Mapping the Surface Heterogeneity of a Polymer Blend: An Adhesion-Force-Distribution Study Using the Atomic Force Microscope

Peter J. Eaton, Paul Graham, James R. Smith, John D. Smart, Thomas G. Nevell, and John Tsibouklis*

School of Pharmacy and Biomedical Sciences, University of Portsmouth, St. Michael's Building, White Swan Road, Portsmouth PO1 2DT, U.K.

Adhesion force mapping using atomic force microscopy has been used to investigate a phase-separated blend of poly(methyl methacrylate) (PMMA) and poly(dodecyl methacrylate) (PDDMA). Comparison of the results from the blend with those from the pure constituent polymers showed that force mapping could identify PMMA- and PDDMA-rich areas in the blend. The adhesion maps produced were deconvoluted from sample topography and contrasted with data obtained from contact angle goniometry.

Introduction

The most promising aspect of the measurement of adhesion forces using the atomic force microscope (AFM) is its capability for sampling small areas of a substrate; the limiting parameter for resolution is the radius of the AFM tip, which is normally in the range 10−20 nm. Furthermore, the combination of the high spatial resolution of AFM coupled with its scanning capability affords a great potential for mapping adhesion forces across a surface.[1]

Kawai et al.[2,3] measured the adhesion forces between a standard, silicon nitride tip and several inorganic materials. In each case, the "jump-to-contact" adhesive force, experienced as the cantilever approaches the surface, and the "pull-off" force, which is the force required to detach the tip from the surface, were determined. The latter forces were found to be much greater.[4] Furthermore, a nonlinear correlation was observed between the "pull-off" adhesion force and surface energy.[5] In an attempt to quantify the relationship between adhesion as measured by AFM, and surface energy, the researchers calculated the surface energies of a series of polymers using the Derjaguin model of a sphere in contact with a flat surface. The calculated surface energy values correlated well with the surface energies measured conventionally by contact angle goniometry. Nonetheless, two methodology limitations were highlighted: the need to use an estimate of the interfacial surface energy and the uncertainty associated with the measurement of the AFM-tip radius.[2,3,6]

In an attempt to construct maps of force curves, Capella et al.[7] examined a sample consisting of fluorescein-isothiocyanate patterns on a silicon substrate. The data, which were presented as "force slices", i.e., a map of the

deflection of the cantilever at set distances into the force curve, were qualitative in that they contained information about the spatial distribution of adhesion, but this property was not deconvoluted from sample topography.[8]

In an effort to construct adhesion maps, patterned monolayers of hydrocarbon, stearic acid, stearyl alcohol, and stearylamine were attached covalently onto a silicon substrate and, using standard silicon nitride tips, relative adhesion was quantified by considering the magnitude of the measured force at the lowest part of the force curve associated with each type of molecule.[9]

Recently, and as part of our work on the synthesis and characterization of novel materials with ultralow surface energy characteristics,[10−13] we examined the relationship between surface roughness, molecular organization, and surface wettability as determined by contact angle goniometry.[12] Our findings have demonstrated that if experimental determinations of surface free energy are to be interpreted with confidence, it is vitally important that the experiments are performed on relatively smooth surfaces (R_a < 10 nm) in which surface heterogeneity is understood down to the sub-micrometer level. Previous attempts to utilize AFM as a means of determining surface heterogeneity have explored the techniques of phase imaging[14] and chemical force microscopy.[15] To further attest the potential of the AFM as a means of quantifying surface heterogeneity, we now apply the technique of adhesion force mapping to a phase-separated blend of poly-(methyl methacrylate) (PMMA) and poly(dodecyl methacrylate) (PDDMA).

Experimental Section

The monomer, dodecyl methacrylate (DDMA), was synthesized by adding dodecan-1-ol (0.01 mol) to a stirred solution of

---

* To whom correspondence should be addressed.

(1) Radmacher, M.; Cleveland, J. P.; Fritz, M.; Hansma, H. G.; Hansma, P. K. *Biophys. J.* **1994**, *66*, 2159.

(2) Kawai, A.; Nagata, H.; Morimoto, H. *Surf. Modif. Technol. VII* **1994**, 343.

(3) Kawai, A.; Nagata, H.; Takata, M. *Jpn. J. Appl. Phys.* **1992**, *4*, 997.

(4) Burnham, N. A.; Colton, R. J.; Pollock, H. M. *Nanotechnology* **1993**, *4*, 64.

(5) Good, R. J. *J. Adhes. Sci. Technol.* **1992**, *6* (12), 1269.

(6) Nie, H. Y.; Walzak, M. J.; Berno, B.; McIntyre, N. S. *Langmuir* **1999**, *15* (19), 6484.

(7) Capella, B.; Baschieri, P.; Frediani, C.; Miccoli, P.; Ascoli, C. *Nanotechnology* **1997**, *8*, 82.

(8) Capella, B.; Dietler, G. *Surf. Sci. Rep.* **1999**, *34*, 1.

(9) Ishino, T.; Hieda, H.; Tanaka, K.; Gemma, N. *J. Electroanal. Chem.* **1997**, *438*, 225.

(10) Stone, M.; Nevell, T. G.; Tsibouklis, J. *Mater. Lett.* **1998**, *37* (1-2), 102.

(11) Thorpe, A. A.; Young, S. A.; Nevell, T. G.; Tsibouklis, J. *Appl. Surf. Sci.* **1998**, *136* (1-2), 99; **1999**, *137* (1-4), 1.

(12) Tsibouklis, J.; Stone, M.; Thorpe, A. A.; Graham, P.; Ewen, R. J.; Nevell, T. G. *Langmuir* **1999**, *15* (20), 7076.

(13) Pullin, R. A.; Nevell, T. G.; Tsibouklis, J. *Mater. Lett.* **1999**, *39* (3), 142.

(14) McMaster, T. J.; Hobbs, J. K.; Barham, P. J.; Miles, M. J. *Probe Microsc.* **1997**, *1*, 43.

(15) Noy, A.; Vezenov, D. V.; Lieber, C. M. *Annu. Rev. Mater. Sci.* **1997**, *27*, 381.

Table 1. Advancing Contact Angles and Receding Contact Angles (in Parentheses) for Water, Diiodomethane (DIM), and Ethylene Glycol (EG) on Pure PMMA, PDDMA, and a Blend of the Two Polymers Coated onto Glass

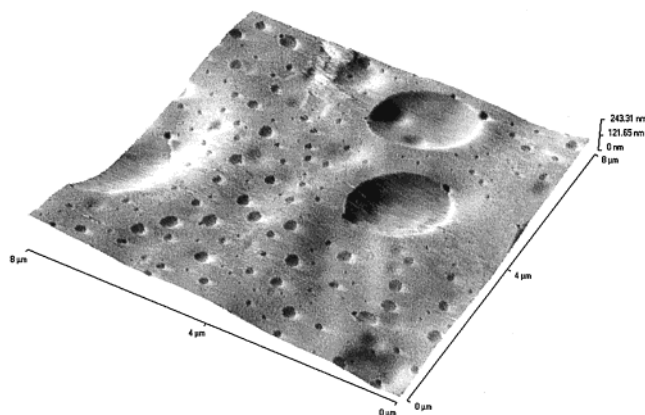|	contact angle, θ/deg		
material	H_2O	DIM	EG
PMMA	71	46	51
PDDMA	106 (65)	96 (20)	96 (40)
PMMA/PDDMA	118 (56)	85 (14)	109 (27)

Figure 1. Contact-mode topographic image of a typical PMMA/PDDMA blend surface.

methacryloyl chloride (0.015 mol) in sodium-dried diethyl ether (50 cm³). Stirring was continued for 24 h, after which time the monomer was purified by column chromatography (silica gel, 4:1 v/v 60−80 °C petroleum ether/diethyl ether). Polymerization was carried out in the bulk (60 °C, nitrogen atmosphere) using freshly recrystallized azobisisobutyronitrile (1% w/w) as the initiator; poly(dodecyl methacrylate), PDDMA, was obtained as an amorphous mass and purified by repeated washings with acetone.

Polymer blend films were produced by dip-coating glass slides (8 mm × 8 mm × 1 mm) into a stirred solution of PDDMA and poly(methyl methacrylate), PMMA, obtained from Goodfellow (Cambridge, U.K.) (1:1 PMMA:PDDMA; 2.5% w/w in chloroform). Prior to AFM investigations, all films were rinsed with ethanol (AnalaR, BDH). Both topography and force measurements were performed using a TopoMetrix TMX2000 Discoverer Scanning Probe Microscope (ThemoMicroscopes, Bicester, U.K.). "V"-shaped, silicon nitride cantilevers of length 200 µm and nominal spring constant (K) 0.032 N m⁻¹, bearing an integrated standard profile tip (part no. 1520-00; ThermoMicroscopes, Santa Clara, CA) were used. Since the actual spring constant of an individual commercial cantilever may differ by up to an order of magnitude from the nominal value, K was determined for the cantilever used in this study, as described elsewhere.[16] To avoid inconsistencies due to variation in tip radii, the same tip was used for all force measurements reported in this paper. Topographic imaging was performed in contact mode, both in air under ambient conditions and in water using a wet cell. Layered imaging was used to obtain force−distance curves over an entire image frame of 8 µm × 8 µm at a resolution of 40 × 40 pixels (1600 force curves) and a scan rate of 1 µm s⁻¹: in this type of imaging each pixel encodes the measured force between the tip and the substrate, effectively, a "slice" through the force−distance curve.[17,18] For each layered image acquired, a corresponding topographic image of identical resolution and spatial orientation was also obtained. Layered images were obtained under ambient conditions.

(16) Cleveland, J. P.; Manne, S.; Bocek, D.; Hansma, P. K. *Rev. Sci. Instrum.* **1993**, *64* (2), 403.

(17) Abbis, T.; Collins, G. *R&D Mag.* **1995**, *37* (9), 57.

(18) Penegar, I.; Toque, C.; Connell, S. D. A.; Smith, J. R.; Campbell, S. A. *Proceedings of the 10th International Congress on Marine Corrosion and Fouling*, Vol. 2, Melbourne, Australia, 8−11th Feb, 1999.
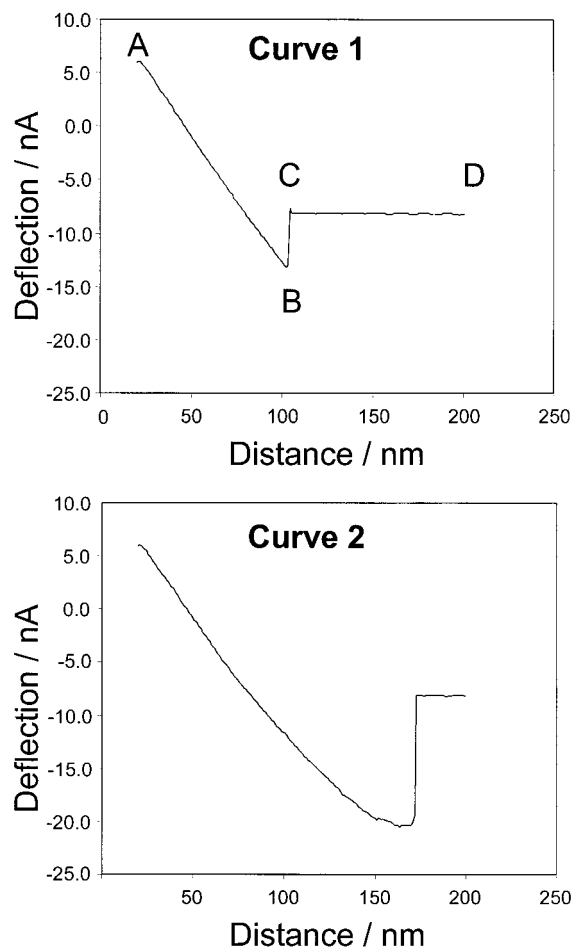

Figure 2. Typical force curves extracted from the layered image data measured on the PMMA/PDDMA blend. Curves 1 and 2 show responses obtained from a "pit" and a raised portion on the surface, respectively. The adhesion was calculated as follows: the pull-off point (B) was obtained from a first-order derivative plot of the adhesion data. This method was used in preference to direct measurement at the lowest point on the curve since it allowed the algorithm to extrapolate measurements beyond the range of the detector (−32 nA) for very large adhesion forces. A straight-line fit was performed on the deflection data between points A and B. Since the sample is infinitely stiff with respect to the cantilever, the gradient between points A and B corresponds to the sensor response (nA/nm). The force of adhesion (nN) was then calculated by the difference between the deflections at points B and C divided by the sensor response and multiplied by the measured spring constant, K (N m⁻¹).

The layered images, as measured, show a combination of topography and adhesion. An adhesion data extraction algorithm, coded in Visual Basic, was written to deconvolute the topography from the force data: This routine operated by locating the position of the "pull-off" region and calculating the adhesion force from the measured values of cantilever deflection, sensor response, and the spring constant. The program then allowed the adhesion force values acquired over the entire 40 × 40 pixel image frame to be plotted as a gray-scale image. Force maps obtained from this method are similar to those reported on the basis of pulsed-force AFM work.[19]

The surface free energies of polymer samples were determined by contact angle goniometry in an enclosed, thermostated cell using a Kruss G10 goniometer interfaced to image capture software. For both advancing (θ_A) and receding (θ_R) contact angle experiments, measurements of droplets (2−10 µL) were recorded at 25 ± 1 °C using doubly distilled water (surface tension γ_L =

(19) Marti, O.; Stifter, T.; Waschipky, H.; Quitus, M.; Hild, S. *Colloids Surf., A: Physicochem. Eng. Aspects* **1999**, *154*, 65.
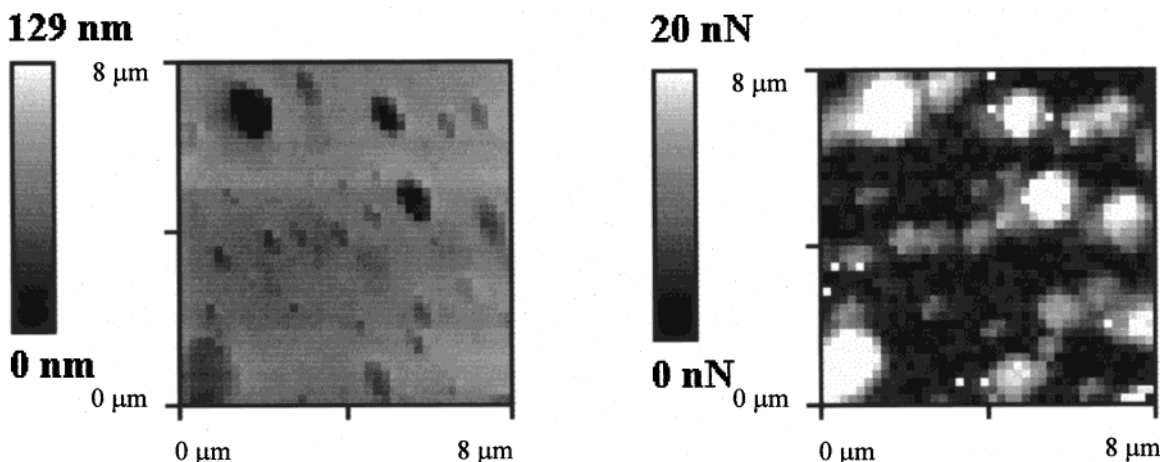
Figure 3. Topography (left) and adhesion (right) images of a typical PMMA/PDDMA blend surface. Both images are reflective of the same area.

73.4 mN m^{-1} at 18.75 °C, lit.[20,21] = 73.05 mN m^{-1} at 18 °C), diiodomethane (>99%; γ_L = 48.7 mN m^{-1} at 18.8 °C, lit.[20,21] = 50.76 mN m^{-1} at 20 °C) and 1,1-ethanediol (ethylene glycol, >99%; γ_L = 47.7 mN m^{-1} at 18.8 °C, lit.[20,21] = 48.40 mN m^{-1} at 20 °C). In the case of receding contact angle experiments, a drop of the probing liquid (8−10 μL) was placed on the surface of the sample and subsequently removed in small increments (0.5 μL) until the drop edge spontaneously contracted to a new stationary position at which the receding contact angle was measured. Hysteresis (*H*) was recorded as ($\theta_A - \theta_R$). Surface energies were evaluated using the surface-tension-component theory, as described elsewhere.[22,23]

Results and Discussion

The contact angle data, Table 1, associated with PMMA films yield a time-independent, total-surface-energy value of 38 mJ m^{-2}; very little contact angle hysteresis (<4°) was observed for such samples, confirming the mechanical smoothness and chemical homogeneity of the film.[12] By contrast, films of pure PDDMA and of the PMMA/PDDMA blend exhibited very large hysteresis values. Since the surface roughness of PDDMA was found to be in excess of 100 nm (R_a), this feature is considered to be mainly, if not entirely, responsible for the observed differences between advancing and receding contact angles. In the case of the blend, it is the combined effect of surface roughness and heterogeneity that is considered responsible for the observed hysteresis but the methodology does not allow the quantification of the relative contribution of these variables. The large values of *H* obtained for PDDMA and PMMA/PDDMA films render this data set unsuitable for the evaluation of their surface energies and highlight the need for the development of alternative methodology, which can be applied meaningfully to the quantification of the surface energy of relatively rough and/or heterogeneous samples. It is worth noting that evaluation of the total surface energy of PDDMA films (surface roughness: $R_a \gg 100$ nm) using advancing contact angle data yields a value of 11 mJ m^{-2} whereas the use of the receding contact angle values determines the same parameter at 48 mJ m^{-2}; for comparison, the same

methodology evaluates the surface energy of poly(tetrafluoroethylene), Teflon, at 21 mJ m^{-2} and that of polyethylene at 30 mJ m^{-2}.[12]

The topography of a typical polymer blend sample, Figure 1, is characterized by a raised surface that is punctuated by irregular pits. The dimensions of the latter features were quite variable, but normally 50−200 nm in depth, and with diameters of up to 5 μm. Considering previous literature reports on the topography of polymer blends,[24−27] a reasonable hypothesis would be that the pits contain one of the constituent polymers with the raised portion containing the other. However, topographic methods do not allow the identification of the polymer associated with each feature. Thus, a combination of adhesion mapping and topographic imaging has been assessed as a means of addressing this issue. Figure 2 shows typical force curves obtained from a pit and a raised region on the polymer blend surface. The pull-off force measured on the pit (curve 2) is significantly greater than that associated with the raised surface (curve 1).

Comparison of the topographic image with the adhesion map presented in Figure 3 confirms the direct relationship between the topographic features and the relative force of adhesion associated with each domain; the pits in the topography image correspond to areas of high adhesion. In parallel, films of pure PMMA and pure PDDMA were prepared in a manner identical to that employed for the fabrication of polymer-blend structures, and force measurements were performed across each film. Histograms of adhesion values obtained for film samples of PMMA and PDDMA are presented in Figure 4, along with those obtained from the layered image displayed in Figure 3; the scatter associated with each set of data may be attributed to local-level molecular organization phenomena, crystallinity, and surface roughness effects.[12,28] The data presented in Figure 4 further demonstrate that the average force of adhesion to PDDMA is much higher than that to PMMA, suggesting that the regions of high adhesion (Figure 3, right) or the "pits" in the topographic image (Figure 3, left) are those of a PDDMA-rich domain. Nonetheless, the value of the adhesive force measured in

(20) Kaye, G. W. C., Laby, T. H., Eds. *Table of Physical and Chemical Constants*, 15th ed.; Longman Scientific and Technical: Harlow, 1992.

(21) Lide, D. R. Ed. *Handbook of Chemistry and Physics*, 76th ed.; CRC Press: 1995.

(22) Good, R. G.; van Oss, C. J. In *Modern Approached to Wettability: Theory and Applications*; Schrader, M. E., Loeb, G., Eds.; Plenum Press: New York, 1991; pp 1−27.

(23) Good, R. G.; Chaudhury, M. K.; van Oss, C. J. In *Fundamentals of Adhesion*; Lee, L. H. Ed.; Plenum Press: New York, 1991; pp 153−172.

(24) Walheim, S.; Böltau, M.; Mlynek, Krausch, G.; Steiner, U. *Macromolecules* **1997**, *30*, 4995.

(25) Walheim, S.; Ramstein, M.; Steiner, U. *Langmuir* **1999**, *15*, 4828.

(26) Stocker, W.; Beckmann, J.; Stadler, R.; Rabe, J. P. *Macromolecules* **1996**, *29*, 7502.

(27) Zhu, S.; Liu, Y., Rafailovich, M. H.; Sokolov, J.; Gersappe, D.; Winesett, D. A.; Ade, H. *Nature* **1999**, *400*, 49.

(28) Glennon, D.; Smith, J. R.; Cox, P. A.; Ewen, R.; Nevell, R. T.; Nevell, T. G.; Tsibouklis, J. *J. Mater. Sci.* **1998**, *33*, 3511.
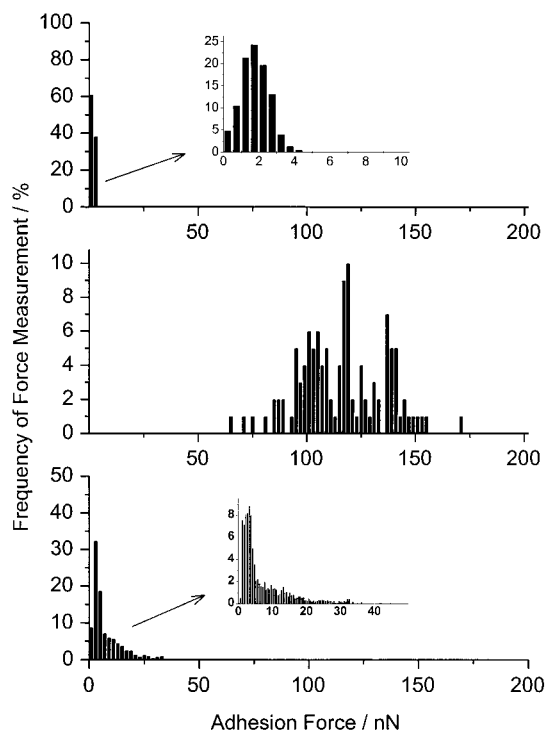
Figure 4. Histogram showing the adhesion forces measured on pure PMMA (top), pure PDDMA (middle), and a 50:50 PMMA/PDDMA blend (bottom). The bars correspond to a force interval of 2 nN in the main picture and 0.5 nN intervals in the inset.

the pits of the structure was lower than that determined for films of pure PDDMA, suggesting either that the polymers are intimately mixed in these areas or that the domains of each polymer are smaller than those apparent from the image. In an effort to assess the resolution limits of the experiment, a higher resolution ($1 \times 1 \ \mu m^2$ scan range) topographic image was obtained but, again, no evidence for the existence of a sub-micrometer-level domain structure could be identified.

Previous AFM work by Mizes et al.[29] has shown that certain topographic features, such as scratches, can lead to increased adhesion values because of the extended area

(29) Mizes, H. A.; Loh, K.-G.; Miller, R. J. D.; Ahuja, S. K.; Grabowski, E. F. *Appl. Phys. Lett.* **1991**, *59*, 2901.

of interaction between the tip and the probed surface. This effect has been shown[29] to become particularly pronounced if the size of the topographic feature approximates that of the tip radius. Thus, differences in surface energy may not be solely responsible for the greater mean force of adhesion measured on films of PDDMA, relative to that determined for PMMA structures, as the former were found to be considerably rougher (R_a: PDDMA $\gg 100$ nm; PMMA $= 4.7$ nm). A further complication, highlighted by Marti et al.[19] who considered polymers below and above their glass transition temperatures, is that increased polymer chain mobility leads to a corresponding increase in AFM-measured forces of adhesion. Since chain mobility is a variable parameter, influenced by chemical structure and temperature of the experiment, its effects would need to be quantified before AFM adhesion measurements could be interpreted with confidence. Nonetheless, the observed differences in force of adhesion are expected to be largely reflective of the relative surface energies associated with the two types of film structure, PDDMA and PMMA. Indeed, for these relatively rough surfaces, pull-off force measurements appear to provide a more powerful means of assessing surface energy than contact angle goniometry.

For this preliminary study, the components of the polymeric blend were selected on the basis of the very large differences in adhesion force recorded with the AFM cantilever; work in progress is attempting to establish the sensitivity, and limitations, of the technique by considering a broader range of homologous polymeric materials.

Conclusions

Topographic imaging and adhesion mapping have been combined to examine the surface heterogeneity in a poly-(methyl methacrylate)/poly(dodecyl methacrylate) blended film structure. In contrast to contact angle goniometry, the technique has been shown to be a suitable probe for the assessment of micrometer-level heterogeneity. Nonetheless, further refinements are required before the method could be applied to the quantification of surface energy.