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Silent Discharge Treatment of Immiscible Polystyrene/ Polycarbonate Polymer Blend Surfaces

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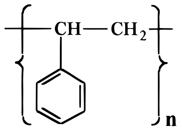
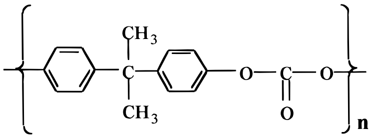
ABSTRACT: Atmospheric dielectric barrier (silent) discharge modification of polystyrene/polycarbonate immiscible polymer blend surfaces has been studied by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). Localized variations in the level of treatment across the surface are evident which can be correlated to the spatial distribution of the respective blend constituents. Subsequent washing of low molecular weight oxidized material from the treated surfaces leaves behind well-defined terraces/wells whose size can be tailored by changing the original polymer blend composition.

Introduction

Many different types of immiscible polymer blend are used in industry.[1] In such systems, phase separation occurs within the bulk of the blends, whilst the surface can be enriched by one of the constituent polymers. The major analytical techniques used in the past to study surface phase morphology of immiscible polymer blends have been optical[2] and electron microscopies.[2−6] The former suffers from poor resolution and the need for a large refractive index difference between the phases of the polymer blend in order to allow phase contrast, whilst the latter technique requires selective etching[3,4] or staining[5,6] which can lead to the introduction of artifacts.[7] More recently, it has been demonstrated that atomic force microscopy (AFM)[8] can be used to investigate the morphology of polymer blends without the prerequisite for any special sample preparation.[9−11] The atomic force microscope works by scanning a very sharp tip across a sample surface and measuring the forces of interaction between the tip and the substrate.[12] AFM itself is insenstive to changes in surface composition; however, variations of this technique can be used to determine the phase morphology, e.g. frictional force microscopy (FFM),[13] force modulation AFM,[14] chemical sensing AFM,[15] and phase modulation AFM.[16]

Quite often polymer blend surfaces require plasma activation prior to bonding.[17] In this article, we use XPS and AFM to study the surfaces of immiscible polystyrene/ polycarbonate blend mixtures before and after atmospheric silent discharge treatment. XPS is used to track the variation in surface chemical composition, whilst phase modulation AFM has assisted with the identification of the respective constituent phases.


Polystyrene (PS)


Bisphenol-A Polycarbonate (PC)

Experimental Section

Thin films of polystyrene (Aldrich, $M_w = 280\,000$)/bisphenol polycarbonate (General Electric, $M_w = 40\,000$) blends were prepared by spin coating from a 5% w/v chloroform solution onto glass slides. Blend compositions are given as bulk weight percent. Immiscible blends generally tend to be cloudy due to the presence of phase boundaries which scatter light;[18] however, the polystyrene/polycarbonate blend mixtures were almost transparent in appearance because of the constituent polymers having similar refractive indices.[19]

Atmospheric silent discharge air plasma treatments were carried out for a duration of 120 s using a home-built parallel plate dielectric barrier discharge reactor[20] operating at 3 kHz and 11 kV, with an electrode gap of 3.00 ± 0.05 mm. Subsequent washing experiments of the treated polymer blend films were carried out using a 50/50 isopropyl alcohol/cyclohexane polar/nonpolar solvent mixture (neither polystyrene nor polycarbonate is soluble in either of these solvents at room temperature[21]).

A Kratos ES300 electron spectrometer equipped with a Mg Kα X-ray source (1253.6 eV) and a concentric hemispherical analyzer was used for XPS surface analysis of the polymer blend surfaces prior to and following plasma treatment. Photoemitted electrons were collected at a take-off angle of 30° from the substrate normal, with electron detection in the fixed retard ratio (FRR, 22:1) mode. XPS spectra were accumulated on an interfaced IBM PC computer. Instrumentally determined sensitivity factors for a unit stoichiometry of C(1s):O(1s) were taken as equaling 1.00:0.62.

A Digital Instruments Nanoscope III atomic force microscope was used to examine the topographical nature of the polymer blend surfaces before and immediately after electrical discharge exposure. All of the AFM images were acquired in air and are presented as unfiltered data. Topographical analysis comprised a combination of tapping mode AFM and phase modulation AFM. Tapping mode AFM employs a stiff silicon cantilever oscillating at a large amplitude near its resonance frequency (several hundred kilohertz). A large root mean square amplitude is used to overcome the capillary attraction of the surface layer, whilst the high oscillation frequency allows the cantilever to strike the surface many times before being displaced laterally by one tip diameter. These features offer the advantage of low contact forces and negligible shear forces. Phase modulation AFM is a variation of tapping mode AFM, where the phase of oscillation is measured with respect to the piezoelectric driver.[16] The phase shift is very sensitive to variations in substrate properties (e.g. adhesion, viscoelasticity, etc.), and therefore regions of different chemical composition can be identified.

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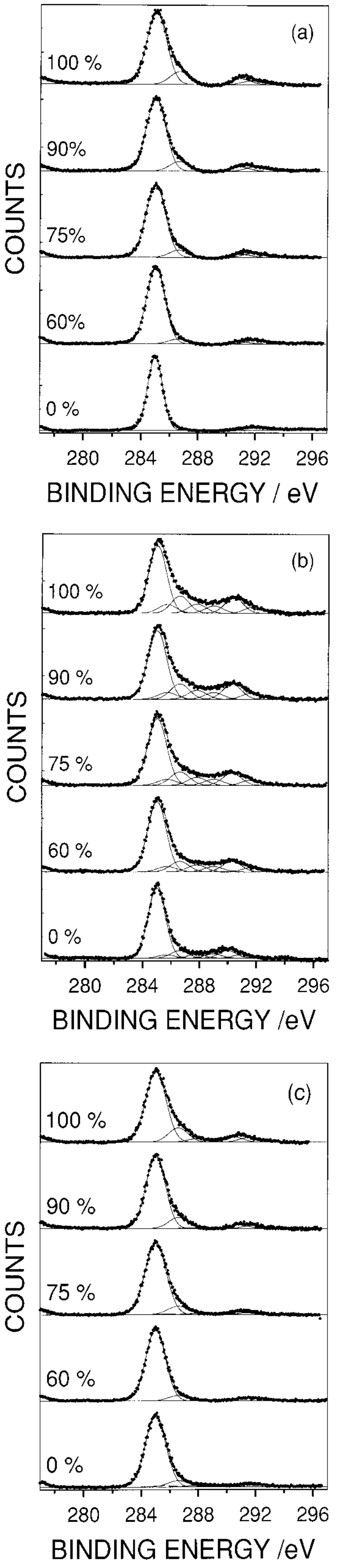


Figure 1. C(1s) peak fitted spectra of polystyrene/polycarbonate blend surfaces as a function of polycarbonate loading: (a) untreated; (b) silent discharge treated; (c) silent discharge treated followed by solvent washing.

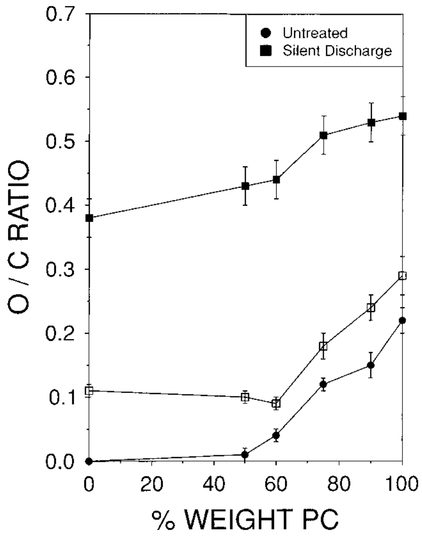
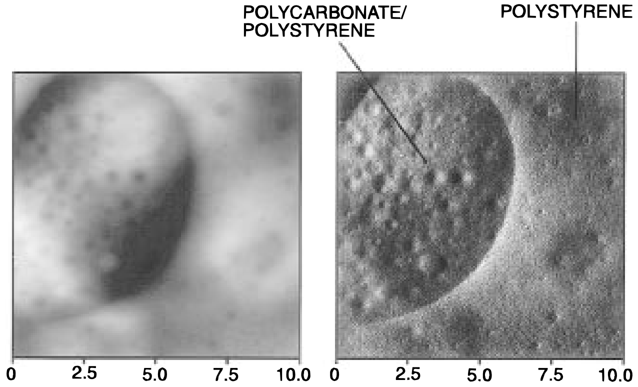


Figure 2. Variation in the O:C ratios for the polystyrene/polycarbonate blend surfaces: untreated; silent discharge treated; silent discharge treated followed by solvent washing (unshaded squares).



(a) TAPPING MODE
Z Range = 100 nm

(b) PHASE IMAGE

Figure 3. 10 μm AFM images of a 60/40 PC/PS blend surface: (a) tapping mode (the degree of shading is a measure of height); (b) phase modulation mode (the degree of shading is respresentative of different phases).

Results

(a) X-ray Photoelectron Spectroscopy. XPS wide-scan spectra were taken to check for the absence of any surface-active inorganic additives. The C(1s) XPS core level spectra were fitted with Gaussian peaks of equal full-width-at-half-maximum (fwhm),[22] using a Marquardt minimization computer program. Binding energies characteristic of different types of carbon moieties were referenced to the hydrocarbon peak ($\underline{C}_x\mathrm{H}_y$) at 285.0 eV:[23] carbon adjacent to a carboxylate group ($>\underline{C}-\mathrm{CO}_2$) at 285.7 eV, carbon singly bonded to one oxygen atom ($>\underline{C}-\mathrm{O}$) at 286.6 eV, carbon doubly bonded to one oxygen atom or carbon singly bonded to two oxygen atoms ($>\underline{C}=\mathrm{O}/\mathrm{O}-\underline{C}-\mathrm{O}$) at 287.9 eV, carboxylate groups ($\mathrm{O}-\underline{C}=\mathrm{O}$) at 289.0 eV, and carbonate carbons ($\mathrm{O}-\underline{C}\mathrm{O}-\mathrm{O}$) at 290.4 eV. The C(1s) envelope for untreated polystyrene can be assigned to a hydrocarbon component, $\underline{C}_x\mathrm{H}_y$ at 285.0 eV, and a $\pi-\pi^*$ shake-up satellite feature at 291.7 ± 0.1 eV (with a different fwhm), which accounts for approximately 5.3 ± 0.2% of the total C(1s) peak area[24] (Figure 1). The experimentally measured O/C ratio for polycarbonate was found to be 0.21 ± 0.02, which is consistent with the theoretically expected value of 0.19; $\underline{C}_x\mathrm{H}_y$ (285.0 eV), $\underline{C}-\mathrm{O}$ (286.6 eV), and $\mathrm{O}-\underline{C}\mathrm{O}-\mathrm{O}$ (290.4 eV) environments were evident in the C(1s) region together with a $\pi-\pi^*$ shake-up satellite at 291.8 eV.

The variation in the measured O/C ratio with polymer blend composition was found to be nonlinear (Figure 2).

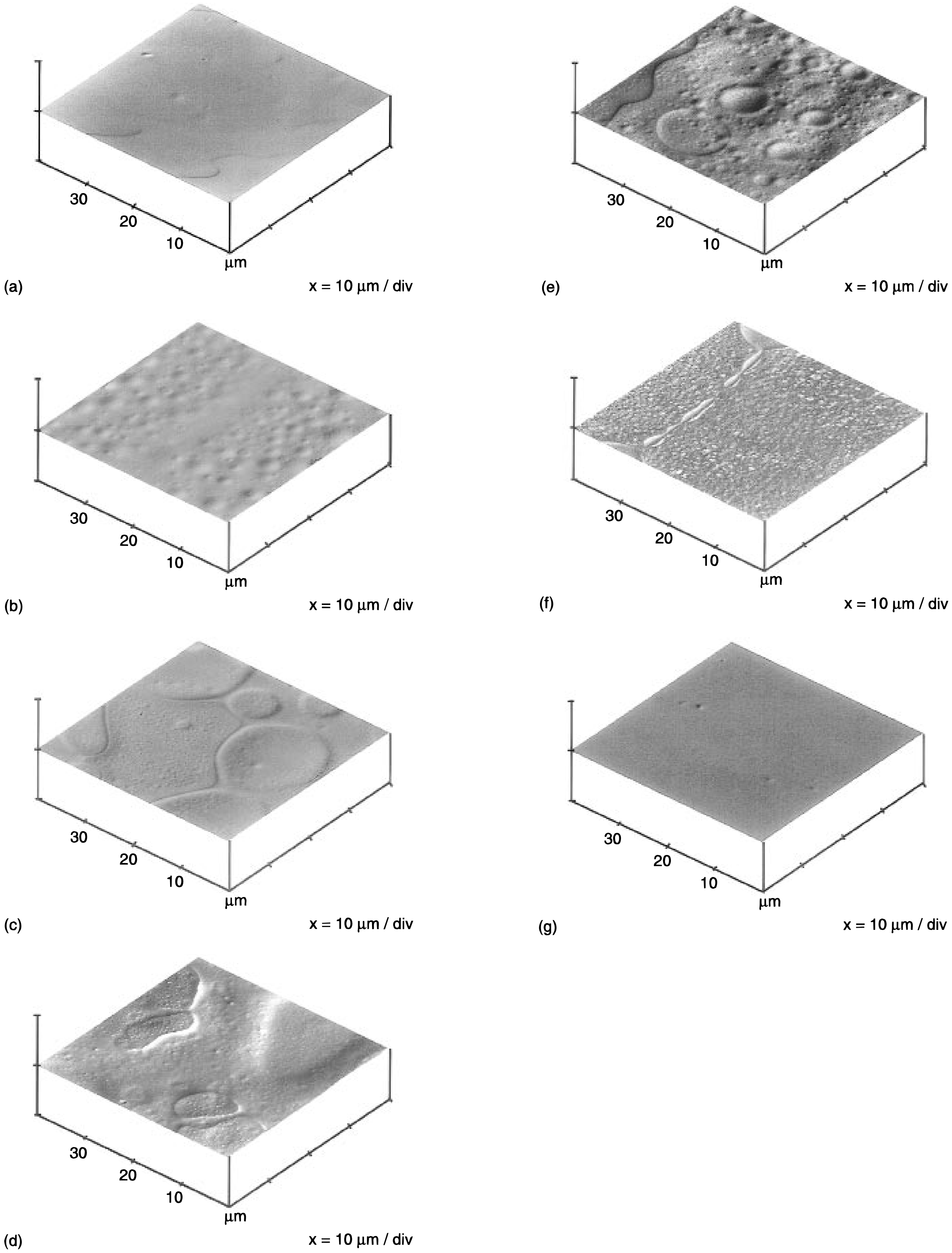


Figure 4. 40 μm phase modulation mode AFM images of untreated blend surfaces: (a) pure PS; (b) 25/75 PC/PS; (c) 50/50 PC/PS; (d) 60/40 PC/PS; (e) 75/25 PC/PS; (f) 90/10 PC/PS; (g) pure PC.

Virtually no O(1s) signal was detected from the surface up to a concentration of approximately 50% polycarbonate; beyond this value, the O/C ratio increased rapidly prior to eventually plateauing off at the value associated with pure polycarbonate. The C(1s) spectra show a corresponding rise in intensity of the *C*—O (286.6

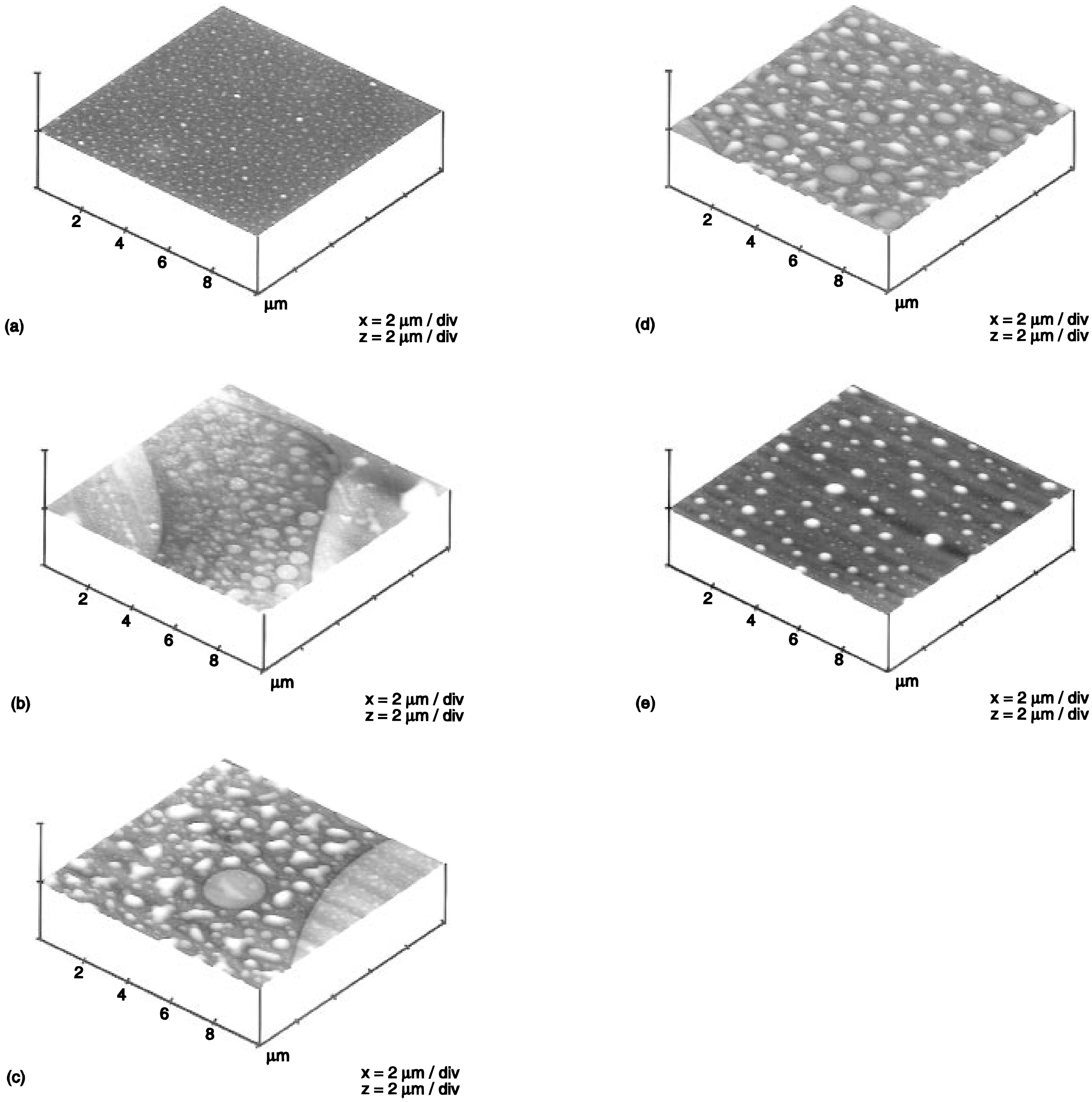


Figure 5. 10 µm tapping mode AFM images of silent discharge-treated blend surfaces: (a) pure PS; (b) 60/40 PC/PS; (c) 75/25 PC/PS; (d) 90/10 PC/PS; (e) pure PC.

eV) and O—*C*O—O (290.4 eV) peaks with increasing bulk polycarbonate content (Figure 1).

Both polystyrene and polycarbonate appear to undergo similar levels of oxidation during silent discharge treatment, with the former being oxidized to a slightly greater extent (Figure 1). The variation in O/C ratio with blend composition followed the same trend as seen previously for the untreated polymer blend mixtures with there being a marked increase in the level of surface oxidation beyond 50% polycarbonate (Figure 2).

Solvent washing of these dielectric barrier discharge-treated polystyrene/polycarbonate blend surfaces led to a drop in the O/C ratio. From these results it can be concluded that soluble low molecular weight oxidized material (LMWOM) is generated during plasma treatment.[25,26]

(b) Atomic Force Microscopy. AFM was used in both tapping and phase modulation modes. Tapping mode AFM analysis of the untreated polymer blend surfaces revealed a two-phase system (Figure 3). The different constituents of the blend were shown more clearly by using phase modulation AFM (Figures 3 and 4). Two types of feature are evident: a *localized* continuous phase (polycarbonate) containing submicron circular nodules (polystyrene) and an *extended* continuous phase (polystyrene).[27] The latter component completely swamps the surface at polystyrene loadings of greater than 40% (Figure 4).

Silent discharge treatment of pure polystyrene film produced smaller globular features compared to those for polycarbonate (Figure 5). These differences were also evident for the corresponding dielectric barrier discharge-modified blend surfaces (thereby aiding in the assignment of the respective blend components). Washing these plasma-treated surfaces with an 2-propanol/cyclohexane solvent mixture removed the low molecular

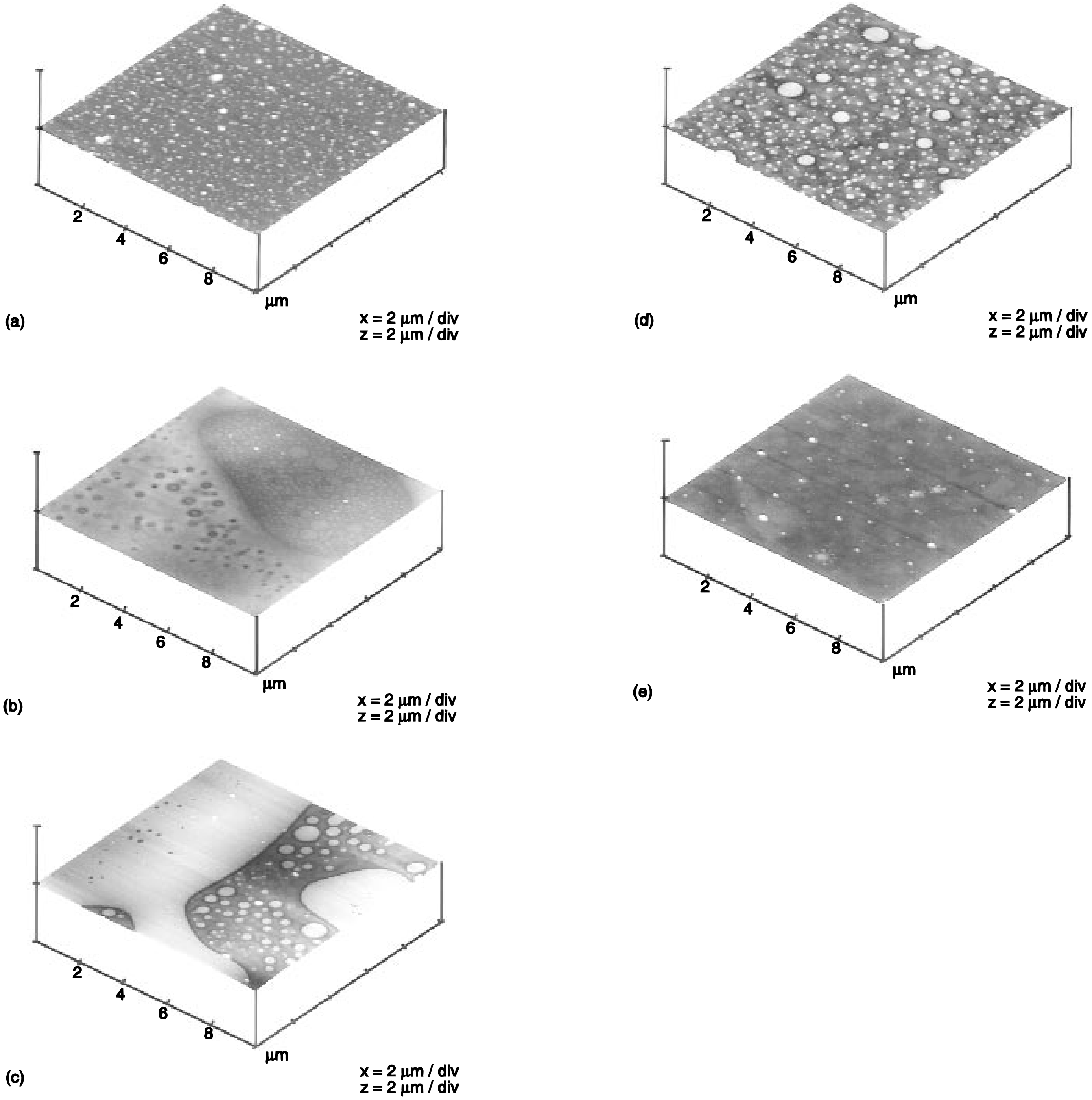


Figure 6. 10 μm tapping mode AFM images of silent discharge-treated blend surfaces followed by solvent washing: (a) pure PS; (b) 60/40 PC/PS; (c) 75/25 PC/PS; (d) 90/10 PC/PS; (e) pure PC.

weight oxidized material to leave behind terraces at different heights (these correspond to an inherent difference in etching rates between the two constituent polymers[28]).

Discussion

XPS samples over a large area and therefore effectively yields an average compositional value of the surface. XPS analysis of the polystyrene/polycarbonate polymer blend mixtures exhibits the classical behavior of an immiscible blend system; a nonlinear variation in the O/C ratio with blend composition is observed, which can be attributed to surface enrichment by polystyrene as a result of its lower surface energy (33 dyn cm^{-1})[29] compared to that for polycarbonate (45 dyn cm^{-1}).[30]

Tapping mode and phase modulation AFM analysis of the untreated polymer blend surfaces also showed that polystyrene tends to form a layer on top of the blend at low concentrations of polycarbonate. The mixed phase regions consist of small circular areas of polystyrene embedded within a continuous polycarbonate host matrix.[27] The polymer blend constituent with the higher surface energy tends to be raised to a higher topography;[17] this is consistent with the host polycarbonate matrix appearing higher within the localized mixed polystyrene/polycarbonate regions (Figure 3).

The silent discharge reactor produces a large quantity of reactive moieties including atomic oxygen, ozone, electrons, and ultraviolet radiation (UV).[31,32] The interaction of these species with an underlying polymer substrate can result in polymer chain scission and the formation of low molecular weight oxidized material (LMWOM), which exists as globules on the surface.[33] A difference in wetting behavior between the LMWOM and the underlying polystyrene/polycarbonate regions helps to identify the respective blend phases.[24] Such oxidative plasma treatment of polymer blend surfaces can lead to preferential etching of one constituent[34,35] as well as chemical modification.[17] The mass rate loss of polycarbonate is approximately twice that of polystyrene during oxidative electrical discharge treatment.[28] This can clearly be seen by AFM analysis of the solvent-washed silent discharge-treated polymer blend surfaces (Figure 6).

Conclusions

Surface enrichment of the polystyrene phase is found to occur for polystyrene/polycarbonate blend mixtures. This is accompanied by polycarbonate forming a continuous bulk phase containing embedded regions of polystyrene. Silent discharge treatment of these polymer blend surfaces produces low molecular weight oxidized material which can be washed off by solvent, to leave behind the polystyrene component raised at a higher topography as a result of polycarbonate having undergone a greater level of degradation during plasma treatment. Depending upon the original polymer blend composition, this gives rise to either terraces or wells at the surface.

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References and Notes

(1) Paul, D. R. In *Polymer Blends*; Paul, D. R., Newman, S., Eds.; Academic: San Diego, 1987; Chapter 1.
(2) Sawyer, L. C.; Grubb, D. T. *Polymer Microscopy*; Chapman and Hall: London, 1987.
(3) Dong, L.; Greco, R.; Orsello, G. *Polymer* **1993**, *34*, 1375.
(4) Mao, L. J.; Zhang, Z. P.; Ying, S. K. *Polym. Commun.* **1991**, *32*, 242.
(5) Goizueta, G.; Chiba, T.; Inoue, T. *Polymer* **1992**, *33*, 886.
(6) Goizueta, G.; Chiba, T.; Inoue, T. *Polymer* **1993**, *34*, 253.
(7) Olabisi, O.; Robeson, L. M.; Shaw, M. T. *Polymer−Polymer Miscibility*; Academic: New York, 1979.
(8) Binning, G.; Quate, C. F.; Gerber, C. *Phys. Rev. Lett.* **1986**, *56*, 930.
(9) Motomatsu, M.; Nie, H.-Y.; Mizutani, W.; Tokumoto, H. *Jpn. J. Appl. Phys., Part 1* **1994**, *33*, 3775.
(10) Nick, L.; Lippitz, A.; Unger, W.; Kindermann, A.; Fuhrmann, J. *Langmuir* **1995**, *11*, 1912.
(11) Viville, P.; Thoelen, O.; Beauvois, S.; Lazzaroni, R.; Lambin, G.; Bredas, J. L.; Kolev, K.; Laude, L. *Appl. Surf. Sci.* **1995**, *86*, 411.
(12) Burnham, N. A.; Colton, R. J. In *Scanning Tunneling Microscopy and Spectroscopy*; Bonnell, D. A., Ed.; VCH: New York, 1993; Chapter 7.
(13) Overney, R. M.; Meyer, E.; Frommer, D.; Brodbeck, D.; Luthi, R.; Howdt, L.; Guntherodt, H.-J.; Fujihira, M.; Taano, H.; Gotoh, Y. *Nature* **1992**, *359*, 133.
(14) Baselt, D. R.; Baldeschwieler, J. D. *J. Appl. Phys.* **1994**, *76*, 33.
(15) Frisbie, C. D.; Rozsnyai, L. F.; Noy, A.; Wrighton, M. S.; Lieber, C. M. *Science* **1994**, *265*, 2071.
(16) Babcock, K. L.; Prater, C. B. Phase Imaging: Beyond Topography. Technical Support Note; Digital Instruments: Santa Barbara, CA, 1995.
(17) Vargo, T. G.; Hook, D. J.; Gardella, J. A.; Eberhardt, M. A.; Meyer, A. E.; Baier, R. E. *J. Polym. Sci., Polym. Chem. Ed.* **1991**, *29*, 535.
(18) Krause, S. In *Polymer Blends*; Paul, D. R., Newman, S., Eds.; Academic: San Diego, 1978; Vol. 1, Chapter 2.
(19) Mobae, A.; Mckay, R. A.; Schaefer, J. *Macromolecules* **1992**, *25*, 4084.
(20) Greenwood, O. D.; Tasker, S.; Badyal, J. P. S. *J. Polym. Sci., Polym. Chem. Ed.* **1994**, *32*, 2479.
(21) Fuchs, O. In *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1989; p 379.
(22) Evans, J. F.; Gibson, J. H.; Moulder, J. F.; Hammond, J. S.; Goretzki, H. *Fresenius' Z. Anal. Chem.* **1984**, *319*, 841.
(23) Clark, D. T.; Dilks, A. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 957.
(24) Greenwood, O. D.; Badyal, J. P. S. *Macromolecules* **1997**, *30*, 1091.
(25) Strobel, M.; Dunatov, C.; Strobel, J. M.; Lyons, C. S.; Perron, S. J.; Morgen, M. C. J. *Adhesion Sci. Technol.* **1989**, *3*, 321.
(26) Briggs, D.; Kendall, C. R.; Blythe, A. R.; Wootton, A. B. *Polymer* **1983**, *24*, 47.
(27) Cheng, T. W.; Keskkula, H.; Paul, D. R. *J. Appl. Polym. Sci.* **1992**, *45*, 1245.
(28) Hansen, R. H.; Pascale, J. V.; deBenedictis, P. T.; Rentzepis, P. M. *J. Polym. Sci. A* **1965**, *3*, 2205.
(29) Toyama, M.; Ito, T.; Moriguchi, H. *J. Appl. Polym. Sci.* **1970**, *14*, 2039.
(30) Lee, L. H. In *Adhesion of High Polymers IV: Relationships Between Surface Wetting and Bulk Properties of High Polymers*; Gould, R. F., Ed.; Advances in Chemistry Series 87; American Chemical Society: Washington, DC, 1968; p 106.
(31) Eliasson, B.; Hirth, M.; Kogelschatz, U. *J. Phys. D, Appl. Phys.* **1987**, *20*, 1421.
(32) Eliasson, B.; Kogelschatz, U. *IEEE Trans. Plasma Sci.* **1991**, *19*, 309.
(33) Boyd, R. D.; Kenwright, A. M.; Badyal, J. P. S. *Macromolecules*, submitted.
(34) Takamatsu, S.; Kobayashi, T.; Komoto, T.; Sugiura, M.; Ohara, K. *Polymer* **1994**, *35*, 3598.
(35) Kushida, M.; Imaizumi, Y.; Harada, K.; Ueno, N.; Sugita, K. *Jpn. J. Appl. Phys.* **1995**, *34*, 4234.
(36) Groeninckx, G.; Chandra, S.; Berghmans, H.; Smets, G. In *Multiphase Polymers*; Advances in Chemistry Series 176; American Chemical Society: Washington, DC, 1979; Chapter 18.

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