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Polymer Viscoelastic Properties Measured by Friction Force Microscopy

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Introduction. Scanning probe microscopies have been developed to examine topography and a variety of physical phenomena with resolutions down to the molecular scale.[1−9] In one of the variations, friction force microscopy (FFM), the lateral force on the probe caused by sliding friction is measured.[10] Interpretation of these data for polymers demands that we understand the cause of frictional energy dissipation on polymer surfaces. In this communication, we present data for poly(ethylene terephthalate) (PET), poly(vinyl alcohol) (PVOH), poly(vinyl acetate) (PVAc), and gelatin which display a correlation between the velocity dependence of frictional force and the viscoelastic loss tangent (tan δ). Earlier frictional studies on polymers suggested a similar correlation particularly vis-à-vis the glass transition. The observation of wear, however, especially under sliding conditions complicated the interpretation, as did the presence of a multiasperity surface.[11]

Experimental Section. An aqueous PVOH solution was prepared by heating a 1 wt % mixture of PVOH (Aldrich, 99% hydrolyzed, M_w = 85 000−146 000) in distilled/deionized water (DW) to 90 °C. Freshly cleaved muscovite mica (New York Mica Co.) substrates were rinsed in DW, immersed in PVOH solution, immediately removed so as to leave a residual puddle of PVOH solution, and dried slowly overnight at 20 °C in moderate humidity (30% < RH < 60%). PVAc (Aldrich, M_w = 113 000) films were prepared similarly using toluene to form a 1 wt % solution. PET (Aldrich) films were prepared by spin coating a 0.08 wt % solution of PET in 2-chlorophenol onto a SiO_2-coated silicon substrate and dried at 60 °C for 2 h.

Backscattering spectrometry[12] of 4.9-MeV helium ions (which exploits the enhanced, non-Rutherford carbon cross section[13]) yielded an approximate PET film thickness of 0.23 μm (employing tabulated stopping powers of He^{2+} in PET[14]). The PVOH film yielded a thickness of 0.47 μm. The much thicker PVAc film was characterized using a 3.0-MeV hydrogen beam and comparing the carbon line width to that from the PET film (with corrections for the respective atomic concentrations of carbon). This procedure yielded a PVAc film thickness of 7 μm.

The Nanoscope III (Digital Instruments) and the PicoSPM (Molecular Imaging) scanning force microscopes with commercial Si_3N_4 tips on 100 μm triangular cantilevers (spring constant = 0.58 N/m) were used to characterize the frictional behavior of the polymer films. The PicoSPM employs an enclosed sample chamber allowing variation of relative humidity (RH) from 5 to 95%. Hydrophobized tips, used in the PET film study, were prepared by exposing probe tips to an oxygen plasma followed by treatment with hexamethyldisilazane (HMDS); this effectively yielded a tip surface comprised of methyl-terminated groups.[15] Hydrophobized tips were less susceptible to spurious polymer adsorption and polymer buildup over long-term scanning. This was determined by the lower contact forces (applied plus adhesive loads) measured over continued scanning of the polymer surface. Probe tips were characterized by scanning electron microscopy (SEM) in order to determine the radius of curvature (r_c), which ranged from 10 to 300 nm.

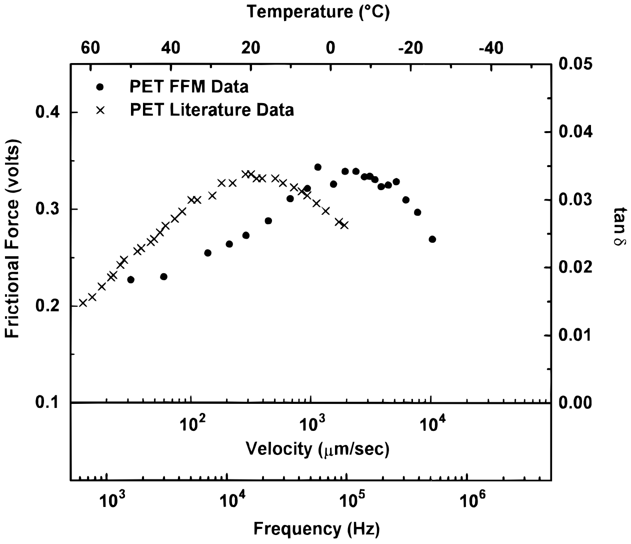

Figure 1. Frictional force versus scanning velocity recorded at a 140 μm scan length for a film of PET, along with an overlay of Takayanagi's viscoelastic data on PET.[24]

Quantitative frictional data were collected in the "y-disabled" mode in which the tip scanned along the fast (x) direction. The frictional force was measured by taking the difference (in volts) between lateral forces scanning left-to-right and right-to-left. Absolute frictional force can be obtained with various calibration methods but such techniques were not necessary in this study.[16,17] Scan velocity, calculated from 2 × (scan length) × (scan frequency), was varied with the independent variables of scan length (0.005−150 μm) and scan frequency (0.1−55 Hz). All data were collected at ambient conditions of ≈20 °C and relative humidity of ≈40%, except for the PVOH and gelatin studies, where the relative humidity was varied.

Results and Discussion. Polymer films completely covered the substrate and appeared flat, having a rms roughness < 1 nm. No detectable alteration of the surface morphology occurred in any of the measurements described in this paper. Figure 1 shows the velocity dependence of frictional force exhibited by crystalline PET. A distinct maximum was observed at a scanning velocity of ≈2000 μm/s. To convert this velocity into a relaxation rate (frequency), we must divide by the length over which the tip force was applied. We approximated this distance using the JKR equation, which utilizes the radius of curvature of the tip (r_c), the applied load (F_{applied}), and the work of adhesion between the polymer and tip (which is related to the adhesive force).[18,19] Using the measured r_c (12

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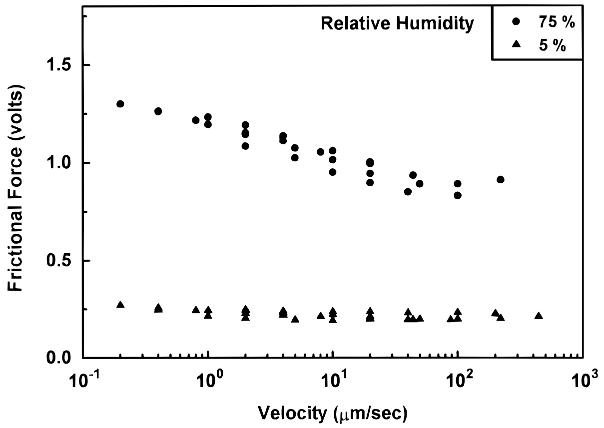

Figure 2. Frictional force versus scanning velocity taken at 5 and 75% relative humidity for a film of PVOH.

nm), F_{applied} (3.5 nN), and F_{adhesive} (26.1 nN), we calculated a contact diameter of 15.4 nm and a corresponding relaxation frequency of $\approx 10^{5.1}$ Hz for PET. The dielectric β process has been studied extensively and was assigned to main chain motions of the polymer involving the COO groups.[20-23] Studies of varying degrees of crystallinity have shown that the frequency–temperature location and shape of the β process were independent of crystallinity.[22,23] Takayanagi measured a relaxation frequency of dry PET at −40 °C to be ≈138 Hz.[24] By using the time–temperature conversion for the β process of PET, 30 °C per order of magnitude in frequency,[25] the viscoelastic data of Takayanagi and our FFM data can be compared and are overlaid with the friction versus velocity data (Figure 1). Takayanagi's measured relaxation corresponds to $\approx 10^{4.14}$ Hz at 20 °C (Figure 1).[25] The loss tangent was scaled arbitrarily to the height of the measured frictional force. The temperature scale corresponds to the literature data only, whereas the relaxation frequency axis is common to the measured FFM data and Takayanagi's result. A qualitative comparison between our frictional data and that reported by Takayanagi also reveals a similar peak shape for the β relaxation. Humidity effects are not as strong in PET as in other more hydrophilic polymers; at 40% relative humidity PET only has a 0.4% water content,[26] which does shift the β relaxation to slightly lower temperatures at a given frequency. Nevertheless we believe we are probing the β relaxation of PET.

Friction force versus scanning velocity at two different humidities for a film of PVOH produced from a 1 wt % solution is shown in Figure 2. No velocity dependence was observed at a relative humidity of 5%, and a gradual increase in friction was observed at velocities < 100 μm/s for RH = 75%. Takayanagi measured the loss compliance (E'') as a function of temperature and assigned the α_a relaxation in PVOH, where the subscript "a" stands for amorphous.[27] The α_a relaxation corresponded to the glass transition and, when measured at a frequency of 138 Hz, occurred at ≈20 °C for 8% water content.[24] Water acts as a plasticizer for PVOH, lowering the temperature at which a particular relaxation occurs[28] or, correspondingly, decreasing the relaxation time. Under our conditions, 20 °C, RH = 5 and 75%, the water content in PVOH should approximately be 1 and 12.5%, respectively, which corresponds to a T_g of 65 and 18 °C.[28] Therefore at 5% RH the glass transition occurs well below our detection limits, whereas at 75% RH we are able to detect the onset of the glass transition. The glass transition for PVOH has a fwhm of ≈40 °C, and a time–temperature conversion of ≈2.5 °C per order of magnitude in frequency;[25] therefore we are unable to measure the full relaxation without temperature variation.

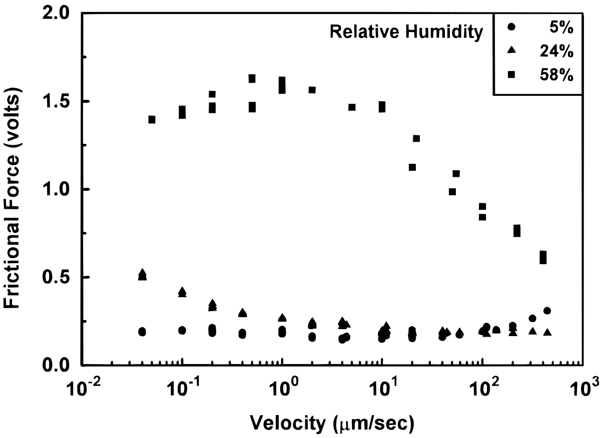

Figure 3. Frictional force versus scanning velocity taken at 5, 24, and 58% relative humidity for a gelatin film.

In an earlier FFM study[7] of gelatin films, we assigned a peak near 1 μm/s in the velocity dependence of friction to the glass transition. In Figure 3 we show the dependence of this peak position on gelatin water content, via the latter's known humidity dependence. The data taken at RH = 58% (≈20% water content[29]) are similar to those previously reported by us at similar measurement humidities,[7] i.e. exhibit a broad peak centered near 1 μm/s. At RH = 24% (≈13% water content) this peak apparently has shifted by approximately 4 decades to lower velocity, residing only partially inside our measurement window. At RH = 5% (≈6% water content) no evidence of this peak is visible, while a secondary peak apparently has moved into the window at the high-velocity end. Interpolation from published gelatin glass transition temperatures yields $T_g \approx 20$, 55, and 120 °C at the water contents of 20, 13, and 6%, respectively. Published time–temperature conversion data do not exist for gelatin to our knowledge; our data suggest a peak shift of (55 °C − 20 °C)/4 ≈ 9 °C per decade of rate, similar in magnitude to tabulated conversions for α relaxations in polyamides like the nylons.[25] The β peak position in amide-linkage polymers typically shifts much less than the α with changing water content.[25]

PVAc films did not exhibit a maximum in the friction vs velocity measurements after >1 day of drying. The α relaxation for 100% PVAc samples occurs at frequencies less than 0.001 Hz at room temperature,[25] and the β mechanism, thought to arise from motions of the $OCOCH_3$ side chains,[30] occurs at $\approx 10^{6.5}$ Hz.[25] Therefore, neither relaxation was accessible at room temperature with our velocity range. Figure 4 shows the effect of drying on a PVAc sample prepared from 1 wt % PVAc in toluene. In order to study plasticizing effects, a thicker film was used allowing for slower loss of solvent. The results measured 12 h after preparation show a frictional maximum at ≈10 μm/s; as the film ages, the peak shifts to lower velocities, yielding no distinguishable maximum after 23 days. Similar frequency shifts due to solvent plasticizing were reported on PVAc in diphenylmethane.[31] In this dielectric study, 11.3 mol % of diphenylmethane shifted T_g ≈2 decades, and 24.1 mol % led to T_g shifting of ≈5 decades of rate.

Conclusions. Using the contact diameter as the velocity-to-frequency conversion length, we suggest a correlation between the friction in films of PET, PVOH,

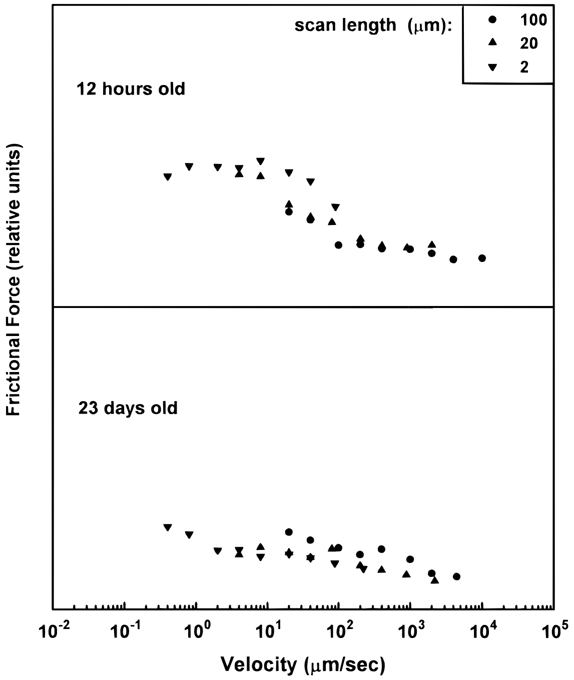

Figure 4. Frictional force versus scanning velocity taken at various scan lengths for a film of PVAc recorded at 12 h (top) and 23 days (bottom) from preparation.

PVAc, and gelatin with their known α and/or β relaxation processes. This method potentially enables assignment of frictional mechanisms, which are due to viscoelastic relaxations, on a nanometer scale.

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References and Notes

(1) Hues, S. M.; Colton, R. J.; Meyer, E.; Guntherodt, H. J. *MRS Bull.* **1993**, *18*, 41.
(2) Overney, R.; Meyer, E. *MRS Bull.* **1993**, *18*, 26.
(3) Hartmann, U.; Goddenhenrich, T.; Heiden, C. *J. Magn. Magn. Mater.* **1991**, *101*, 263.
(4) Burnham, N. A.; Dominguez, D. D.; Mowery, R. L.; Colton, R. J. *Phys. Rev. Lett.* **1990**, *64*, 1931.
(5) Weisenhorn, A. L.; Maivold, P.; Butt, H. J.; Hansma, P. K. *Phys. Rev. B* **1992**, *45*, 11226.
(6) Blackman, G. S.; Mate, C. M.; Philpott, M. R. *Phys. Rev. Lett.* **1990**, *65*, 2270−2273.
(7) Haugstad, G.; Gladfelter, W. L.; Weberg, E. B.; Weberg, R. T.; Jones, R. R. *Langmuir* **1995**, *11*, 3473.
(8) Frisbie, C. D.; Rozsnyai, L. F.; Noy, A.; Wrighton, M. S.; Lieber, C. M. *Science* **1994**, *265*, 2071.
(9) Florin, E. L.; Moy, V. T.; Gaub, H. E. *Science* **1994**, *264*, 415.
(10) Mate, C. M.; McClelland, G. M.; Erlandsson, R.; Chiang, S. *Phys. Rev. Lett.* **1987**, *59*, 1942.
(11) Ludema, K. C.; Tabor, D. *Wear* **1966**, *9*, 329.
(12) Chu, W. K.; Mayer, J. W.; Nicolet, M. A. *Backscattering Spectrometry*; Academic Press: San Diego, 1978.
(13) Feng, Y.; Zhou, Z.; Zhou, Y.; Zhou, G. *Nucl. Instrum. Methods B* **1994**, *86*, 225.
(14) Feldman, L. C.; Mayer, J. W. *Fundamentals of Surface and Thin Film Analysis*; North-Holland: New York, 1986.
(15) Hertl, W.; Hair, M. L. *J. Phys. Chem.* **1971**, *75*, 2181.
(16) Haugstad, G.; Gladfelter, W. L.; Weberg, E. B.; Weberg, R. T.; Weatherill, T. D. *Langmuir* **1994**, *10*, 4295.
(17) Noy, A.; Frisbie, C. D.; Rozsnyai, L. F.; Wrighton, M. S.; Lieber, C. M. *J. Am. Chem. Soc.* **1995**, *117*, 7943.
(18) Johnson, K. L.; Kendall, K.; Roberts, A. D. *Proc. R. Soc. London A* **1971**, *324*, 301.
(19) The JKR equation

$$a^3 = \frac{r_c}{K}[F + 3\pi r_c W_{12} + (6\pi r_c W_{12} F + (3\pi r_c W_{12})^2)^{1/2}]$$

where a is the contact radius, r_c is the radius of curvature, K is the elastic modulus, R is the applied load, and W_{12} is the work of adhesion, was used to calculate the contact diameter ($2a$). W_{12} was calculated from $F_{\text{adhesion}} = (-{}^3/_2)W_{12}\pi r_c$ using the measured adhesive force. Future refinements of this method will attempt to account more accurately for the distance over which the force of the tip is felt. Due consideration will have to be given to the contact force, the tip shape, and the mechanical properties of the polymer.
(20) Ward, I. M. *Trans. Faraday Soc.* **1960**, *56*, 648.
(21) Illers, K. H.; Breuer, H. *J. Colloid Sci.* **1963**, *18*, 1.
(22) Saito, S. *Res. Electrotech. Lab.* **1964**, *No. 648*.
(23) Ishida, Y.; Yamafuji, K.; Ito, H.; Takayanagi, M. *Kolloid Z.* **1962**, *184*, 97.
(24) Takayanagi, M. *Mem. Fac. Eng. Kyushu Univ.* **1963**, *23*, 1.
(25) McCrum, N. G.; Read, B. E.; Williams, G. *Anelastic and Dielectric Effects in Polymeric Solids*; Wiley: London, 1967.
(26) Langevin, D.; Grenet, J.; Saiter, J. M. *Eur. Polym. J.* **1994**, *30*, 339.
(27) Takayanagi, M.; Nagai, A. *Rep. Prog. Polym. Phys. (Jpn.)* **1964**, *7*, 249.
(28) Finch, C. A. *Polyvinyl Alcohol: Properties and Applications*; Wiley: London, 1973.
(29) Mees, C. E. K.; James, T. H. *The Theory of the Photographic Process*: Macmillan Publishing Co.: New York, 1966; p 45.
(30) Ishida, Y.; Matsuo, M.; Yamafuji, K. *Kolloid Z.* **1962**, *180*, 108.
(31) Broens, O.; Muller, F. H. *Kolloid Z.* **1955**, *140*, 121.

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