Substrate and Chain Size Dependence of Near Surface Dynamics of Glassy Polymers

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(Received 28 February 2008; published 26 August 2008)

We use nanohole relaxation to study the surface relaxation of films of glassy isotactic poly (methyl methacrylate) (*i*-PMMA) films. These measurements allow us to obtain the time dependent relaxation function at a number of different sample temperatures for the first 2–3 nm of the free surface in a system often used as a model system for the effect of the substrate on thin film dynamics. The surface is observed to relax at temperatures up to 42 K below the bulk T_g value, even on systems where the thin film T_g is known to be greater than the bulk value. We are able to determine the range over which the substrate directly affects the free surface relaxation, and determine a surprisingly large (M_w independent) limiting thickness of ~180 nm where the free surface relaxation is not affected by the substrate. For thick films ($h > 200$ nm) we find an unexpected linear M_w dependence of the near surface relaxation time.

DOI: 10.1103/PhysRevLett.101.096101 PACS numbers: 68.47.Mn, 68.03.Hj, 68.35.bm, 68.37.Ps

The physical properties of thin polymer films remains an area of significant interest and activity. For a number of polymer materials, thin films have measured glass transition temperatures (T_g) that exhibit significant deviations from the bulk material [1,2]. In some materials, such as atactic polystyrene, the measured T_g values decrease as the film thickness decreases with little apparent dependence on substrate material or polymer molecular weight [3,4]. Despite considerable theoretical interest, an adequate description of these observations remains elusive [5]. In addition, there are some polymers [such as poly (methyl methacrylate) (PMMA)] where the film thickness dependence of the T_g values exhibit a significant dependence on the substrate material [6–8]. A popular explanation for these differences is that the interfacial properties are the underlying cause of observed T_g anomalies. In particular the free surface region causes a local enhancement of dynamics that results in an overall lowering of the T_g value, and the substrate inhibits local dynamics leading to an overall increase of the T_g value. It is surmised that the material dependent competition between these two effects causes the differences among different polymers. Despite some controversy, there is growing evidence that the free surface region of polymers exhibits enhanced dynamics relative to the bulk [9–14] and that this enhancement is directly related to the reduced T_g values of thin films [15,16]. Recent computer simulations also support this idea [17]. Comparison of the T_g value of supported and free standing films of polystyrene (PS) have suggested that the effects of the interfaces may be simply additive [18], but this ignores possible interaction between the two interfaces which can be important for films with thickness of a few tens of nm. Experiments of Ellison *et al.* using a fluorescently labeled layer incorporated into a thin film have shown that the local T_g of the near free-surface region can be affected by the presence of the substrate [16]. This result indicates a possible interaction between the two interfacial regions over a surprisingly large distance of a few 10's of nm. Measurements of the T_g value provide a convolution of time and temperature dependence and average over a region of the size of the labeled film (14 nm in Ref. [16]), and are limited in the sense that when the total film thickness is the thickness of that of the labeled layer, there is no ability to distinguish between the substrate and free surface region. Even for films that have a thickness of a few times the labeled layer, this may be an important consideration. In order to isolate the near surface dynamics it is necessary to employ a technique that can measure independently the time and temperature dependent dynamics with nm resolution.

In this Letter we report the application of our recently developed nanohole relaxation technique to directly measure the surface relaxation of *i*-PMMA, and how this surface relaxation can be affected by a substrate. We chose *i*-PMMA because it is a model system that has been well studied and shown to have a film thickness dependent T_g value that depends on the nature of the substrate [7,15]. The nanohole relaxation technique [14] is well suited to this study as we obtain the time dependent relaxation function at a number of different sample temperatures for the first 1–3 nm of the free surface. By studying the film thickness dependence of the near-free surface relaxation for films on different substrates we are able to determine the range over which the substrate directly affects the free surface relaxation. This also allows us to determine a limiting thickness where the free surface relaxation is not affected by the substrate. For films with thickness greater than this limiting value, we determine the M_w dependence of the relaxation time of the near free surface region and find a surprising linear M_w dependence.

Three kinds of isotactic poly(methyl methacrylate) were used for the present work ($M_w = 212.4$k, $M_w/M_n = 1.21$, ISO $> 98\%$; $M_w = 436$k, $M_w/M_n = 1.4$, ISO $> 98\%$;

$M_w = 889\text{k}$, $M_w/M_n = 1.15$, ISO $> 95\%$; all from Polymer Source, Inc.). Thin *i*-PMMA films were produced by spin-coating from solutions in toluene onto two kinds of substrates. One substrate was single side polished silicon wafers (from Silicon Quest International; orientation: $\langle 100 \rangle$) with the native oxide layer left intact. The other substrate had these Si wafers coated with a thermally evaporated aluminum (99.99% purity) layer (100 nm in thickness; 1.3 nm in surface roughness). All *i*-PMMA films were annealed in dry nitrogen gas for more than 16 h at a temperature of 336 K (13 K above T_g). We use our previously described technique [14] to produce nanometer spherical-cap holes on polymer surfaces. In the present study, the gold nanoparticles, with an average diameter of 20 nm, were spin-cast onto surfaces of the annealed *i*-PMMA films, embedded into film surfaces [at $T = T_g(\text{bulk}) + 4$ K] to a depth of ~ 3 nm, and then dissolved using mercury in a purge of dry nitrogen. After removing the mercury, the samples were immediately imaged using atomic force microscopy (AFM) (typical tip curvature radius ~ 7 nm) in tapping mode to track the annealing of surface holes. A key difference between this study and our previous work on PS is that relatively low value of bulk T_g for *i*-PMMA leads to much higher surface mobility at ambient temperature. Because of this enhanced mobility, if the mercury removal process is done at room temperature, the holes are fully annealed out before measurements can be carried out. As a result, the dissolution of gold particles by mercury for these studies on *i*-PMMA is done at a temperature of 275–276 K for 2 h.

Figure 1 shows the result of surface hole relaxation of 60 nm thick 212.4k *i*-PMMA on silicon substrate at a temperature of 287 K. Every data point represents the average hole depth of more than 100 surface holes. The inset of Fig. 1 shows a typical AFM image of surface holes. The surface holes have surrounding rims which help distinguish artificially produced nanoscale surface holes from natural polymer surface roughness. The rims have a lifetime that is significantly larger than the holes (due to the larger radius of curvature). This allows one to know that a hole is (was) present even if the actual depth is too small to be measured. This is important as the average depth of holes is used to determine the lifetime, and the inability to count holes with immeasurably small depth would skew the hole distribution to large values. The depth of surface holes was defined as the distance from the average local polymer surface height to the bottom of such holes. This imaging was done at a number of different times until the sample had evolved to the point where most of the holes were no longer visible. The solid curve is a single exponential fit to the data. In all cases the data was well described by a single exponential. If the Kohlrausch-Williams-Watts equation is applied to fit the experimental data, values of β between 0.8 and 1.0 could all be used to provide reasonable fits to the data. It is remarkable that even at 287 K, more than 30 K below the bulk T_g value, complete surface relaxation is observed in less than 100 minutes.

Figure 2 shows the temperature dependence of the hole relaxation time over the range of temperature 281 to 289 K, for thick films ($h > 180$ nm). Because of the relatively low T_g value of the *i*-PMMA and correspondingly fast surface relaxation, this was the limited temperature range available for these surface relaxation studies. The solid curve is from Ref. [19] for bulk *i*-PMMA given by the equation $\log(\tau_\alpha/100) = -41.41 + 55.17(T - T_\infty)^{-0.1143}$ where $T_\infty = 311$ K, and the symbols are lifetimes that have been derived from the experimental lifetimes through the

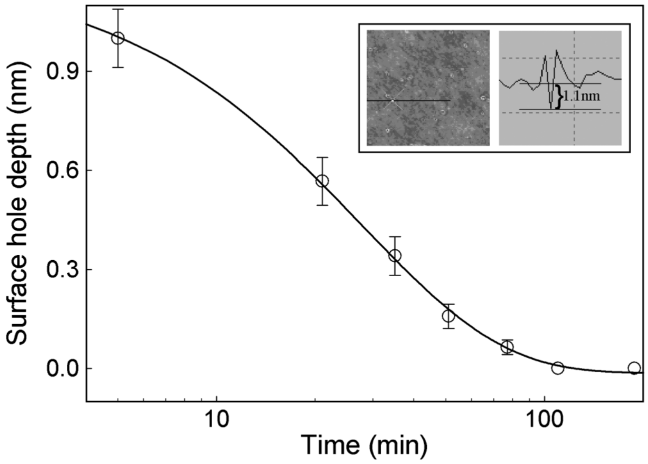

FIG. 1. Surface hole relaxation at 287 K of 60 nm thick *i*-PMMA (Mw = 212.4k) film on Si; the solid curve is the single exponential fit. The inset shows some surface holes in the AFM image (left) and the line scan (right) for one surface hole (marked as a cross).

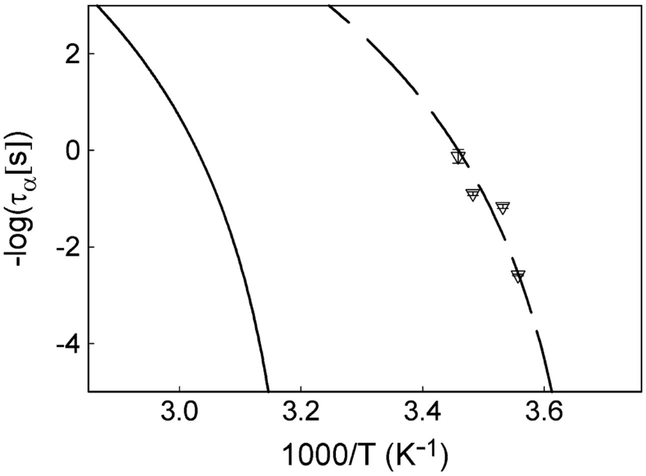

FIG. 2. Temperature dependence of the average lifetime for the first few nm of the M_w 889k *i*-PMMA surface for films with $h \gtrsim 180$ nm. The solid curve is the relaxation curve for bulk *i*-PMMA [19] and the dashed curve is the same curve with T_∞ shifted by 41 K from the bulk curve.

relation [14]

$$\tau_\alpha = \frac{\tau_{\text{measured}}}{1+\frac{RG_0}{2\gamma}} \qquad (1)$$

where τ_{alpha} is the characteristic relaxation time of the system, and τ_{measured} is the lifetime of the nanohole relaxation. While we use this relation to estimate an alpha relaxation time from the hole relaxation to compare to bulk data, the central results of this Letter are not model dependent. One way to consider the data is to ask by what temperature we have to shift the solid bulk curve in order to get agreement with our data. We find that a shift of 41 K in T_∞ provides good agreement between the solid curve and our experimental data, as shown by the dashed line. A possible interpretation of this is that in this temperature region, the surface is acting as if it has a T_g value that is $\simeq 41$ K less than that of bulk *i*-PMMA. Over this limited range, a simple shift in the temperature is sufficient to produce coincidence of the bulk and surface lifetimes. This is similar to Ref. [11] and distinct from that observed in nanohole relaxation in PS [14], and suggests that while many (if not all) polymers exhibit enhanced surface relaxation, there remain significant material dependent features. From this data, we chose a temperature of 287 K for a detailed study of thickness, substrate, and M_w dependence of hole relaxation in *i*-PMMA films.

Figure 3 combines the dependence of measured surface hole lifetime (at 287 K) as a function of *i*-PMMA film thickness, substrate material, and molecular weight. The surface hole lifetimes for *i*-PMMA with different M_w values are normalized using corresponding surface hole lifetimes of thick films ($h > 180$ nm), which are not affected by the substrate materials, as a reference lifetime. The value of 1 in the vertical axis of the main panel corresponds to about 14 min for $M_w = 212.4$k, 36 min for $M_w = 436$k, and 53 min for M_w 889k *i*-PMMA. There is a clear difference in lifetimes between the relaxation time of the surface deformations for thin films on Si (with native oxide) versus the same film thickness on an Al coated wafer (with a native Al oxide as well). We note that complete relaxation of the surface is always observed more than 30 K below bulk T_g in particular even for films as thin as 10 nm on silicon substrates. Such films have been previously reported to exhibit overall T_g [7,20] values greater than the bulk value which indicates slower overall dynamics. This disparity between surface properties and whole film properties suggests highly heterogeneous dynamics in such systems. We note the similarity between the substrate-dependent difference in surface relaxation time and measured T_g values for *i*-PMMA on the same substrate materials [7,8]. Despite the similarity, there are significant quantitative differences. For example, for 20 nm films, the measured T_g value for *i*-PMMA on a Si substrate is 10–40 K greater than the bulk value [7,20], while the surface relaxation time increases by only a factor of 3. While T_g values are often said to average over the whole film, and include effects on dynamics due to a near-substrate region and free-surface region, the effect of the substrate on the free surface shown in Fig. 3 allows for the possibility that the substrate effects enter only indirectly in how they affect the free surface (though Ref. [16] shows strong evidence for a direct substrate effect). The dependence on substrate material of surface relaxation could be compared with differences observed in the conformational changes for PMMA at an Al interface [21], but in this case the free surface is 180 nm away from the solid interface. It is remarkable that this substrate dependence of surface relaxation times persists to a film thickness value of ~180 nm before the hole relaxation time is the same for films on different substrates. This observation means that the rheological properties of the first 2–3 nm of the *i*-PMMA surface are strongly affected by the substrate even when the substrate is over 100 nm away from the free surface, and the bulk of the film is completely glassy. This is consistent with measurements of physical aging near the surface of PMMA films that predicted long range interactions between the surface and the substrate [22], and measurements of dynamics of filled elastomer systems [23]. It is also possible that this surface sensitivity to the substrate material results from the fact that the strain field on embedding can persist to a depth of ~10 times the contact area and the dynamics of the near surface region could be affected [24].

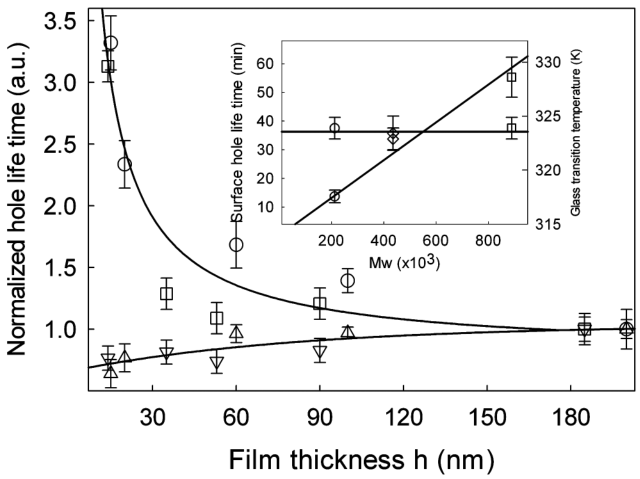

FIG. 3. Normalized surface hole lifetime vs thickness of *i*-PMMA films of different molecular weights on two kinds of substrates: 212.4k *i*-PMMA on Si (○), 889k *i*-PMMA on Si (□), 212.4k *i*-PMMA on Al (△), 889k *i*-PMMA on Al (▽); the solid curves serve as guides for the eye. The inset shows the surface hole lifetimes, and ellipsometrically measured T_g values of thick *i*-PMMA films ($h \gtrsim 180$ nm) on Si for three molecular weights: 212.4k (○), 436k (◇), and 889k (□).

Equally remarkable is how the "thick film" value of surface relaxation time at $T = 287$ K depends on the molecular weight of the polymer (inset of Fig. 3) while T_g

values are the same within an uncertainty of ±1 K. This means that the surface relaxation times are unlikely to be related to any M_w dependence of the bulk T_g value. If the near surface region is treated as a viscous fluid the leveling time varies as $\tau \sim \frac{\eta x}{\gamma}$, where x is the size of the surface perturbation, and so our observation implies that $\eta \sim N$. Even though the thick film surface relaxation times depend on the M_w of the *i*-PMMA, the limiting film thickness where this dependence vanishes does not appear to. Given the factor of 4 difference in the M_w values used, it is very unlikely that the dependence on substrate material is due to chain confinement over the whole film. Since only the near surface region of the polymer surface (of the order of a few nm) is able to relax at the measurement temperature, and the size of this region is much smaller than the molecular size, only a small fraction of the monomer units of any molecule should be in the mobile surface region (for ideal chains near an interface) [25]. It is interesting to note that this observation of Rouse-like dynamics is the same as that observed for high M_w PS confined to 2 nm confinement [26]. The M_w dependence for *i*-PMMA is distinct from that observed for PS mixtures [27], as those can be explained in terms of chain ends acting as diluents which are only affected by the static spatial distribution of chain ends. The molecular weight dependence in the surface relaxation dynamics of glassy *i*-PMMA could be a specific property of *i*-PMMA, because of its molecular structure and possible short range ordering of the chains near the surface [28]. Similar studies on the M_w dependence of surface relaxation of other polymers such as atactic polystyrene are needed to lead to a definitive conclusion. Clearly, this is an observation that will benefit substantially from more theoretical consideration.

We have used nanohole relaxation studies to probe the rheological properties of the near free surface region of *i*-PMMA with different film thicknesses, substrate materials, and M_w values. The results show an enhanced surface mobility compared to the bulk under all conditions, but the actual relaxation time reveals a number of surprising features. The relaxation time of the first few nm of the surface appears to be strongly affected by the substrate such that for films with $h \sim 20$ nm there is a factor of 3 difference in the relaxation time between films with the same thickness but different substrate. The substrate dependence of the surface relaxation time persists to a film thickness of ≃200 nm. The surface relaxation time is dependent on the M_w value of the polymer. In the range $200\text{k} < M_w < 800\text{k}$ this dependence appears to be linear. It is not possible from this data to distinguish between a surface region of near 2-dimensional chains or a M_w dependent surface structure that leads to the observed relaxation behavior.

Financial support from Natural Sciences and Research Council of Canada (NSERC) is gratefully acknowledged.

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