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Non-isothermal O_2 Plasma Treatment of Phenyl-Containing Polymers

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ABSTRACT: A variety of phenyl-containing polymer surfaces have been oxidized using low pressure non-equilibrium O_2 glow discharges. Characterization by X-ray photoelectron spectroscopy has shown that the level of oxygen incorporation can be correlated to the intensity of the C(1s) $\pi-\pi^*$ valence transition measured for the untreated parent polymer. In all cases, a globular surface texture is observed by atomic force microscopy following O_2 plasma treatment. These chemical and topographical changes can be explained in terms of the susceptibility of phenyl groups contained within the parent polymer structure toward oxidative glow discharge attack.

Introduction

Traditional methods for improving polymer surfaces encompass wet chemical, hot press, flame, abrasion, and graft treatments.[1,2] Non-isothermal plasma processing offers many advantages over these other techniques including the modification of just the outermost atomic layers of a substrate,[3,4] selection of desired chemical reaction pathways,[5] minimization of thermal degradation,[5] rapid treatment,[6] and negligible waste.[7] Often it can prove to be the only way of achieving desired surface performance. Such cold plasma treatment of polymeric materials comprises bombardment of the substrate surface by electromagnetic radiation, electrons, ions, metastables, and ground state species.[8] Most of the previous studies in this field have tackled only one or two polymers at a time under comparable experimental conditions, and therefore it has been difficult to draw any valid mechanistic conclusions concerning the importance of substrate structure.[9−12] For instance, a recent study based on contact angle measurements reported that O_2 plasma treatment improves aluminum adhesion to a variety of phenyl-containing polymers;[13] however, the relative variations were not correlated to parent polymer structure.

In this article, the interdependence between surface reactivity and parent polymer structure during low pressure non-isothermal O_2 plasma treatment is investigated for seven phenyl-containing polymers using X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM).

Experimental Section

Small strips of polystyrene (BP), poly(ethylene terephthalate) (Hoechst), poly(ether ether ketone) (ICI), poly(bisphenol carbonate) (General Electric Plastics), poly(bisphenol sulfone) (Westlake Plastics Co.), and poly(ether sulfone) (Westlake Plastics Co.) were ultrasonically cleaned in a 50:50 nonpolar (cyclohexane):polar (propan-2-ol) solvent mixture for 30 s. Poly(dimethylphenylene oxide) (Aldrich) was spin coated onto clean glass slides from a 2% chloroform solution.

Low pressure plasma treatments were carried out in an electrodeless cylindrical reactor (4.5 cm diameter, 460 cm^3 volume, with a leak rate better than 4×10^{-3} cm^3 min^{-1}) enclosed in a Faraday cage.[14] This was fitted with a gas inlet, a Pirani pressure gauge, and a 27 L min^{-1} two-stage rotary pump attached to a liquid nitrogen cold trap. A matching network was used to inductively couple a copper coil (4 mm diameter, 9 turns, spanning 8−15 cm from the gas inlet) wound around the reactor to a 13.56 MHz radio frequency (rf) generator. All joints were grease-free. Gas and leak mass flow rates were calculated assuming ideal gas behavior.[15]

Each experimental run comprised initially scrubbing the reactor with detergent, rinsing with propan-2-ol, and oven drying, followed by a 30 min high-power (50 W) air plasma cleaning treatment. At this stage, a strip of polymer was inserted into the center of the reactor (i.e., the glow region), and the reactor was pumped down to a base pressure of 3×10^{-3} mbar. Subsequently O_2 (99.9% purity, BOC) was introduced into the reaction chamber at 2×10^{-1} mbar pressure and a flow rate of 1.0 cm^3 min^{-1}. After 5 min of purging with O_2 gas, the glow discharge was ignited at 20 W for 30 s. Upon termination of treatment, the rf generator was switched off, and the reactor was flushed with O_2 gas for a further 5 min to allow quenching of residual free-radical centers at the surface and then finally vented to air prior to surface characterization.

In addition, O_2 plasma treated polymer strips were rinsed for 2 min in a 50:50 mixture of cyclohexane:propan-2-ol (nonpolar and polar solvents, respectively) and dried in air prior to surface analysis. None of the parent polymers are reported to be soluble in either of these washing solvents.[16]

A Kratos ES300 electron spectrometer equipped with a Mg Kα X-ray source (1253.6 eV) and a concentric hemispherical analyzer was used for surface analysis by X-ray photoelectron spectroscopy (XPS). Photoemitted electrons were collected at a take-off angle of 30° from the substrate normal (which corresponds to a sampling depth of ~2 nm in polymers[17]), with electron detection in the fixed retarding ratio (FRR, 22:1) mode. XPS spectra were accumulated on an interfaced IBM PC computer. Sensitivity factors for unit stoichiometry were experimentally determined to be C(1s):O(1s):S(2p) = 1.00:0.62:0.54.

Atomic force microscopy (AFM) allows non-destructive topographical characterization of electrically insulating surfaces in the range 10^{-4}−10^{-10} m, without the need for any special sample preparation.[18] All of the AFM images were acquired in air using the tapping mode[19] 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). The 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. AFM was used to examine each of the polymer substrates at the three stages (i.e., clean, O_2 plasma treated, and O_2 plasma treated followed by solvent washing). The sizes of topographical feature were measured using cross-sectional analysis.

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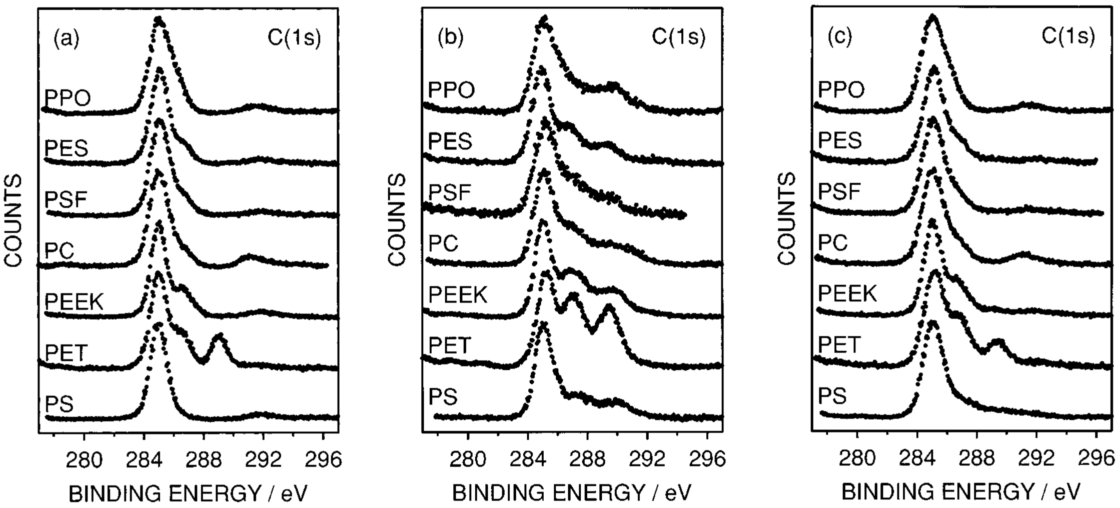
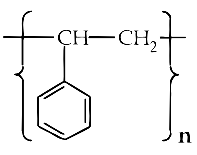


Figure 1. C(1s) XPS spectra of (a) untreated, (b) O_2 plasma treated, and (c) solvent washed/O_2 plasma treated polymers.

Results

***(a)* XPS.** The cleanliness of each substrate and the absence of any surface-active inorganic additives were verified by XPS wide-scan spectra. O_2 plasma treated polymer substrates yielded only carbon and oxygen features (with additional signals for sulfur in the case of polysulfone and poly(ether sulfone)). Mg K$\alpha_{1,2}$ C(1s) XPS core-level spectra were fitted with Gaussian peaks of equal full width at half-maximum (fwhm),[20] using a Marquardt minimization computer program. Energies distinctive of different types of carbon moieties were referenced to the hydrocarbon peak ($-\underline{C}_xH_y-$) at 285.0 eV:[21,22] carbon singly bonded to one sulfur atom ($-\underline{C}-S$, in the case of polysulfone and poly(ether sulfone)) at 285.6 eV, carbon adjacent to a carboxylate group ($-\underline{C}-CO_2-$) at 285.7 eV, carbon singly bonded to one oxygen atom ($-\underline{C}-O-$) at 286.6 eV, carbon doubly bonded to one oxygen atom or carbon singly bonded to two oxygen atoms ($>\underline{C}{=}O/{-}O{-}\underline{C}{-}O{-}$) at 287.9 eV, carboxylate groups ($-O-\underline{C}{=}O$) at 289.0 eV, and carbonate carbons ($-O-\underline{C}O-O-$) at 290.4 eV. The $\pi-\pi^*$ phenyl ring shake-up satellite present at ~291.7 eV for all of the substrates under investigation was fitted with a Gaussian peak of different fwhm in order to assess the level of aromaticity present in the untreated polymers.[23]



Polystyrene (PS)

The C(1s) XPS envelope for untreated polystyrene can be assigned to a hydrocarbon component, $-\underline{C}_xH_y-$ at 285.0 eV, and a $\pi-\pi^*$ shake-up satellite feature is discernible at 291.7 ± 0.1 eV which accounts for approximately 5.3 ± 0.2% of the total C(1s) peak area[23-26] (Figure 1). Low-pressure O_2 electrical discharge treatment of polystyrene produced the greatest uptake of oxygen among all of the polymers under investigation (Figure 2); this was accompanied by an attenuation of the $\pi-\pi^*$ shake-up satellite intensity to 3.3 ± 0.5% of the total C(1s) peak area. A total of 37 ± 5% of the incorporated oxidized carbon functionalities were removed by solvent washing (Figures 1 and 2).

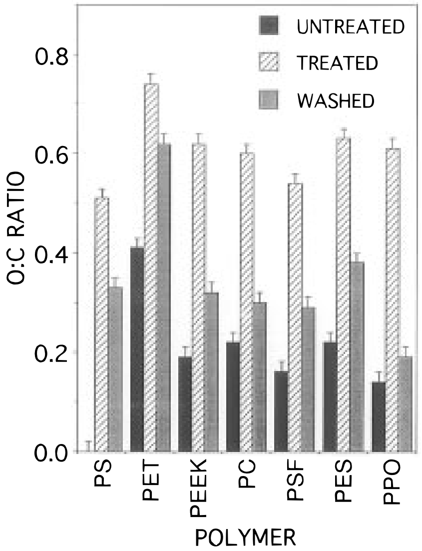
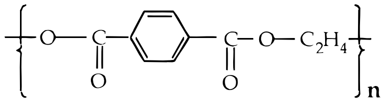


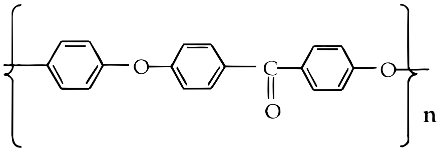
Figure 2. Variation in XPS O:C ratio with parent polymer structure for untreated, O_2 plasma treated, and solvent washed/O_2 plasma treated polymers. Error bars represent standard deviations.



Polyethyleneterephthalate (PET)

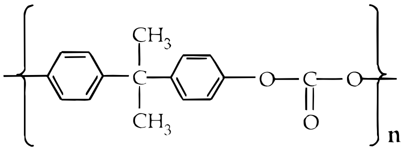
In the case of untreated poly(ethylene terephthalate) (PET), the $-\underline{C}_xH_y-$, $-\underline{C}-O-$, and $-O-\underline{C}{=}O$ environments (in a 3:1:1 ratio) are clearly discernible in the C(1s) spectrum (Figure 1). The $\pi-\pi^*$ shake-up satellite accounts for 3.5 ± 0.2% of the overall C(1s) envelope.[27] O_2 plasma treatment of PET produced the highest O:C ratio among all the polymers screened in the present study; this was despite the relative change in O:C ratio with respect to the untreated polymer being the smallest (Figure 2). Plasma oxidation was accompanied by a loss in the $\pi-\pi^*$ shake-up satellite intensity to 2.3 ± 0.5% of the total C(1s) envelope. The various types of oxygenated functionalities were noted to be fairly evenly distributed (Figure 1). Solvent washing of the O_2

plasma treated PET surface removed 36 ± 5% of the oxygen added by plasma treatment (Figure 2).



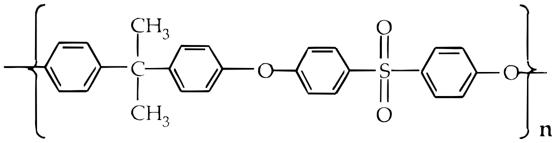
Polyetheretherketone (PEEK)

Poly(ether ether ketone) (PEEK) contains two phenyl centers linked by ether groups and one benzophenone group per polymer repeat unit. The C(1s) envelope comprises $-\underline{C}_x\mathrm{H}_y-$, $-\underline{C}-\mathrm{O}-$, and $>\underline{C}{=}\mathrm{O}$ carbon functionalities (Figure 1). O_2 plasma treatment of PEEK led to a large increase in O:C ratio (Figure 2) combined with a reduction in the $\pi-\pi^*$ shake-up satellite signal from 5.9 ± 0.2 to 3.5 ± 0.5% of total C(1s) peak area. Solvent washing of the treated PEEK surface removed 71 ± 5% of the added oxygen, accompanied by a large increase in the proportion of $-\underline{C}-\mathrm{O}-$ groups at the expense of the other three types of oxidized carbon environments (i.e., $>\underline{C}{=}\mathrm{O}/-\mathrm{O}-\underline{C}-\mathrm{O}-$, $-\mathrm{O}-\underline{C}{=}\mathrm{O}$, and $-\mathrm{O}-\underline{C}\mathrm{O}-\mathrm{O}-$) (Figure 1).



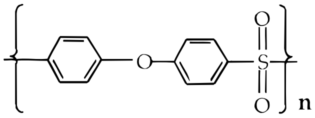
Polybisphenolcarbonate (PC)

$-\underline{C}_x\mathrm{H}_y-$, $-\underline{C}-\mathrm{O}-$, and $-\mathrm{O}-\underline{C}\mathrm{O}-\mathrm{O}-$ environments can be identified in the C(1s) XPS spectrum of clean polycarbonate together with a $\pi-\pi^*$ shake-up satellite contributing 4.2 ± 0.2% of the total C(1s) signal intensity (Figure 1). Attenuation of the C(1s) $\pi-\pi^*$ shake-up satellite to 3.2 ± 0.5% and an increase in oxygen content occurred during O_2 glow discharge treatment (Figure 2). The rise in the number of $-\underline{C}-\mathrm{O}-$ and $>\underline{C}{=}\mathrm{O}/-\mathrm{O}-\underline{C}-\mathrm{O}-$ groups was accompanied by a drop in the amount of carbonate ($-\mathrm{O}-\underline{C}\mathrm{O}-\mathrm{O}-$) centers. These results are in agreement with previous reports which have shown that polycarbonate is more susceptible to plasma oxidation than PET and less so than polystyrene.[28] Solvent washing the treated polycarbonate surface removed 79 ± 5% of the incorporated oxygen. Once again, structural environments associated with the parent polymer reappeared upon solvent washing (Figure 1); i.e., a large increase in the number of $-\underline{C}-\mathrm{O}-$ groups was observed in conjunction with a decrease in the proportion of $>\underline{C}{=}\mathrm{O}/-\mathrm{O}-\underline{C}-\mathrm{O}-$ functionalities.



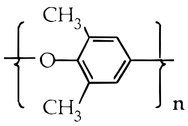
Polybisphenolsulfone (PSF)

The surface of untreated polysulfone (PSF) was found to contain 82 ± 2% carbon, 15 ± 2% oxygen, and 3 ± 1% sulfur, which is in keeping with the bulk parent polymer structure (the theoretical composition being 84.4% carbon, 12.5% oxygen, and 3.1% sulfur). Ether ($-\underline{C}-\mathrm{O}-$) linkages constitute the only oxidized carbon groups in untreated polysulfone, while oxygen is also present as doubly bonded to sulfur. The $\pi-\pi^*$ shake up intensity accounted for 4.4 ± 0.2% of total C(1s) intensity (Figure 1). A significant level of oxygen incorporation was noted during O_2 plasma treatment (Figure 2) combined with an attenuation of the $\pi-\pi^*$ shake-up satellite down to 1.6 ± 0.5% of total C(1s) intensity. Solvent washing the oxidized polysulfone surface removed 73 ± 5% of the added oxygen. A large rise in the $-\underline{C}-\mathrm{O}-$ group contribution was seen at the expense of the other types of oxidized carbon environments (Figure 1).



Polyethersulfone (PES)

Poly(ether sulfone) (PES) has a greater oxygen (20 ± 2%) and sulfur (6 ± 2%) content compared to its structurally related polysulfone counterpart, since the former lacks any dimethyl carbon linkages within its repeat unit. Also, the $\pi-\pi^*$ shake-up satellite was found to be more intense for poly(ether sulfone) (Figure 1), constituting 5.8 ± 0.2% of the total C(1s) peak intensity. O_2 plasma treatment of poly(ether sulfone) resulted in oxygen incorporation at the surface (Figure 2) and complete loss of the $\pi-\pi^*$ shake-up satellite[29] (Figure 1). Solvent washing poly(ether sulfone) removed 54 ± 2% of the oxygen added during O_2 plasma treatment. This was accompanied by the C(1s) envelope reverting back toward the parent polymer spectrum (Figure 1). It is interesting to note that the absolute value of the change in O:C ratio upon solvent washing, $\Delta(\mathrm{O{:}C}) = -0.25 \pm 0.02$, is the same for both sulfur-containing polymers.



Poly(2,6-dimethyl-1,4-phenyleneoxide)

Poly(dimethylphenylene oxide) (PPO) contains a phenyl ether linkage along its backbone with two pendant methyl groups per polymer repeat unit. The C(1s) XPS spectrum comprised 28 ± 2% of carbon atoms in $-\underline{C}-\mathrm{O}$ environments; this is consistent with the parent polymer structure (Figure 1). The $\pi-\pi^*$ shake-up satellite peak contributed 6.9 ± 0.2% toward the total C(1s) peak area. O_2 plasma treatment of poly(dimethylphenylene oxide) produced a large increase in O:C ratio (Figure 2) accompanied by an attenuation of the C(1s) $\pi-\pi^*$ shake-up signal to about half of its original value (Figure 1). A significant proportion (89 ± 2%) of the oxygen added during O_2 plasma treatment was lost from the poly(dimethylphenylene oxide) surface during solvent rinsing, leading to the largest change in O:C ratio upon washing. Once again the C(1s) envelope reverted to being reminiscent of the untreated polymer (Figure 1).

(b) AFM. Atomic force microscopy showed that the relatively smooth untreated surfaces were roughened by O_2 plasma treatment to produce an even distribution of more or less hemispherical protrusions (Figures 3 and 4). Polystyrene, PET, and PEEK displayed topographi-

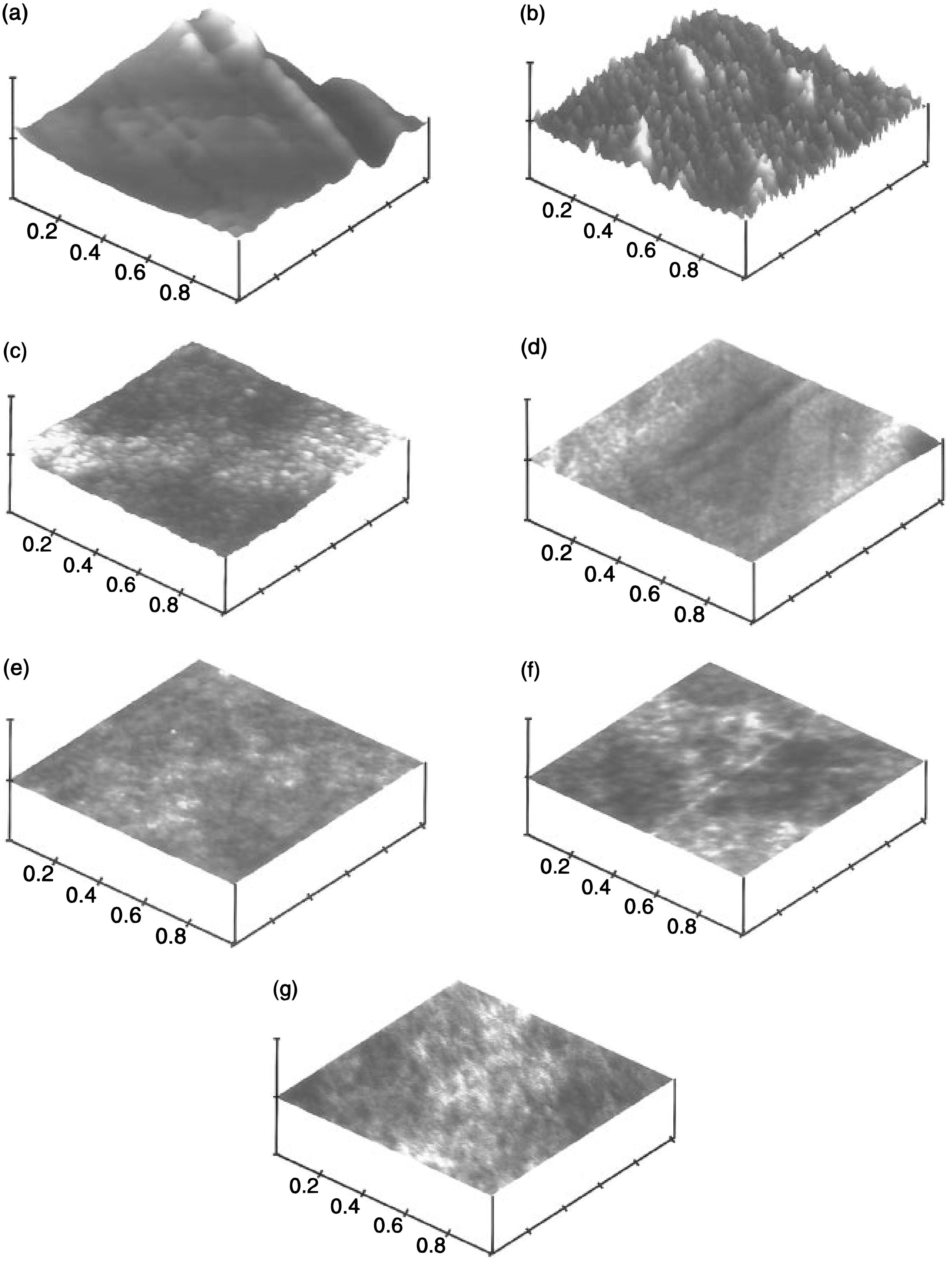


Figure 3. Atomic force micrographs of untreated (a) polystyrene, (b) poly(ethylene terephthalate), (c) poly(ether ether ketone), (d) poly(bisphenol carbonate), (e) poly(bisphenol sulfone), (f) poly(ether sulfone), and (g) poly(dimethylphenylene oxide). $x = 0.2$ μm/div, $z = 0.1$ μm/div.

cal features prior to plasma treatment, and these must have been introduced into the surface during film manufacture (Figure 3): PET has an even distribution of narrow, non-hemispherical protrusions; PEEK displays an array of relatively low height, circular features; and polystyrene exhibits a small number of relatively low height ridges. The globules seen on O_2 plasma treated polysulfone were found to be slightly irregular

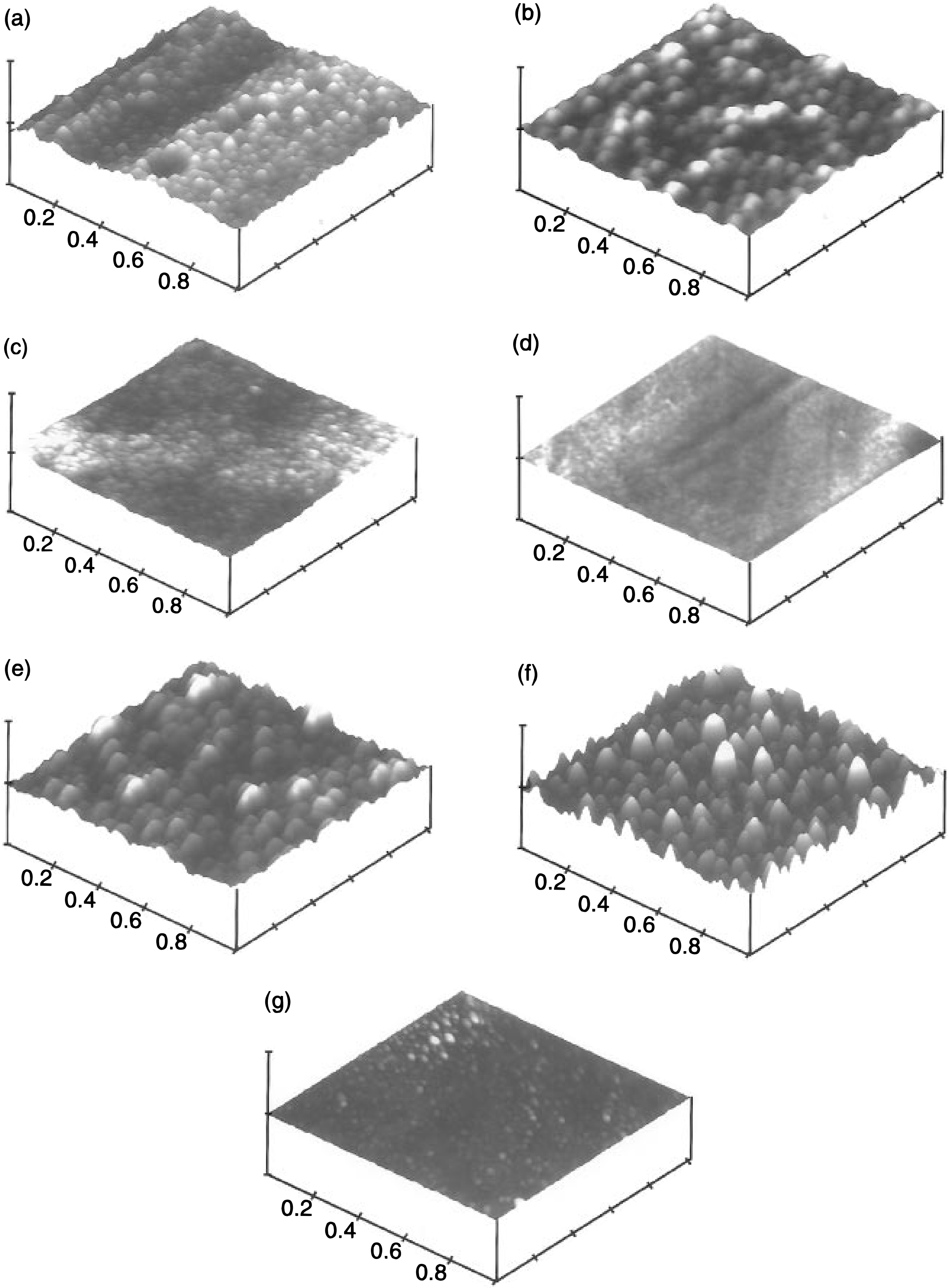


Figure 4. Atomic force micrographs of O_2 plasma treated (a) polystyrene, (b) poly(ethylene terephthalate), (c) poly(ether ether ketone), (d) poly(bisphenol carbonate), (e) poly(bisphenol sulfone), (f) poly(ether sulfone), and (g) poly(dimethylphenylene oxide). $x = 0.2$ μm/div, $z = 0.1$ μm/div.

in shape.[30] Solvent washing resulted in a diminishing of the globular features introduced during O_2 plasma treatment to give rise to an overall smoothing of the surface texture (Figure 5).

Discussion

Intense $\pi-\pi^*$ satellite shake-up lines appear on the high binding energy side of XPS core photoelectron

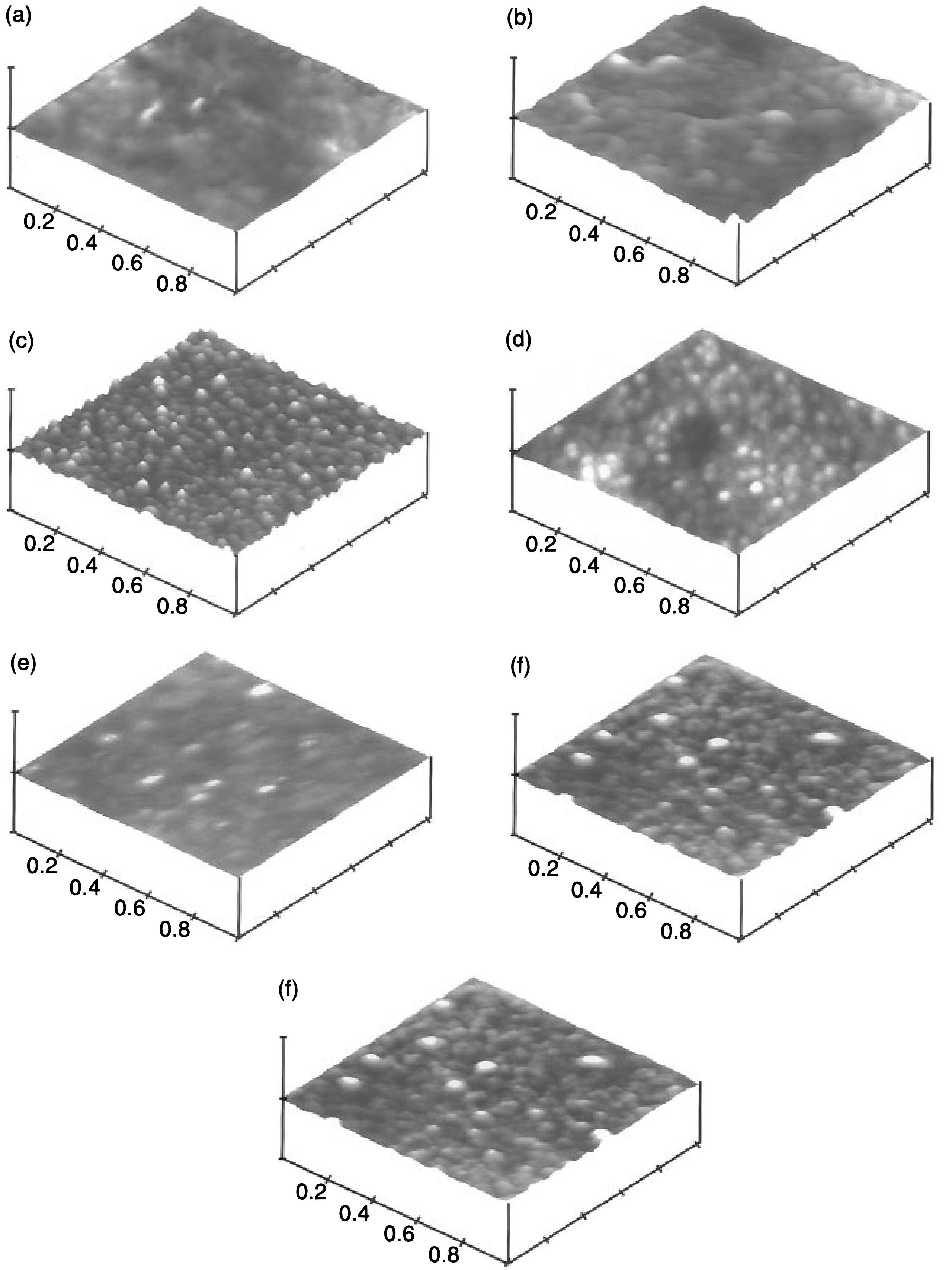


Figure 5. Atomic force micrographs of solvent washed/O_2 plasma treated (a) polystyrene, (b) poly(ethylene terephthalate), (c) poly(ether ether ketone), (d) poly(bisphenol carbonate), (e) poly(bisphenol sulfone), (f) poly(ether sulfone), and (g) poly(dimethylphenylene oxide). $x = 0.2$ μm/div, $z = 0.1$ μm/div.

emission lines for unsaturated systems, due to valence orbital excitations during the ejection of core-level photoelectrons.[31,32] The high degree of delocalization contained in phenyl π ring orbital systems yields well-resolved C(1s) $\pi-\pi^*$ shake-up structures.[33] A correlation is found between the C(1s) $\pi-\pi^*$ shake-up intensity for clean polymers and the proportion of carbon centers located in a phenyl environment for the untreated

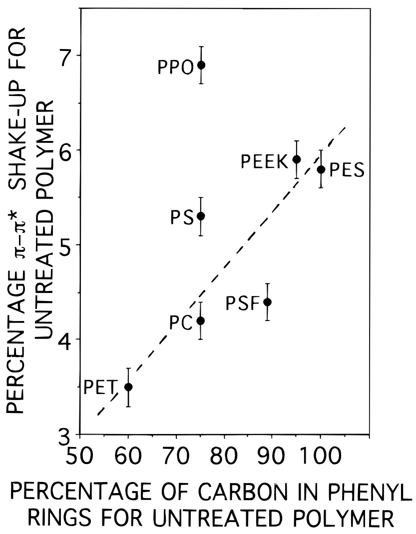


Figure 6. Percentage $\pi-\pi^*$ shake-up of total XPS C(1s) intensity for the untreated polymer versus percentage of carbon centers in phenyl environments in the untreated polymer. Error bars represent standard deviations.

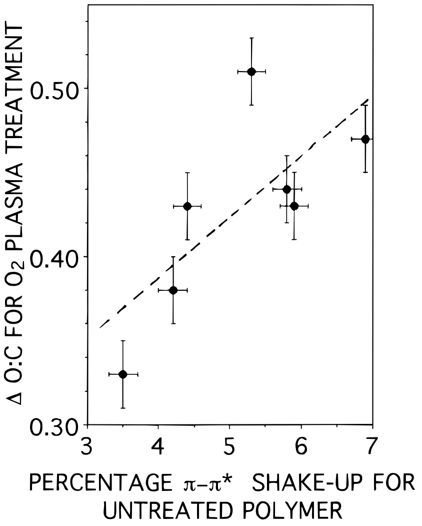


Figure 7. Extent of oxidative attack (before solvent washing) versus percentage $\pi-\pi^*$ shake-up of total XPS C(1s) intensity for the untreated polymer. Error bars represent standard deviations.

polymer structure (Figure 6). The anomalously high $\pi-\pi^*$ shake-up peak observed for poly(dimethylphenylene oxide) may result from a greater net charge density on the phenyl carbon atoms, due to electron donation into the aromatic ring system from the adjacent methyl groups.[34]

Substrate–plasma reactivity can be expected to be influenced by the chemical structure[35] and aromaticity[36] of the underlying polymer. Previous extended-Hückel molecular orbital calculations have predicted that phenyl-containing polymers are more resistant toward oxygen plasma etching compared to saturated polymers and are therefore more likely to become highly oxygenated during oxygen plasma treatment.[37] Our results have shown that the extent of oxygenation obtained during O_2 plasma treatment is directly dependent upon $\pi-\pi^*$ shake-up intensity measured in the C(1s) XPS spectrum for the untreated polymer (Figure 7).

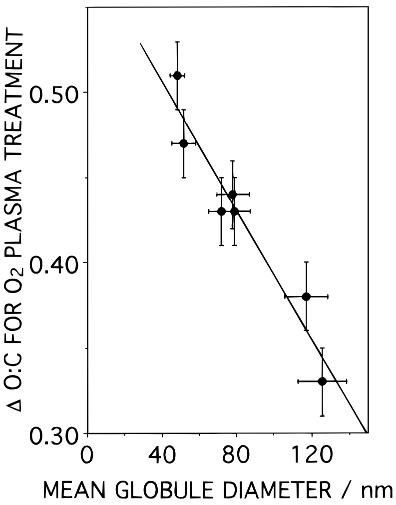


Figure 8. Extent of oxidative attack (before solvent washing) versus mean globule size. Error bars represent standard deviations.

Low pressure O_2 glow discharges contain a range of energetic species which are capable of reacting with polymer surfaces: molecular, atomic, and electronically excited oxygen moieties, in addition to electrons, ions, and electromagnetic radiation.[38] Oxygen atoms are produced mainly by collisions of ions, electrons, and photons with O_2 molecules contained in the plasma and are believed to be the prominent reactive chemical species.[39] Also since the level of gas ionization[40] is less than 1 in 10^5 and retarding collisions in the plasma boundary further attenuate the chance of ions reacting with the polymer surface,[41] it must be a combination of vacuum UV irradiation and oxygen atoms which gives rise to most of the observed polymer oxidation.[42] Electromagnetic radiation generated by the O_2 glow discharge includes an intense line at 130 nm,[43,44] which can lead to photoexcitation of π electrons located in the polymer phenyl rings to antibonding π^* orbitals.[45,46] Such singly occupied π orbitals are highly susceptible to attack by incident nucleophiles (e.g., atomic oxygen).[41,47] Hence the ease of $\pi-\pi^*$ transitions observed by XPS for each untreated polymer can be used as a good measure of polymer reactivity toward an O_2 plasma. Attenuation of the $\pi-\pi^*$ shake-up signal during O_2 plasma treatment of all of the polymers studied confirms substantial oxidative attack at phenyl centers.[48,49]

Modification of surface morphology by O_2 plasma treatment is believed to be a combination of vigorous reactions between the polymer and atomic oxygen,[50] as well as photon- and ion-induced physical degradation,[50] melting and recrystallization,[51] and agglomeration of the surface species formed during plasma oxidation and chain scission.[51,52] Globular features were evident for all the polymers following oxygen plasma treatment, regardless of the level of crystallinity present in the bulk of the polymer. A correlation is evident between the mean diameter of globules and the extent of plasma oxidative attack, Δ(O:C), measured by XPS for each treated polymer (Figure 8). This interdependency between surface chemical and topographical characteristics for O_2 plasma treatment of polymer surfaces suggests that the degree of oxygenation determines the final surface morphology. The majority of the XPS signal (sampling depth $\sim$ 2 nm) is measured from the O_2 plasma generated surface texture.[17] No trend was established between O_2 plasma modified surface topography and parent polymer melting point or glass transition temperature; this confirms that surface physical modification does not occur exclusively via a polymer melting mechanism. The observation of globules on the surface of corona-treated polypropylene[51,52] and the removal of oxidized surface species upon solvent washing of discharge-treated polymers[53−56] has been attributed to aggregation and solvation, respectively, of low molecular weight oxidized material formed during electrical discharge treatment. Conglomeration of plasma-oxidized polymer material is driven by minimization of polar surface energy at the interface with the underlying unmodified substrate.[57] One would expect the contact angle of the globules of modified material to increase and the mean diameter of globules to decrease[58] with increasing level of oxygenation (Figure 8). The proportion of oxygenated material and globular features which remained intact during rinsing in a polar/nonpolar solvent mixture must have undergone either extensive cross-linking or minimal chain scission.[53,57,59,60]

Conclusions

Polymer chemical structure can bear a strong influence upon the level of surface oxygenation attained during O_2 plasma treatment. The C(1s) π−π* shake-up intensity measured for phenyl-containing polymers is a good measure of their reactivity toward an O_2 glow discharge. This can be accounted for in terms of vacuum UV photoexcitation of phenyl rings followed by reaction with plasma-generated oxygen atoms. Polymer chain scission produces oxidized low molecular weight material, which rearranges to form small globules in order to minimize polar surface energy. A correlation has been found between mean globule size and the extent of surface oxygenation.

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