Friction, Surface Oxidation, and Polar Free Energy for Polymer Surfaces by Chemical Force Microscopy

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The surfaces of polystyrene (PS) films and polystyrene/poly(methyl methacrylate) (PS/PMMA) blend films have been studied using atomic force microscopy with probe tips coated with specific chemical functional groups (chemical force microscopy). PS films have been surface oxidized using an ultraviolet/ozone technique to give substrates with total surface oxygen levels between 0 and 20 atom % measured using XPS. XPS has also been used to study the chemistry of these substrates. AFM tips carrying hydroxyl-terminated (polar) and methyl-terminated (apolar) groups have been produced and used to characterize the statistical effects of oxidation surface chemistry. Scans have been acquired in frictional force mode with the tip moving orthogonal to the long axis of the cantilever. The torsional constant of the AFM cantilever has been used to derive absolute friction values for the systems studied. Increased frictional force is observed when surfaces of increasing polarity (defined by the oxygen level measured by XPS or by the water contact angle) are probed using the hydroxyl-terminated polar tips. Absolute coefficients of friction are shown to be directly proportional to the surface oxygen level and to the water contact angle, and these can therefore be used to approximate changes in polar free energy caused by oxidation. The phase-separated domains of PS and PMMA in blend thin films can be resolved at a submicrometer level using the CFM approach with a polar tip.

1. Introduction

The application of scanning probe microscopy in atomic force mode to materials surface studies can now be regarded as a relatively mature technique. Since its first use in the early 1980s to provide topographical information[1] it has now also been developed to provide local surface information on friction,[2] adhesion,[3] modulus,[4] and thermal[5] properties for a wide variety of materials. In addition, by utilizing the variations in force which result when the probe tip carries different surface chemistries, it is also possible to probe substrate surface chemistry by using tips carrying known functional groups (CFM).[6,7] This approach can be used to provide information about relative surface polarities or, as shown in the work presented here, by calculation of the cantilever torsion, to derive absolute friction and surface free energy data.

Various approaches are currently used to deposit specifically terminated chemical groups and to control AFM tip chemistry. Self-assembled monolayers (SAMs) of a range of organic species such as alkanesilanes and alkanethiols have been widely used to deposit covalently bonded specifically terminated layers.[8] In contrast is the approach used in our present work, first described by Ito et al.,[9] whereby the silicon nitride (Si_3N_4) tip is subjected to a silanolization treatment using ultraviolet/ozone cleaning followed by immersion in sodium hydroxide, then hydrochloric acid, and then sodium hydroxide. This treatment produces hydrophilic tips which can subsequently be made hydrophobic by the adsorption of methyl-terminated alkylsilane.

Initially the use of CFM has been restricted to the identification of the relative chemical properties of idealized surfaces such as those resulting from the SAM approach applied to substrates, i.e., to homogeneous systems of known composition.[6] Studies of chemically and energetically heterogeneous surfaces such as oxidized polymer films are scarce and only now beginning to appear in the literature.[7] However, the development of the technique to include such applications is desirable since it will extend the overall range of information that can be derived using probe microscopy. When polymer surfaces of differing oxidation level, for example, achieved by controlled exposure to a plasma source are dealt with,

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the differing mechanical properties of the surface must also be considered as this may affect the tip contact area. Since the energies of interaction of some organic functional groups are extremely similar (e.g., ref 6), absolute identification of different groups when in juxtaposition (chemical force spectroscopy) is still some way away. Currently, the data which result from CFM lead to a relative polarity being defined by the frictional property of the surface under study. This is an average statistical behavior of the surface expressed as a numerical output of the AFM position-sensitive photodiode. If the torsional response of the tip cantilever and photodiode are known, then an absolute friction can be calculated as we demonstrate in this paper. Where changes in frictional force result from surface chemical modification, the approach that is applied to classical surface free energy models can be employed to understand the surface behavior. In such treatments the total free energy of a solid surface (γ_s^t) is described by the sum of all free energy interactions which apply to a particular surface. The principal ones are dispersion (γ_s^d) or polar (γ_s^p) in nature, giving the general equation proposed by Fowkes:[10]

$$\gamma_s^{\,t} = \gamma_s^{\,d} + \gamma_s^{\,p} \tag{1}$$

This assumes that the polar interaction can be approximated to a geometric mean value for the surface as in the case of the nonspecific dispersion force. By analogy it follows that the total surface polar free energy will result from the combined interactions of all surface polar groups, which possess a permanent dipole; thus, for oxidation

$$\gamma_s^{\,p} = \gamma_s^{\,-OH} + \gamma_s^{\,C=O} + \gamma_s^{\,COOR} \text{ etc.} \tag{2}$$

but the friction-loop method of measurement does not distinguish these group types and presently provides only an average frictional analysis of the surface.

Combination of this approach with contact angle (θ) data for suitable liquids of interfacial free energy (γ_{lv}) as described by Young[11] leads to the Owens and Wendt treatment[12] whereby solution of

$$(1 + \cos\theta)\gamma_{lv} = 2(\gamma_s^{\,d}\gamma_{lv}^{\,d})^{1/2} + 2(\gamma_s^{\,p}\gamma_{lv}^{\,p})^{1/2} \tag{3}$$

allows calculation of the dispersion and polar components of the surface free energy of a solid from contact angle data of polar and nonpolar liquids.

Oxidative modification of surfaces, for example, by plasmas, flames, and corona discharges, is used extensively in modern materials technology. Two typical applications are to enhance adhesion and biocompatibility. Many surface studies have been performed in these areas, and there exists substantial evidence that γ_s^p and consequently the contact angle for polar liquids (e.g., water) change markedly with oxidation level, while γ_s^d remains constant or decreases slightly.[13,14] Where this is the case, there is a direct relationship between substrate surface oxygen level (polarity) or contact angle behavior for a polar liquid and the frictional force measured using a probe tip terminated with a polar end group. Consequently friction will vary directly with surface oxygen level and can be used as a measure of polar free energy.

In this paper we apply chemical force microscopy using hydroxyl (−OH) and methyl ($-CH_3$) terminated probe tips to PS films and report briefly on chemical-based imaging data for PS/PMMA blend films which have been cast from chloroform. We have produced PS film substrates with a range of surface oxygen levels using an ultraviolet/ozone technique previously described.[15,16] We discuss the relative statistical frictional behavior of these systems with reference to the chemical nature of the tip for these chemically heterogeneous surfaces and with reference to the oxygen chemisorption isotherm and functional group content measured using XPS. We also consider the water contact angle behavior of these films. In addition we show that CFM is capable of producing submicrometer spatially resolved information about the chemically distinct PS and PMMA phases in a PS/PMMA blend system.

2. Experimental Section

The surfaces of the PS films (cut from 60 mm cell culture dishes supplied by LP Italiana, Milan) were oxidatively modified using a modular benchtop UV/ozone (UVO) reactor. This contains a high-intensity low-pressure mercury grid lamp with an emission spectrum showing high transmission at 184.9 and 253.7 nm wavelengths. This produces oxygen radicals which combine with molecular oxygen to form ozone and also photosensitizes the polymer surface by carbon bond scission, the overall quantum yield being 0.5.[17] All oxidized surfaces were washed in Milli-Q deionized water for 5 min prior to analysis to remove low molecular weight oxidized material formed by oxidative scission of the PS structure. This material is known to form a “soft” or fluid layer on the polymer surface which is deformable by intrusive AFM, i.e., operation in contact mode with tip loads of >50 nN.

All CFM work was carried out using Digital Instruments Si_3N_4 cantilevers with integrated tips which were functionalized in-house using a method described by Ito et al.[9] Tips were cleaned to remove adsorbed hydrocarbon and water by UVO exposure in the reactor described above for 15 min. This process probably also leads to further oxidation of the native oxide which terminates the Si_3N_4 layer on the tip. Hydroxylation to produce polar tips was carried out by immersing cleaned tips into 0.5 M NaOH for 20 min followed by immersion in 0.1 M HCl for 10 min and finally by immersion in 0.5 M NaOH for a further 10 min. Tips were then washed in Milli-Q deionized water and dried in a vacuum for 10 min at 373 K. The overall process results in silanolization of the tip surface[9,18] and a decrease in the water contact angle (measured for a model surface) from 60° to 25°. Nonpolar tips were produced by adsorbing a methyl-terminated alkylsilane monolayer onto hydroxylated tips by immersing them in 5 mM *n*-dodecyltrichlorosilane ($CH_3(CH_2)_{11}SiCl_3$) dissolved in a 4:1 mixture of hexadecane and chloroform for 3 h. This produces a SAM which is covalently bonded to the Si_3N_4 surface via a

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condensation reaction as a result of hydrolysis at the terminal $SiCl_3$ group.[19,20] These silanated tips were washed in chloroform and then in deionized water to remove unreacted silane and then vacuum-dried at 353 K for immediate use. Tip radii are quoted at 20−60 nm.[21] SEM confirms this and reveals no evidence for shape change or broadening postfunctionalization.

Surface elemental compositions and the chemistry of native and oxidized PS films and PS/PMMA blend films were measured by X-ray photoelectron spectroscopy (XPS) using a KRATOS Axis five-channel spectrometer with monochromated Al Kα radiation (1486.6 eV) at a power of 150 W in a residual vacuum of 10^{-9} Torr. Charge neutralization was employed during all spectrum acquisitions. Composition data were derived from the areas of carbon 1s (C1s) and oxygen 1s (O1s) peaks from survey spectra collected at a pass energy of 80 eV using Kratos relative sensitivity factors (errors in atom percent compositions have been evaluated at ±5% by analysis of standards). Surface chemical data have been obtained by analysis of C1s envelopes measured at a pass energy of 20 eV using Kratos software and also version 1.5 of the Spectral data processor (XPS International).

CFM/AFM was performed on a Digital Instruments Multimode SPM system (Nanoscope IIIa) using a fluid cell. Lateral force imaging was performed simultaneously with topographical imaging in contact mode using 200 mm long V-shaped cantilevers of nominal spring constants 0.06 and 0.12 N/m.[21] The sensitivity of the laser beam detector to vertical and lateral displacement of the tip was calibrated in accordance with the procedure of Liu et al.[22] Lateral (torsional) spring constants (k_l) have been evaluated from the formula proposed by Hazel et al.[23] which gave $k_l/k_n = 1449$ for the 200 mm V-shaped cantilevers with narrow legs. Values for the normal spring constant, k_n, were determined by measuring unloaded resonance frequencies of the cantilevers.[24] Scans were made at a constant rate of 4 μm s^{-1} in the direction orthogonal to the long axis of the cantilever. To allow meaningful intercomparisons of trends, all scans were made with the same tips. Control images were collected in tapping mode to ensure that wear or plastic deformation did not occur during force imaging. Frictional forces were evaluated from the analysis of friction loops measured in scope mode,[25] with the friction at a given load being taken as half the difference between forward and reverse signals. All force imaging was carried out under Milli-Q deionized water to avoid capillary effects of water adsorbed on the substrate surfaces.

3. Results and Discussion

Pure polystyrene contains no oxygen, and the XPS survey scans and high-resolution carbon 1s peak envelopes confirm that the surfaces of the unoxidized PS films used in this study are oxygen free. The survey spectra from the unoxidized PS contain only a single C1s line. The high-resolution C1s peak envelope is a single symmetrical chemical peak at a binding energy of 285 eV which is characteristic of only C−C/C−H bonding. In addition, the C1s envelope also contains a $\pi-\pi^*$ shakeup structure at shifts of 6−8 eV from the main peak due to the interaction of excited electrons with the aromatic segment of the PS prior to emission.

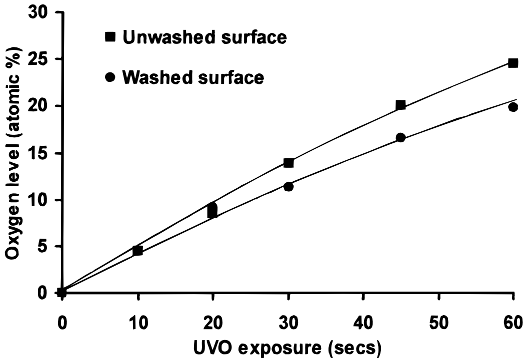

Figure 1. Oxygen chemisorption levels for PS surfaces derived from XPS C1s and O1s peak intensities.

Table 1. Surface Chemical Compositions of Unoxidized and Oxidized PS Derived from XPS C1s Data[a]

	percentages in the C1s envelope (atom %)				
exposure time (s)	C−C/C−H	C−O	C═O	O−C═O	$\pi-\pi^*$
0	92.9	0	0	0	7.1
20	88.1	3.5	2.6	0.7	5.1
40	78.1	5.7	8.3	4.3	3.6
60	69.4	9.3	11.5	6.6	3.2

[a] All oxidized surfaces were washed prior to analysis.

The oxygen chemisorption levels as a function of UVO exposure time have been calculated from oxygen 1s line intensities in the survey spectra and are given in Figure 1. In previous studies we have shown that UVO oxidation leads to PS chain scission and the formation of a low molecular weight oxidized material (LMWOM) which is softer than the unoxidized PS. We have also observed that the intensity of the $\pi-\pi^*$ shakeup structure decreases with oxidation, suggesting some loss of aromaticity also occurs.[26]

For PS the LMWOM can be deformed by contact mode AFM using a standard tip with high loading forces (>100 nN).[26] The oxidized surface is highly likely to have differential mechanical characteristics depending on the oxidation level. The LMWOM can be removed by water washing, leaving a surface which is still oxidized but which is not plastically deformable under normal tip conditions. Figure 1 shows the oxidation levels achieved before and after washing. The washed surfaces were used in the CFM experiments reported here. Overall, an unoxidized surface and three oxidized surfaces with respective oxygen levels of 0, 9, 15, and 20 atom % oxygen have been used in this work.

Analysis of C1s peak envelopes for the oxidized PS surfaces used reveals that the oxidation process proceeds via the formation of hydroxyl/ether, carbonyl, and carboxylic acid/ester species which give rise to chemically shifted peaks which lie 1.5, 3.0, and 4.5 eV from the main hydrocarbon peak. As a detailed XPS analysis of the surface oxidation chemistry of PS has been given elsewhere, for brevity the C1s envelopes are not given here, but the resulting surface's chemical data for the oxidation levels used in this study are shown in Table 1. In this paper we concentrate on frictional force/chemical force behavior in relation to increases in mean surface oxygen levels and therefore polarity. The general trend in oxidation chemistry for the PS materials used

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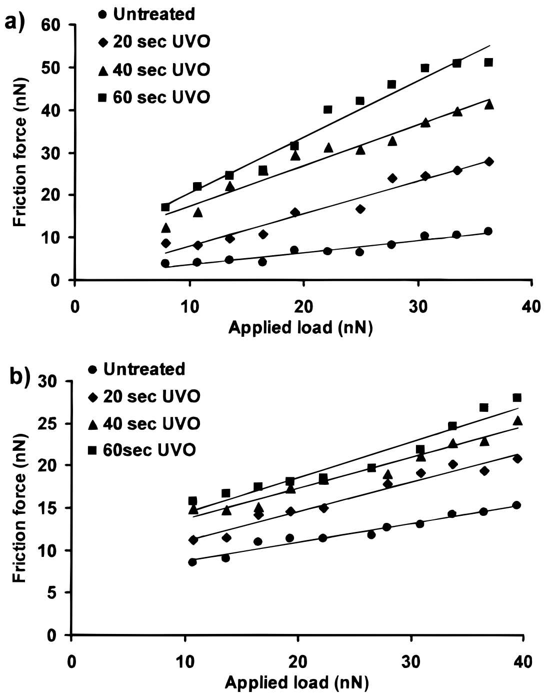

Figure 2. Load−friction data for PS surfaces obtained using (a) hydroxylated (polar) and (b) methylated (apolar) tips.

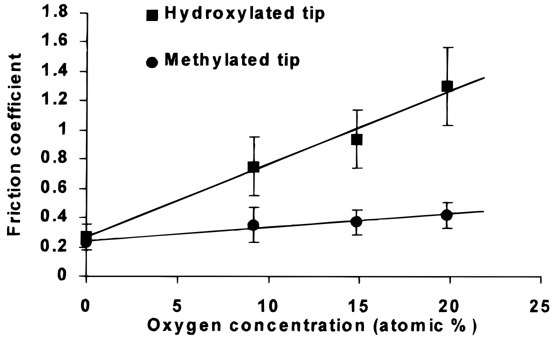

Figure 3. Relationships between friction coefficients (derived from Figure 2) and PS surface oxygen levels.

as substrates (i.e., washed) is that at low oxidation times (<60 s) the formation of oxygen species (C−O−R) and $R_2C{=}O$ is favored, while at higher treatment times more carboxyl (RO−C=O) is produced. We have discussed this process/mechanism in detail elsewhere for a wide range of treatment levels.[26] Since the materials used in this study are only oxidized at low levels and then washed, the dominant oxygen species are C−OR and $R_2C{=}O$.

We have previously reported that probing PS surfaces using CFM with either methyl- or hydroxyl-terminated tips and varying the applied load leads to classical friction−load behavior whereby arbitrary friction, derived solely from the numerical output of the AFM position-sensitive photodiode, increases linearly with load.[7] We have also shown that higher relative friction levels are recorded for the oxidized materials when probed with the hydroxylated (polar) tip.

It is also significant that the data measured with the $-CH_3$-terminated tip are still differentiated according to surface oxygen content. We believe this to result in part from incomplete coverage of the tip by $-CH_3$, resulting in some residual polarity at the probe surface.

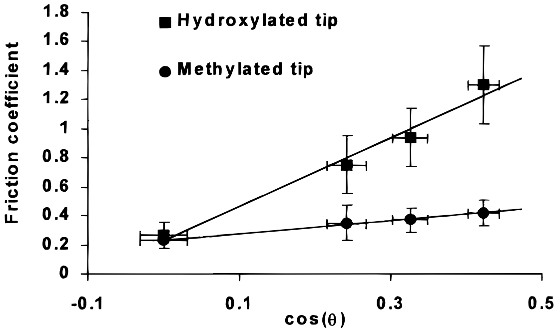

Figure 4. Relationships between friction coefficients and water contact angle (cos θ) for oxidized PS surfaces.

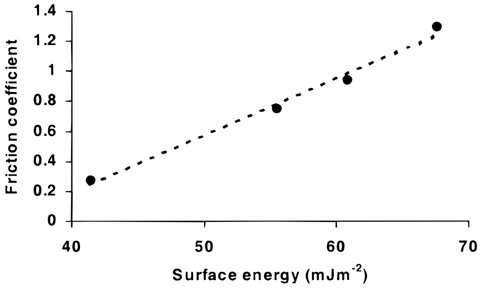

Figure 5. Changes in friction coefficients and development of polar free energy due to surface oxidation of PS. Polar free energy changes derived using eq 3.

In addition, the surface mechanical property changes which result from oxidation may lead to increasing tip−sample contact as a function of oxidation level for a given tip load.

Using the torsional spring constants derived using the method of Hazel et al.,[23] we have now been able to derive absolute friction values for oxidized PS as shown in Figure 2. Variations in the values shown are on the order of 20% and arise due to uncertainties in cantilever normal and torsional spring constants plus FFM calibration. The interaction between the hydroxylated tip and the unoxidized PS gives the lowest friction value (≈4 nN) due to the unlike interaction between the tip which carries predominantly polar groups and the apolar unoxidized PS which is therefore characterized by a strong dispersion (induced dipole−induced dipole) energy. The values derived for the interaction between the methylated tip and unoxidized PS appear to be intermediate (≈9 nN) and are due to dispersion forces, although this effect will not be optimized since the methylation of the tip appears to be incomplete. The values for the hydroxylated tip and the most oxidized surfaces are the highest recorded for this system (≈51 nN) due to the relatively strong polar (dipole−dipole) energy. This is totally consistent with the established theories of intermolecular forces and with previous work involving AFM force−distance-type adhesion measurements for chemically engineered surfaces,[6] although, as far as we know, this is the first reporting from the frictional imaging/CFM approach as applied to a real system. By comparison of this behavior with that reported for other materials systems subjected to surface oxidations and then probed by surface energy techniques (immersion calorimetry and wetting force tests),[13,14,26] it appears that friction, as used in force microscopy, can be understood in a way similar to that of classical free energy. Hence, the total friction mea-

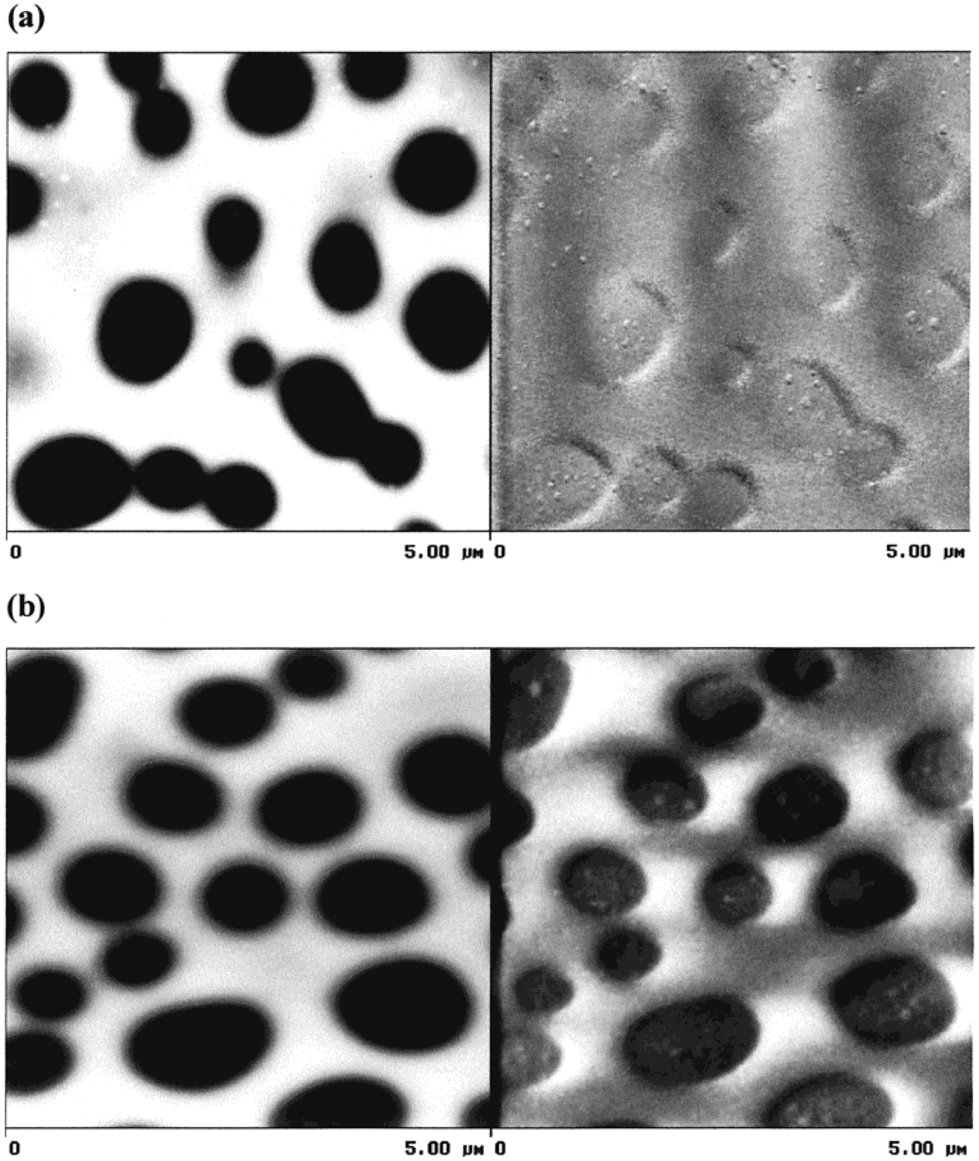

Figure 6. Topographical (left, *z* range 150 nm) and frictional force (right, *z* range 0.2 V) images of the PS/PMMA blend taken with unfunctionalized (a) and hydroxylated (b) tips. Note improved differentiation of polar PMMA continuous phase and apolar PS pits achieved using the CFM approach.

sured will result from both a nonpolar (dispersion) interaction and a chemical (polar) interaction between the probe tip and surface, the total friction (F_t) will be given by

$$F_t = L(f^d + f^p) \tag{4}$$

where f^d and f^p refer, respectively, to the dispersion and polar contributions to total friction, and the proportionality between the two force types will depend on the precise surface chemistry of both the tip and substrate. In the present work an increase in friction due to the increased polarity of the substrate is observed.

By taking into account the dual (i.e., polar and dispersion) interactivity of both the tip and substrate, the total friction will be given by an equation of form similar to that of eq 3

$$F_t = L[2(f_s^d f_t^d)^{1/2} + 2(f_s^p f_t^p)^{1/2}] \tag{5}$$

where again F_t is the total friction experienced by the probe tip, f^d and f^p refer to the dispersion and polar contributions to total friction, the subscripts s and t denote the substrate and tip, respectively, and L is the applied tip loading. If the dispersion contributions change little over moderate levels of oxidation, then the major increase in friction is due to polar chemical interactions.

We have observed that the hydroxylated tip allows identification of the oxidized surfaces via the characteristic friction values which are highest for the most oxidized surfaces and show a greater change with applied load than those obtained using the methylated tip. Friction coefficients (μ) for this system have been derived by linear least-squares analysis of the data given in Figure 2. Their change with surface oxidation is most marked for the hydroxylated (polar) tip chemistry as shown in Figure 3 (errors shown arise from the standard deviations of three data sets). The small increase in μ observed with the methylated tip we think to be due to residual polarity on this tip caused by incomplete coverage of the $Si_3N_4/Si(OH)_4$ terminating layer of the Si_3N_4 tip and/or some increase in tip−sample contact area due to sample surface "softening" with oxidation. In previous surface oxidation−surface energy studies using heat of immersion calorimetry,[13] we have observed a slight decrease in dispersion free energy with increasing surface oxidation as would be expected if the gross dispersion and polar interactivity between any probe and substrate are mutually exclusive on a geometric mean area basis. Thus, this slight positive slope observed in Figure 3 for the friction data recorded with the methylated tip is an artifact of our measurement, and the true chemical effect is represented by the differential between the two sets of data. In future work we shall be studying the relative contributions to the energy of interaction for film coatings of varied compositions.

It follows directly from the behavior observed in Figure 3 that μ values measured using a polar tip will vary in a similar way when plotted against any sufficiently sensitive probe of surface polarity. Hence, the measurement of water contact angle data for the four PS surfaces leads to Figure 4. Since the surface free energy of PS is known to be 42.0 mJ/m^2 [27] ($\gamma_s^d = 41.4$ mJ/m^2 and $\gamma_s^p = 0.6$ mJ/m^2 at 293 K), from eq 3 we can calculate the differential values of γ_s^p for the PS due to oxidation as shown in Figure 5, and to a first-order approximation the surface energy of the system can be obtained from CFM friction data. Using the approach which leads to eq 4, and assuming that the frictional forces are proportionally equivalent to, but numerically different from, polar free energy obtained from water contact angle data (mJ/m^2), a shift from a 99% dispersion force based friction, for unoxidized PS, to a mixed interaction of, respectively, 26%, 33%, and 39% of the frictional force due to polar interaction is observed as oxidation increases. Use of eq 5 to give a more detailed analysis of the relative tip−substrate contributions to both friction types is presently precluded due to lack of knowledge about the relative dispersion/polar interactivities of the tip coatings.

Functionalized tips have also been used to produce topographical (contact mode) and frictional force images of PS/PMMA blends. The blend films cast from chloroform were annealed at 145 °C in a vacuum oven for 3 h to promote phase separation of the two polymers. In this situation the difference in friction between nonpolar PS and the polar PMMA has been used to distinguish the separated phases of these materials as shown in Figure 6. This distinction cannot be made using a normal (unfunctionalized) tip or the methylated tip since the frictional difference between the two phases is not great enough. The effect observed in Figure 6b is therefore chemical in nature and due to the increase in f_t^p brought about by tip oxidation.

4. Conclusions

CFM using either hydroxyl (polar) or methyl (nonpolar) terminated Si_3N_4 tips has been used to distinguish the frictional behavior of a PS surface containing oxygen levels between 0 and 20 atom %. Absolute friction values have been derived by calibration of the torsional response of the cantilever to friction and the resulting signal output of the photodiode. Data for both tip types show classical mechanical behavior in terms of tip loading as previously reported. The friction values derived from the polar tip are greater than those of the CH_3 tip for oxidized surfaces. A linear increase in the coefficient of friction against surface oxygen level and water contact angle is observed at ambient temperature. By using simple thermodynamic relationships between surface polarity and wetting by a polar liquid, frictional measurements can be used to derive polar free energy data. Friction imaging using chemically functionalized tips allows the polar and nonpolar phases of PS/PMMA blends to be distinguished with submicrometer resolution. Frictional force is determined by chemical and physical surface properties. Since surface treatments, such as UVO, can result in modification of both of these properties, the use of chemically different probes, which allows isolation and characterization of specific surface changes, has great potential.

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