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Nonequilibrium Plasma Treatment of Miscible Polystyrene/Poly(phenylene oxide) Blends

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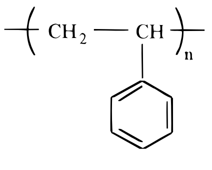
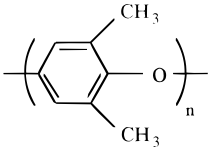
ABSTRACT: Oxidative low-pressure and atmospheric plasma modification of polystyrene/poly(2,6-dimethyl-1,4-phenylene oxide) miscible polymer blend surfaces has been studied using X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The extent and stability of surface oxygenation is found to be critically dependent upon both the type of electrical discharge employed and the bulk polymer blend composition.

Introduction

Economically it is much cheaper to just mix together two or more existing polymers, rather than having to develop a polymer for each new application. Indeed, this approach can offer scope for the tailoring of important surface properties, e.g., thermal behavior, adhesion, gas barrier, electrical conductivity, etc. For instance, the well-known polystyrene/poly(2,6-dimethyl-1,4-phenylene oxide) miscible blend system finds widespread commercial use in the thermoplastics industry.[1−3] The surface characteristics of such polymer blend mixtures need not necessarily be a straightforward weighted average of the values known for the respective constituents. In this study, the surface chemistry and topography of polystyrene/poly(phenylene oxide) miscible blend mixtures is investigated following low-pressure (glow discharge) and atmospheric pressure (dielectric barrier discharge) nonequilibrium plasma modification. In particular, we address the issue of whether oxidative plasma treatment of this miscible blend system results in just a straightforward average of the changes seen for the respective parent polymers or if some unusual physicochemical behavior occurs at the surface.



Polystyrene (PS)



Poly (2,6-dimethyl 1,4-phenylene oxide (PPO)

Experimental Section

Thin films of polystyrene (Aldrich; $M_W = 280,000$)/poly(phenylene oxide) (Aldrich; $M_W = 244,000$) polymer blends were prepared by spin coating from a 5% w/v chloroform solution onto glass slides. All blend compositions are quoted in terms of percentage weight. Visual examination indicated that the films were completely transparent, with no clouding, irrespective of the blend composition; this can be taken as being consistent with a single-phase polymer blend, since any phase separation should lead to light scattering.[4]

Low-pressure oxygen glow discharge modification of the polymer blend films was carried out in a cylindrical electrodeless reactor, with a base pressure of 5×10^{-3} mbar and a leak rate of lower than 1×10^{-10} kg s^{-1}. The reactor was fitted with a gas inlet, a Pirani pressure gauge, and a two-stage mechanical rotary pump attached to a liquid nitrogen cold trap. All joints were grease free. A 13.56-MHz rf generator was inductively coupled to the gas via an LC matching circuit and a copper coil (0.5-cm diameter, 10 turns) wound externally around the reaction chamber spanning 8−16 cm from the gas inlet. Prior to each experiment, the reaction vessel was scrubbed with detergent, rinsed with isopropyl alcohol, oven-dried, and then cleaned with a 50-W air plasma at a pressure of 0.2 mbar for 30 min. Next, a glass slide coated with polymer was placed in the central region of the copper coils. The reactor was purged with oxygen (99.99%, BOC) at 0.2 mbar for 600 s prior to igniting the glow discharge. Plasma treatments were carried out at 10 W of power for 60 s in all cases. Upon termination, the reaction zone was flushed with oxygen for a further 120 s and then vented to air. This was found to result in a limiting level of surface modification.

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[5] operating at 3 kHz, 11 kV, with an electrode gap of 3.00 ± 0.05 mm.

Subsequent washing experiments of both types of plasma-treated blend films were carried out using a 50/50 isopropyl alcohol/cyclohexane polar/nonpolar solvent mixture (neither polystyrene nor poly(phenylene oxide) are soluble in either of these solvents at room temperature[6]).

A Kratos ES300 electron spectrometer equipped with a Mg Kα source (1253.6 eV) and a concentric hemispherical analyzer was used for XPS surface analysis of the polymer blend surfaces before 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 the unit stoichiometry of C(1s):O(1s) were taken to equal 1.00:0.62.

A Digital Instruments Nanoscope III atomic force microscope was used to examine the topographical nature of the polymer blend surfaces prior to and immediately following electrical discharge exposure. All of the AFM images were acquired in air using the Tapping mode and are presented as unfiltered data. This technique employs a stiff silicon cantilever oscillating at a large amplitude near its resonance frequency (several hundred kilohertz). A large RMS amplitude is used to overcome the capillary attraction of the surface layer, while 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. RMS roughness values were obtained from unfiltered images.

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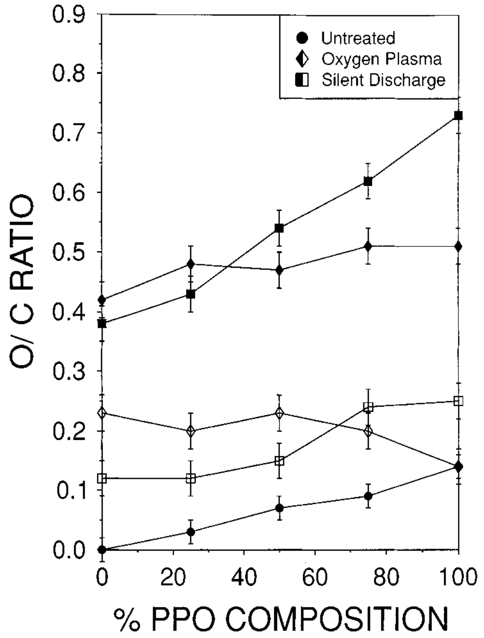

Figure 1. Variation in the O/C XPS ratio for the various treatments (the unshaded symbols correspond to solvent washing).

Results

(a) X-ray Photoelectron Spectroscopy. Only carbon and oxygen XPS lines were evident for untreated, low-pressure oxygen plasma treated, and atmospheric silent discharge treated polymer blends. The C(1s) XPS spectrum for each blend mixture was peak fitted with Gaussian peaks of equal full width at half maximum (FWHM),[7] using a Marquardt minimization computer program. Energies distinctive of different types of oxidized carbon moieties were referenced to the hydrocarbon peak (—C_xH_y—) at 285.0 eV:[8] carbon adjacent to a carboxylate group (>CCO$_2$—) at 285.7 eV, carbon singly bonded to one oxygen atom (>CO—) at 286.6 eV, carbon singly bonded to two oxygen atoms or carbon doubly bonded to one oxygen atom (—OCO—/>C=O) at 287.9 eV, carboxylate groups (—OC=O) at 289.0 eV, and carbonate carbons (—OCOO—) at 290.4 eV. An additional peak at 291.6 eV, with a different FWHM, corresponded to the π–π* shake-up satellite associated with phenyl ring centers.[9] Clean polystyrene exhibited a main peak at a C(1s) binding energy of 285.0 eV along with a π–π* transition satellite. The O/C ratio for untreated poly(phenylene oxide) was measured to be 0.14 ± 0.02, in good agreement with the theoretical value of 0.13 expected from the parent polymer repeating unit. A linear variation in the O/C ratio was found for the blend mixtures with increasing poly(phenylene oxide) concentration, Figure 1. This was accompanied by a corresponding change in shape of the C(1s) envelope, Figure 2.

Low-pressure oxygen plasma treatment of all the polymer blend mixtures resulted in oxygen incorporation at the surface, Figure 1. If one takes into account the oxygen present beforehand due to poly(phenylene oxide), then both of the parent polymers appear to have undergone oxygenation to a similar extent. The O/C ratio varies in approximately a linear fashion with increasing poly(phenylene oxide) concentration; this is indicative of no preferential oxidation or etching of either blend component. C(1s) peak-fitted XPS spectra of plasma-treated blend mixtures are shown in Figure 3a. Washing of these glow discharge modified polystyrene/poly(phenylene oxide) blends in a cyclohexane/isopropyl alcohol solvent mixture resulted in a decrease in the amount of oxygen present at the surface, Figures 1 and 3b. This suggests that low-pressure oxygen plasma treatment generates low molecular weight oxidized material (LMWOM) which can be washed off. Interestingly, the trend seen in the O/C ratio during low-pressure oxygen plasma treatment is reversed on solvent washing, with polystyrene retaining a greater proportion of its incorporated oxygen species compared to poly(phenylene oxide).

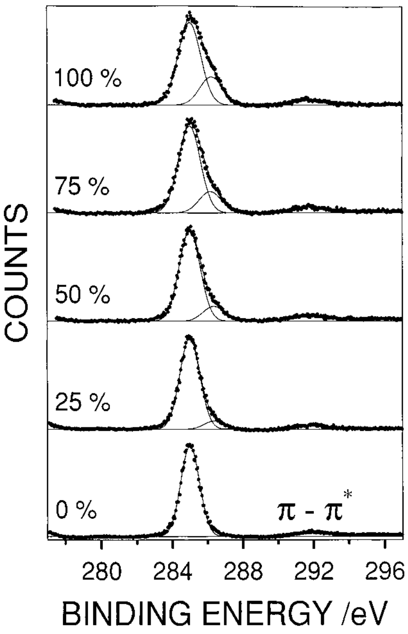

Figure 2. C(1s) peak-fitted spectra for untreated polystyrene/poly(phenylene oxide) blend mixtures with increasing poly(phenylene oxide) content.

Atmospheric silent discharge treatment of the miscible blend mixtures also exhibits a linear rise in the O/C ratio with increasing poly(phenylene oxide) concentration; however, the rate of change with blend composition is markedly greater compared to the untreated and low-pressure oxygen plasma treated polymer blends, Figure 1. C(1s) peak-fitted XPS spectra for silent discharge treated polymer blend mixtures reflect this linear variation, Figure 4a. Solvent washing of the silent discharge treated polystyrene/poly(phenylene oxide) blends removed a significant amount of modified polymeric material, Figures 1 and 4b. In this case, the trend in the O/C ratio did follow the behavior for the unwashed case, although it is clearly evident that modified poly(phenylene oxide) material is more readily removed in comparison to oxygenated polystyrene. Contrary to low-pressure oxygen plasma treatment, washing of atmospheric dielectric barrier discharge treated blend surfaces did not completely remove the oxidized poly(phenylene oxide) species.

(b) AFM. Polystyrene exhibits a fine granular surface structure, while poly(phenylene oxide) appears to be coarser in texture, Figure 5 and Table 1. Therefore, the surface morphology of spin-coated films is influenced by the polymer itself as well as by the preparation technique. AFM micrographs taken of the polystyrene/poly(phenylene oxide) blends on a 10-μm scale showed no new types of morphological feature at the surface (i.e., no evidence for any phase separation). Rather, increasing the poly(phenylene oxide) concentration in the blend mixtures led to the gradual collapse of the fine granular polystyrene morphology.

Low-pressure oxygen plasma treatment resulted in the formation of globular features which increased in

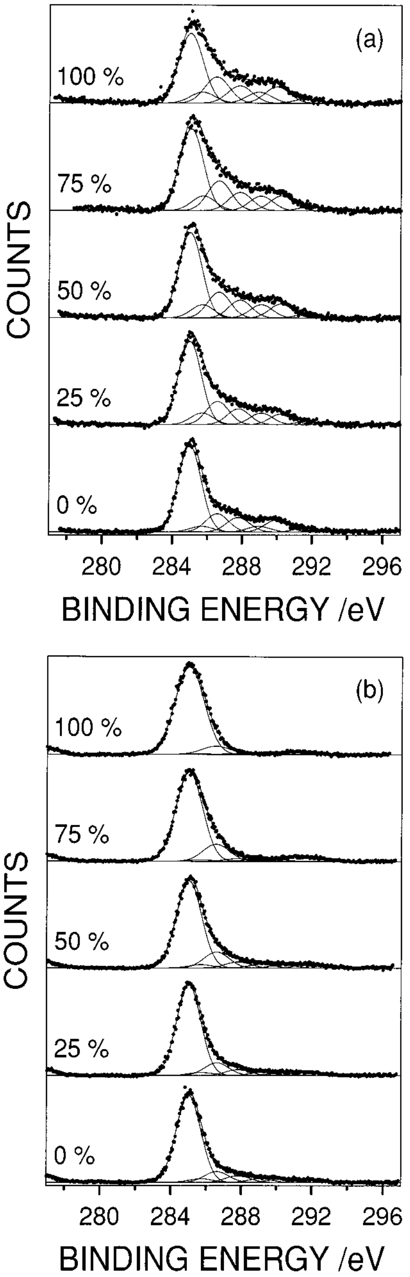

Figure 3. XPS data for low-pressure oxygen plasma treated PS/PPO polymer blends with increasing poly(phenylene oxide) content: (a) C(1s) peak-fitted spectra and (b) C(1s) peak-fitted spectra after washing.

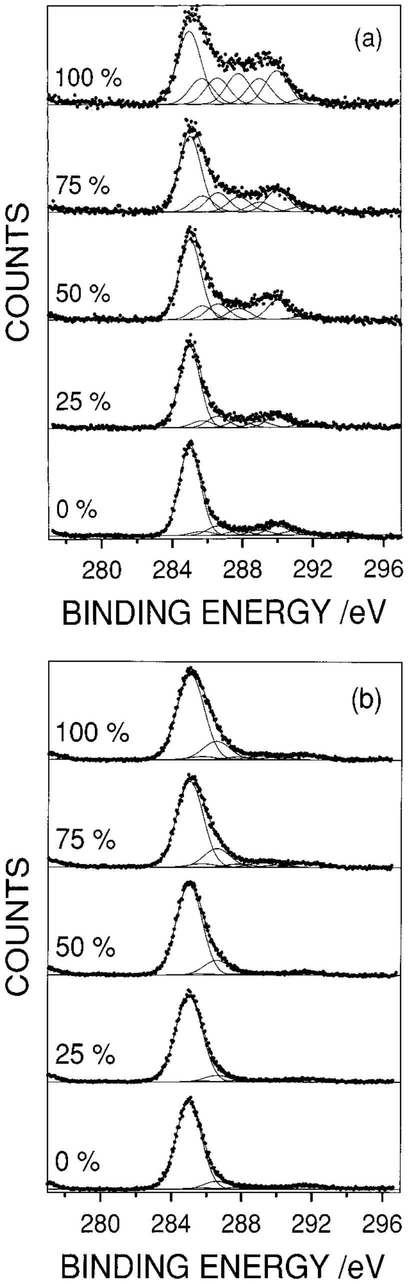

Figure 4. XPS data for atmospheric pressure silent discharge treated PS/PPO polymer blends with increasing poly(phenylene oxide) content: (a) C(1s) peak-fitted spectra and (b) C(1s) peak-fitted spectra after washing.

size with poly(phenylene oxide) content, Figure 6. This was accompanied by a loss of the original blend surface texture, Table 1. Solvent washing of the low-pressure plasma-treated polymer blend surfaces resulted in an increase in surface roughness, Figure 6 and Table 1.

Atmospheric silent discharge treatment of poly(phenylene oxide) and polystyrene also produced globular features, Figure 7. The average globular size becoming greater with increasing poly(phenylene oxide) content. Washing of the silent discharge treated polymer blend surfaces removed the large globular features to leave behind a smoother surface (this is contrary to what was observed during low-pressure oxygen glow discharge modification), Figure 7 and Table 1.

Discussion

Miscibility over the entire composition range for polystyrene/poly(phenylene oxide) blends has been known for a long time and widely investigated using a variety of techniques (e.g., glass transition temperature,[10] neutron scattering studies,[11] etc.). Infrared[12] and ultraviolet[13] spectroscopic studies have shown that this high miscibility arises from strong interactions between the phenyl rings contained in poly(phenylene oxide) and polystyrene. Pure polystyrene or blends with a high polystyrene content tend to be brittle. However, blends with a poly(phenylene oxide) content of greater than 30% are ductile glasses.[14] This variation in mechanical properties has been attributed to the intermolecular disruption of stacks of polystyrene polymer chains by poly(phenylene oxide).[15] These interactions can be used to account for the observed disappearance of the parent polystyrene granular surface morphology upon blending with poly(phenylene oxide).

Typically for a polymer blend, one would expect surface enrichment of the component with the lowest surface energy.[16] Polystyrene and poly(phenylene oxide) have surface energies of 33 and 41 dyn cm^{-1}, respec-

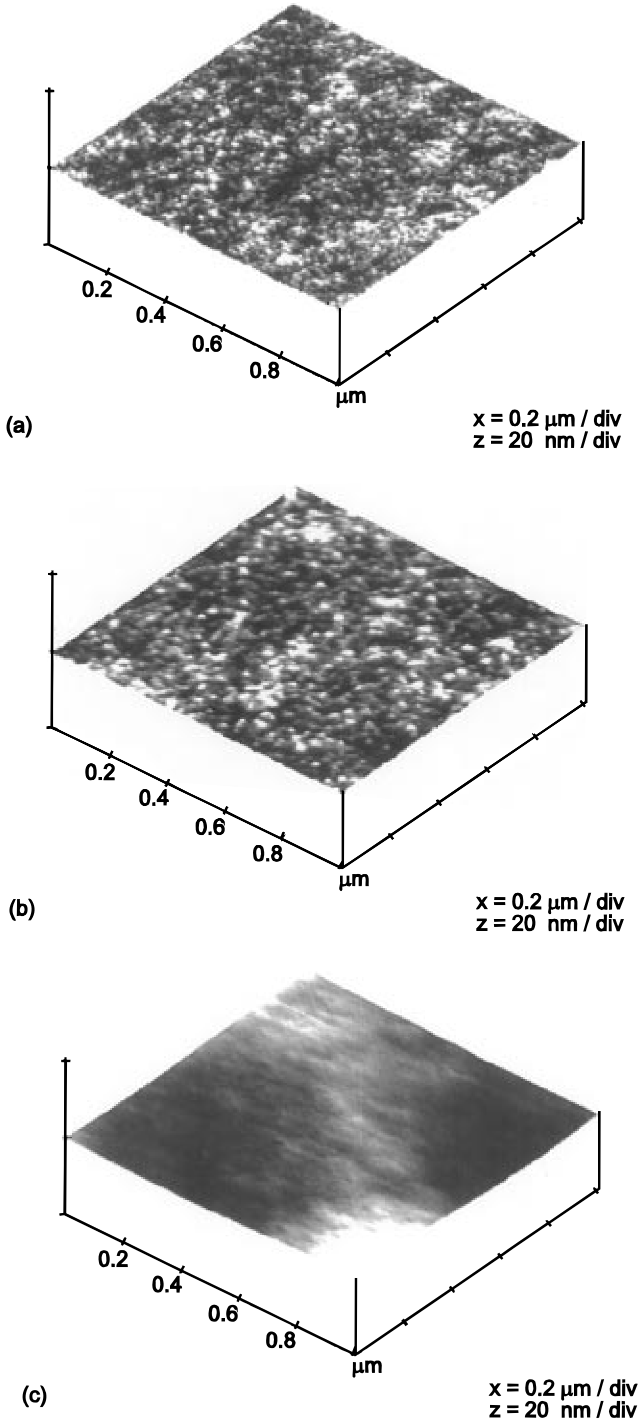

Figure 5. AFM micrographs of untreated blend mixtures: (a) pure PS; (b) 50/50 PS/PPO; (c) pure PPO.

Table 1. Summary of RMS Surface Roughness Measurements

comp/% PPO	untreated/ nm	low-pressure plasma treated/nm unwashed	low-pressure plasma treated/nm washed	atm silent discharge treated/nm unwashed	atm silent discharge treated/nm washed
0	0.26	0.56	0.74	3.2	2.9
25	0.22	0.35	0.51	5.2	0.81
50	0.21	0.32	0.71	5.0	1.1
75	0.20	0.37	0.87	5.2	0.76
100	0.34	0.61	0.20	14.3	0.51

tively.[17,18] Therefore, surface enrichment of polystyrene would be expected in the case of polystyrene/poly(phenylene oxide) blend mixtures. The observed linear variation in poly(phenylene oxide) content at the surface with blend composition suggests that no surface segre-

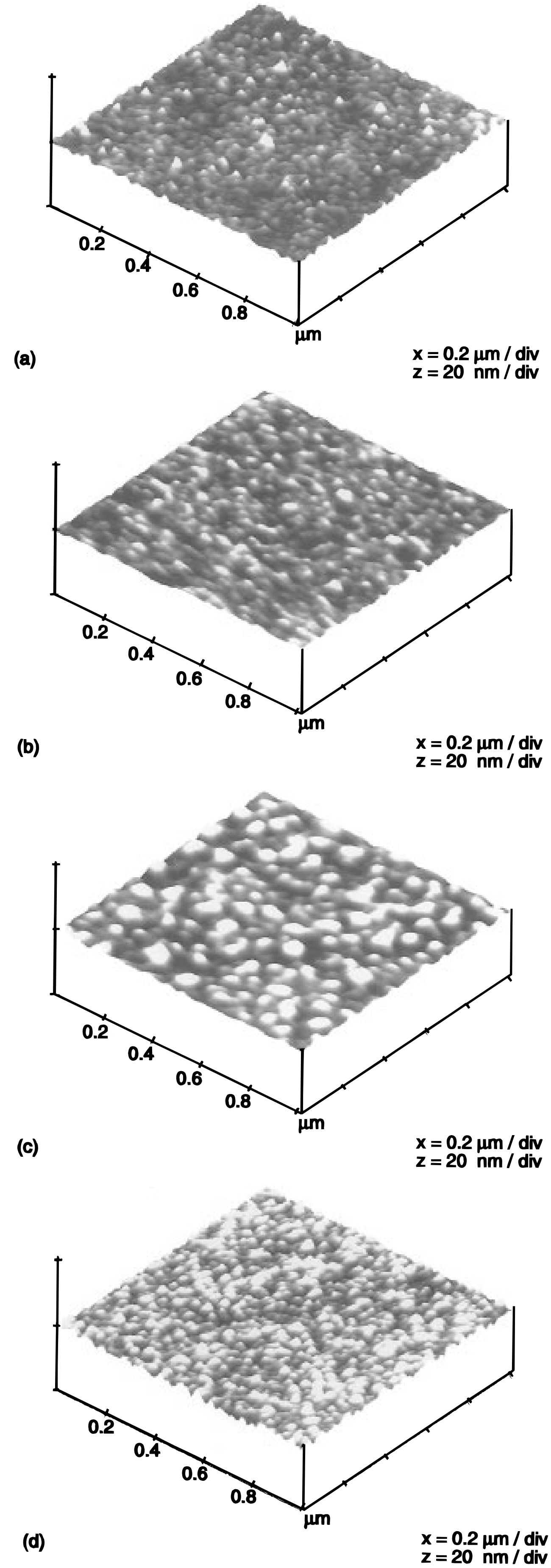

Figure 6. AFM micrographs of oxygen plasma treated blend mixtures: (a) pure PS; (b) 50/50 PS/PPO; (c) pure PPO; (d) following solvent washing of b.

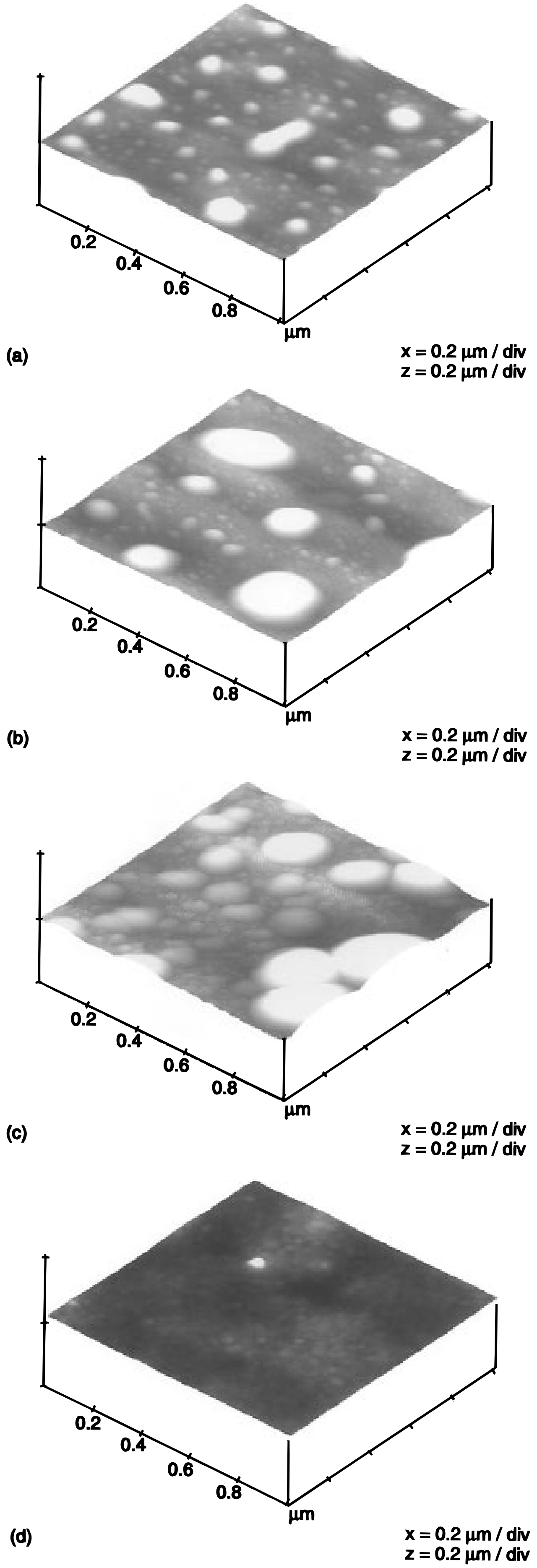

Figure 7. AFM micrographs of silent discharge treated blend mixtures: (a) pure PS; (b) 50/50 PS/PPO; (c) pure PPO; (d) following solvent washing of b.

gation of either component of the polymer blend is occurring within the XPS sampling depth (2 nm). The lack of surface enrichment might be due to phenyl ring interactions between the two polymer constituents hindering the migration of polystyrene toward the surface[13] combined with molecular entanglements.[19] Alternatively, fast evaporation of the chloroform solvent during spin coating may be preventing the blend from reaching thermodynamic equilibrium.[16]

Low-pressure oxygen and atmospheric silent discharge plasma treatment can increase the wettability of the polymers due to the formation of polar groups at the surface.[20–22] In the former case, this occurs as a result of bombardment of the substrate by glow discharge generated free radicals, ions, metastables, and vacuum ultraviolet radiation (vacuum UV),[23] while for the latter, surface activation by electron streamers and UV radiation in the presence of atomic oxygen and ozone are the predominant reaction pathways.[24–27] For both parent polymers, electrical discharge treatment results in the formation of $\underline{C}$O, O$\underline{C}$O, $\underline{C}$=O, O$\underline{C}$=O, and O$\underline{C}$OO functionalities at the surface. Attenuation of the $\pi-\pi^*$ shake-up satellite during plasma modification is indicative of the phenyl centers being attacked during treatment.[24–26,28,29] Chain scission along the polymer backbone can be taken as being responsible for the formation of low molecular weight oxidized material.[22,28,30,31] Solvent-washing experiments have shown that there is a greater loss of oxygenated material from electrical discharge treated poly(phenylene oxide)-rich blend mixtures. This can be attributed to poly(phenylene oxide) being more susceptible toward chain scission as a consequence of its phenyl ring being located within the polymer backbone rather than being pendant (as is the case for polystyrene): aromatic pendant groups promote stability of the polymer backbone by enhancing radiationless deactivation.[32] Also, the polar C—O bond along the poly(phenylene oxide) backbone will be susceptible to nucleophilic attack by plasma-generated oxygen species. In the case of atmospheric silent discharge treatment, vacuum UV radiation of lower energy is generated, and this leads to less chain scission within the subsurface region and therefore helps to explain why some of the oxygenated functionalities remain in tact during solvent washing of the poly(phenylene oxide)-rich blends. However, in the case of solvent-rinsing low-pressure oxygen plasma modified polystyrene-rich mixtures, the low molecular weight poly(phenylene oxide) fraction is easily removed.

The higher oxygen content associated with the low molecular weight oxidized material makes it incompatible with the underlying untreated polymer due to a large difference in their respective surface energies, and this leads to the formation of globules at the surface.[33–35] It appears that the amount of globular material increases with the proportion of poly(phenylene oxide) incorporated into the blend mixture, which is consistent with the greater level of oxygenation measured by XPS. Although silent discharge modification causes a greater perturbation of surface topography,[36] this does not hold true following solvent washing of the respective treated surfaces, Table 1; an increase in roughness is found for low-pressure plasma modification of the polymer blend surfaces, while the converse was noted for silent discharge treatment.

Conclusions

No significant surface enrichment is found within the XPS sampling depth of either parent component for polystyrene/poly(phenylene oxide) blends. The surface topography characteristic of each constituent is destroyed upon mixing due to the disruption of phenyl ring stacking associated with polystyrene by interpenetrating poly(phenylene oxide) chains. Atmospheric dielectric barrier treatment of the polymer blends leads to a larger amount of low molecular weight oxidized globular material being produced in comparison to low-pressure oxygen plasma modification. For both types of treatment, these oxidized moieties can be partially washed off by solvent, which leads to a change in both the chemical composition and topography at the surface. From the point of view of incorporating oxygen into the surface (which is not associated with low molecular weight oxidized material), low-pressure oxygen plasma treatment is better suited for polystyrene-rich compositions, whereas silent discharge modification is more appropriate for poly(phenylene oxide)-rich blends. Hence, it has been demonstrated that a desired level of surface oxygenation can be attained by selecting the appropriate combination of polymer blend composition and type of plasma treatment.

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