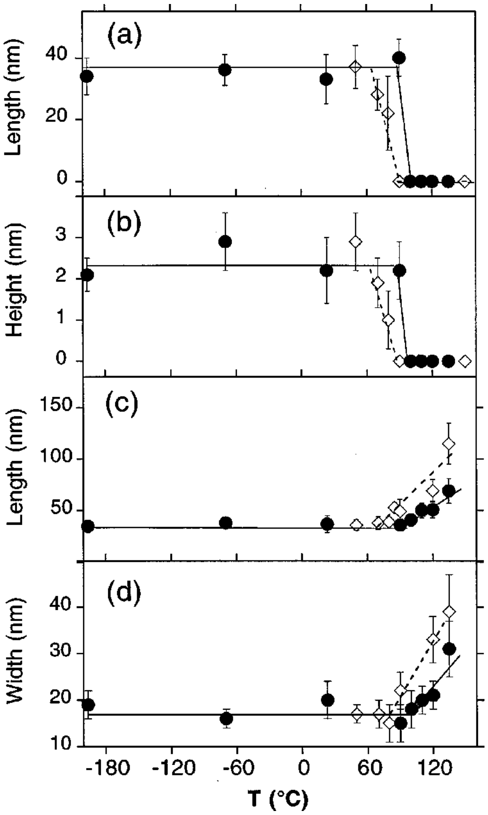

FIG. 3. Average dimensions of surface features induced by 20 MeV Au ions impacting PMMA thin films as a function of target temperature and cooling rate: (a) hillock length, (b) hillock height, (c) crater length, (d) crater width. Slow cooling data are depicted as open diamonds and fast cooling data as circles. The solid and dashed lines are just to indicate the trend of the two relaxation conditions. Mean values were obtained from data collected from around 100 impact sites for each temperature, using different SFM tips.

In summary, SFM images of MeV heavy-ion impacts can be used to characterize the response of PMMA thin films to a sudden and localized energy perturbation. Plastic deformation is not seen above a critical temperature, after which the horizontal scale of impact craters also rapidly increases. As the changes in the impact feature dimensions occur over a narrow temperature range, it is possible to determine the temperature for a transition from a glassy to a viscoelastic behavior in polymeric systems. This would be important in studies of high modulus (e.g., cross-linked) polymers that are difficult to characterize by traditional stress-strain and dynamic mechanical analysis. Moreover, ion impact features may also be applicable for discrimination of nanometer phases of copolymers, polymer blends, and composites. The mobility of polymer chains on a segmental level and the kinetics of relaxation of nanodeformations in polymers can be investigated in more detail by carefully controlling the cooling rate of bombarded films.

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*Corresponding author. Email address: papaleo@pucrs.br

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[17] As the size of the hillocks on films bombarded at 70 °C and which undergo a slow cooling is identical to the ones irradiated at room or lower temperatures (Fig. 3), hillock relaxation is considered to be virtually frozen when the targets reach a temperature of approximately 70 °C. The dimensions of the hillocks on bombarded films kept for several years at room temperature (which can be higher than 35 °C) did not show any significant change.

[18] The interpretation of phase contrast is still a subject of discussion, but there are a number of significant experiments connecting phase shifts to variations in mechanical properties, as in Y. Thomann, H.-J. Cantow, G. Bar, and M. -Whangbo, Appl. Phys. A: Mater. Sci. Process. **66**, S1233 (1998).