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Surface Segregation and Plasma Oxidation of Poly(dimethylsiloxane)-Doped Polyolefins

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ABSTRACT: The surface segregation behavior of poly(dimethylsiloxane)/polyethylene (PDMS/PE) and poly(dimethylsiloxane)/polypropylene (PDMS/PP) blends has been studied using X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). It is shown that the overall concentration of silicon-containing species at the surface in these systems can be controlled by solvent washing, annealing, and plasma treatment. In the case of plasma oxidation, well-adhered SiO_x coatings are produced.

1. Introduction

The physicochemical nature of polymer surfaces is important for many everyday applications[1] (e.g., adhesion, wettability, friction, dye uptake, gloss, biocompatibility, gas permeability, etc.). Blending two or more polymers is one widely practiced route for making new polymeric materials with surface and bulk properties which are different compared to the parent homopolymers. For some polymer blend systems, preferential enrichment of one component at the surface may occur as a consequence of differences in surface energy, with the lowest surface energy constituent becoming preferentially adsorbed at the air−solid interface.[2] In addition, polymer−polymer miscibility factors within the bulk often also need to be taken into account.[3]

Poly(dimethylsiloxane)/polyolefin blends are a case in point, where the lower surface energy poly(dimethylsiloxane) component can migrate toward the surface. Such poly(dimethylsiloxane) enrichment can be beneficial for lowering friction, acting as an antiblocking agent,[4,5] fire proofing,[6] and improving release behavior.[7] In this article, the surface segregation behavior of poly(dimethylsiloxane)/polyethylene and poly(dimethylsiloxane)/polypropylene melt-blown films is compared in order to determine to what extent the nature of the polyolefin host influences surface composition. Plasma oxidation of these blends has also been explored with the aim of generating a well-adhered SiO_x surface layer, thereby providing an alternative and more direct route for making SiO_x-coated substrates compared to conventional approaches (e.g., PECVD,[8] electron beam evaporation,[9] etc.).

2. Experimental Section

Linear poly(dimethylsiloxane) (PDMS) containing a $-SiMe_2-CH{=}CH_2$ end block (Dow Corning, $M_w = 500\,000$ and $T_g = 146$ K) was mixed with linear low-density polyethylene/low-density polyethylene (LLDPE/LDPE) or polypropylene (PP) during film extrusion via the bubble-film process (Table 1).

Table 1. Physical Properties of Polyolefin Constituents[a]

polymer	$M_n \times 10^3$	$M_w \times 10^3$	M_w/M_n	T_g/K	T_m/K
LDPE/LLDPE	29	104	3.6	148	390.5
PP	49	204	4.2	265	437.5

[a] M_n = number-average molar mass, M_w = weight-average molar mass, M_w/M_n = heterogeneity index, T_g = glass transition temperature, and T_m = melting point.

Solvent washing studies were carried out on these films for 30 s using an ultrasonic bath containing mixtures of cyclohexane (BDH, 99.5% purity)/propan-2-ol (BDH, 99.7% purity). Subsequent annealing experiments were undertaken in a vacuum oven (LTE, Qualivac). Oxygen plasma treatment of these polymer blend surfaces entailed 60 s exposures at powers ranging from 2 to 20 W in a cylindrical glass reactor (4.5 cm diameter, 505 cm^3 volume) enclosed in a Faraday cage. The chamber was fitted with a gas inlet, a thermocouple pressure gauge, and a two-stage mechanical rotary pump attached to a liquid air cold trap (base pressure of 2×10^{-3} mbar and a leak rate better than 1.2×10^{-3} cm^3 min^{-1}). A copper coil (5 mm diameter, 10 turns, spanning 8−16 cm from the gas inlet) wound externally around the reactor walls was coupled to a 13.56 MHz rf power supply via an LC matching circuit. Prior to each treatment, the chamber was cleaned with a 40 W air plasma at 0.2 mbar pressure for 10 min. Next, a piece of the polymer substrate was placed into the center of the reactor and purged with oxygen (BOC, 99.6% purity) at 0.8 mbar pressure for 10 min, followed by plasma ignition at 0.2 mbar pressure and 1 cm^3 min^{-1} flow rate. Upon completion of plasma treatment, oxygen gas was allowed to continue to flow over the substrate for a further 5 min, prior to bringing the reactor up to atmosphere.

A Kratos ES300 electron spectrometer equipped with a Mg Kα X-ray source (1253.6 eV) and a concentric hemispherical analyzer (CHA) was used for XPS analysis. Photoemitted electrons were collected at a takeoff angle of 30° from the substrate normal, with electron detection in the fixed retarding ratio (FRR, 22:1) mode. XPS spectra were accumulated on an interfaced PC computer and fitted to Gaussian peak shapes with equal full width at half-maximum (fwhm)[10] using a Marquardt minimization algorithm. Instrument sensitivity factors were taken as C(1s):O(1s):Si(2p) equals 1.00:0.57:0.72.

AFM micrographs of the polymer blend film surfaces were acquired with a Digital Instruments Nanoscope III operating

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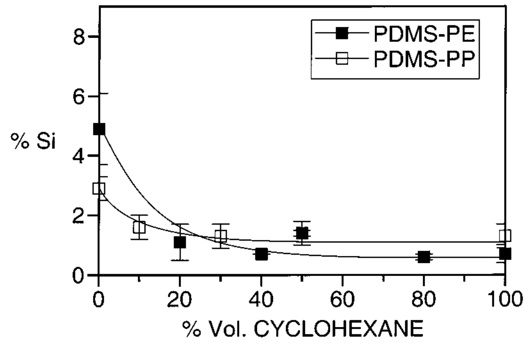

Figure 1. Variation in silicon concentration at the surface of 2.5 wt % PDMS-doped polyethylene and polypropylene films following washing in cyclohexane/propan-2-ol solvent mixtures for 30 s.

in Tapping Mode.[11] These studies used a stiff silicon cantilever oscillating at close to its resonance frequency. In addition to height images, the corresponding phase images reflecting the mechanical properties of the surface were obtained by choosing a set point: free amplitude ratio of 0.5 (set point = 50 nm; free amplitude = 100 nm).[12] All images were acquired in air at room temperature and are presented as unfiltered data. Large area scans were also taken on the 100 μm × 100 μm scale in order to check that the reported images were representative of the whole surface. Cross-sectional microtoming studies of the polymer blend films were carried out at 243 K using a cryogenic microtoming apparatus (Leica RM 2165).

Sessile drop contact angle measurements at 20 °C were made with a video capture apparatus (A.S.T. Products VCA2500XE). The chosen probe liquid was high-purity water (B.S. 3978 Grade 1).

3. Results

The amount of poly(dimethylsiloxane) removed from the polymer blend surfaces by washing was found to be dependent upon the binary solvent mixture composition (Figure 1). This constituted combining cyclohexane and propan-2-ol (known to be good and bad solvents, respectively, for poly(dimethylsiloxane), based upon standard solubility parameter arguments). XPS analysis showed that more silicon-containing material was lost from the surface with increasing nonpolar (cyclohexane) content. This trend provided a means for controlling the surface composition of the PDMS-doped polyolefin substrates. It was found that washing in a 50/50 cyclohexane/propan-2-ol solvent mixture for 30 s resulted in virtually all the poly(dimethylsiloxane) species being lost from the top 3–5 nm of the substrate (i.e., the Si(2p) XPS sampling depth[13]). These conditions were taken as being optimum for removal of poly(dimethylsiloxane) from the surface region of the polymer blend, without significant effect upon the bulk composition.

Subsequent annealing in a vacuum oven for 30 min gave rise to the diffusion of poly(dimethylsiloxane) material from the near-surface region toward the surface (Figure 2). A temperature dependency was found which reached a maximum at around 100 °C for polyethylene and 80 °C for polypropylene. In the latter case, the amount of poly(dimethylsiloxane) detected by XPS dropped off at higher annealing temperatures. In fact, surface segregation of PDMS was always greater for the polyethylene-based blend compared to its polypropylene counterpart and was also found to correlate to the overall bulk poly(dimethylsiloxane) content at low concentrations (Figure 3). A maximum level of segregation was reached at concentrations above ca. 1.0 wt % bulk loading of PDMS. The absence of any binding energy shift in the Si(2p) spectra from 102.0 eV confirmed that poly(dimethylsiloxane) species were not undergoing oxidation during annealing and migration toward the air–solid interface. Consecutive solvent washing followed by annealing cycles eventually gave rise to almost total exhaustion of PDMS species from the near-surface region (i.e., heating could no longer replenish the surface with poly(dimethylsiloxane) moieties after solvent washing) (Figure 4).

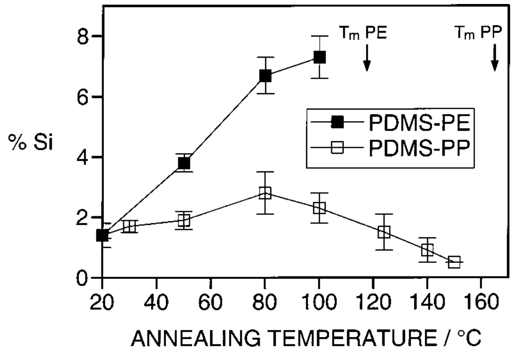

Figure 2. Silicon concentration at the surface of 2.5 wt % PDMS-doped polyethylene and polypropylene films following washing in a 50/50 cyclohexane/propan-2-ol solvent mixture for 30 s and then annealing at various temperatures for 30 min.

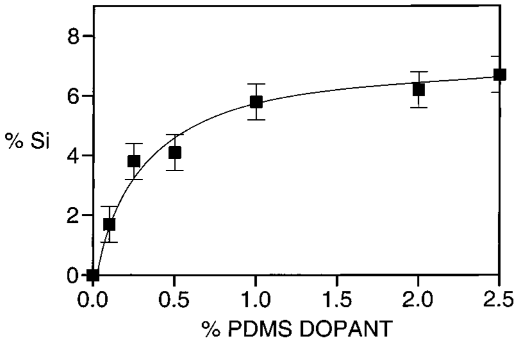

Figure 3. Silicon concentration at the surface of PDMS-doped polyethylene films as a function of bulk poly(dimethylsiloxane) loading (wt %), following washing in 50/50 cyclohexane/propan-2-ol solvent mixture for 30 s and then annealing at 80 °C for 30 min.

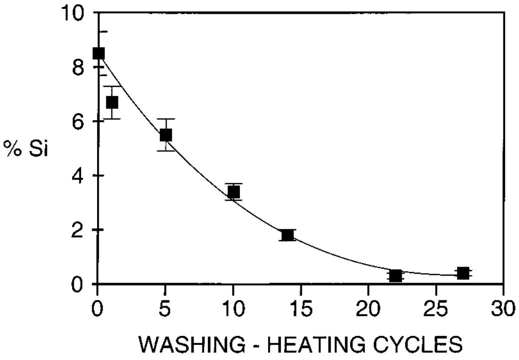

Figure 4. Variation in XPS silicon concentration at the surface of 2.5 wt % PDMS-doped polyethylene film as a function of the number of washing–heating cycles.

Oxygen plasma treatment of poly(dimethylsiloxane)-doped polyolefin films which had previously undergone one solvent washing/annealing cycle (i.e., contained a well-defined quantity of poly(dimethylsiloxane) at the surface) resulted in surface oxidation (Figure 5). Interestingly, the surface composition following oxygen plasma treatment was found to be very similar for both the

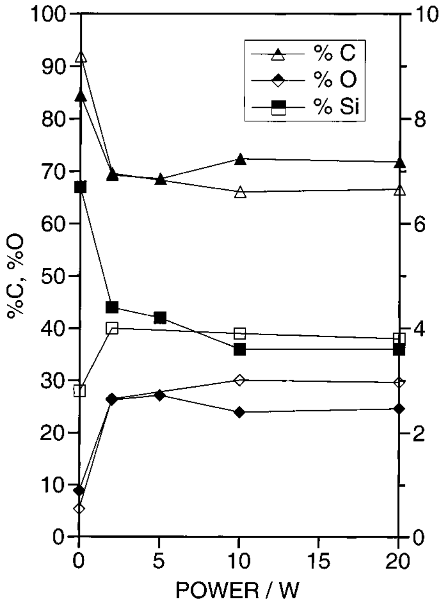

Figure 5. Change in elemental composition at the surface of 2.5 wt % PDMS-doped polyethylene (shaded symbols) and polypropylene (unshaded symbols) films as a function of oxygen glow discharge power level.

polyethylene and polypropylene hosts, despite the former containing a much larger concentration of poly(dimethylsiloxane) at the surface prior to plasma exposure. In addition, the Si(2p) peak shifted from 102.0 eV (poly(dimethylsiloxane)) to 103.4 ± 0.1 eV (SiO_x)[14,15] (Figure 6). This was accompanied by the appearance of oxidized C(1s) moieties:[14] $\underline{C}{-}CO_2$ at 285.7 eV, $\underline{C}{-}O{-}$ at 286.6 eV, $\underline{C}{=}O$, $O{-}\underline{C}{-}O$ at 287.8 eV, $-O{-}\underline{C}{=}O$ at 289.0 eV, and $-O{-}\underline{C}O{-}O{-}$ at 290.0 eV. Also, a broadening of the O(1s) envelope toward higher binding energies was noted; however, accurate deconvolution of O(1s) spectra was not possible due to the close overlap of various different oxygen environments:[14-17] e.g., polysiloxane at 532.6 eV, $Si\underline{O}_2$ at 532.5–533.2 eV, $C{-}\underline{O}{-}$ at ~532.6 eV, $C{=}\underline{O}$ at ~532.3 eV, $-\underline{O}{-}C{=}O$ at ~533.6 eV, $-\underline{O}{-}CO{-}\underline{O}{-}$ at ~533.9 eV, etc. Control plasma oxidation experiments using undoped polyolefin films did not yield any silicon at the surface, thereby ruling out the possibility of plasma-assisted sputtering off the reactor walls.

Washing low-power plasma oxidized 2.5 wt % poly(dimethylsiloxane)-doped polyethylene surfaces in a 50/50 cyclohexane/propan-2-ol solvent mixture for 30 s gave rise to an overall increase in the proportion of silicon-containing species at the surface (Figure 7). This is most likely to be due to the removal of low molecular weight oxidized polyolefin material, as confirmed by the characteristic attenuation of the high binding energy shoulder in the C(1s) envelope.[18] Annealing of these plasma-treated surfaces at 80 °C gave rise to a substantial buildup of poly(dimethylsiloxane) at the surface. Some of this poly(dimethylsiloxane) material could subsequently be removed by washing in the binary solvent mixture (this being more prevalent for the polypropylene substrate). However, the amount of oxidized silicon species (SiO_x) appeared to be resilient toward solvent washing and annealing; rather, it was the mobile poly(dimethylsiloxane) constituent which altered the overall concentration of elemental silicon detected by XPS at the polymer blend surface.

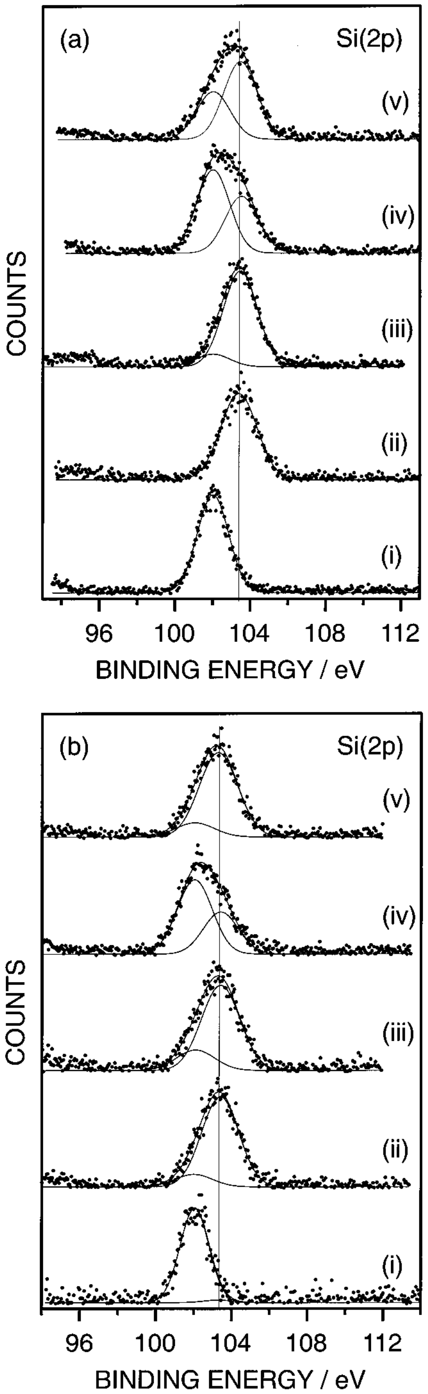

Figure 6. Si(2p) XPS spectra of PDMS-doped (a) polyethylene and (b) polypropylene, where (i) washed in 50/50 cyclohexane/propan-2-ol solvent mixture for 30 s and then heated at 80 °C for 30 min; (ii) 2 W O_2 plasma treatment for 60 s; (iii) 2 W O_2 plasma treatment for 60 s followed by washing in 50/50 cyclohexane/propan-2-ol solvent mixture for 30 s; (iv) 2 W O_2 plasma treatment for 60 s followed by annealing at 80 °C for 30 min; and (v) 2 W O_2 plasma treatment for 60 s followed by annealing at 80 °C for 30 min and then washing in 50/50 cyclohexane/propan-2-ol solvent mixture for 30 s. (All spectra have been normalized.)

Consecutive plasma oxidation followed by annealing cycles was undertaken in order to maximize SiO_x formation at the polymer blend surfaces (Figure 8). This buildup of SiO_x reached limiting values after four cycles, with poly(dimethylsiloxane)-doped polyethylene yielding approximately twice as much SiO_x at the surface compared to its polypropylene counterpart.

Phase imaging atomic force microscopy clearly showed the presence of poly(dimethylsiloxane) regions on the

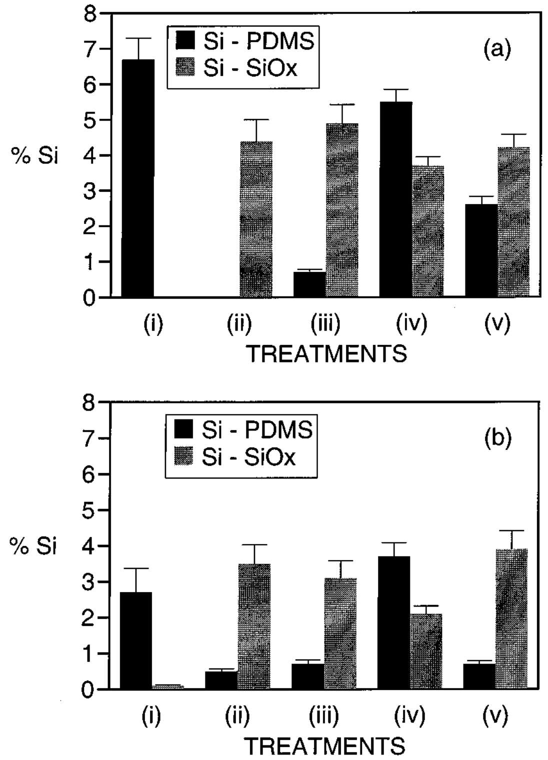

Figure 7. Relative amount of silicon associated with PDMS vs SiO_x at the surface of 2.5 wt % PDMS-doped: (a) polyethylene and (b) polypropylene, where (i) solvent washed and then heated at 80 °C for 30 min; (ii) 2 W O_2 plasma treatment for 60 s; (iii) 2 W O_2 plasma treatment for 60 s followed by washing in 50/50 cyclohexane/propan-2-ol solvent mixture for 30 s; (iv) 2 W O_2 plasma treatment for 60 s followed by annealing at 80 °C for 30 min; and (v) 2 W O_2 plasma treatment for 60 s followed by annealing at 80 °C for 30 min and then washing in 50/50 cyclohexane/propan-2-ol solvent mixture for 30 s.

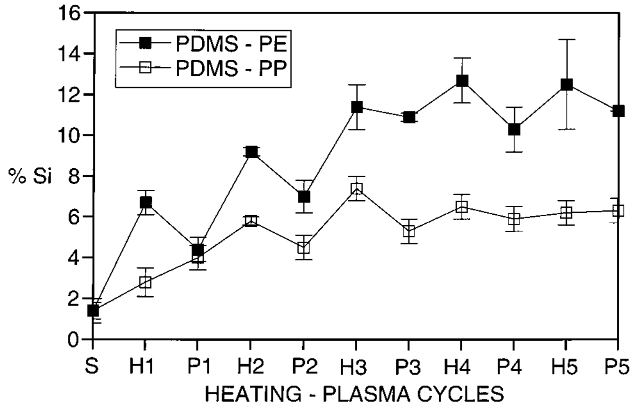

Figure 8. Amount of silicon present at the surface of 2.5 wt % PDMS-doped polyethylene and polypropylene films as a function of the number of heating–plasma cycles (S = solvent washing in 50/50 cyclohexane/propan-2-ol mixture for 30 s; H = annealing at 80 °C for 30 min; P = 2 W O_2 plasma treatment for 60 s).

surface of the as-prepared films (Figure 9). The size of these areas corresponded to the intensity of the Si(2p) XPS signal. Solvent washing caused these phase contrast patches to disappear, while subsequent annealing gave rise to their reemergence at the surface. Plasma oxidation produced silicon oxide domains, which were found to be stable toward solvent washing. AFM phase images also confirmed that repetitive annealing followed by oxygen plasma treatment cycles resulted in the buildup of silicon oxide moieties across the poly(dimethylsiloxane)/polyolefin blend surfaces in accordance with the rise in the corresponding Si(2p) XPS signal.

Cross-sectional analysis of the bulk of these films demonstrated that the poly(dimethylsiloxane) is present as separated microphases (1–4 μm in length and 1 μm in width for 2.5 wt % poly(dimethylsiloxane)/polyethylene film, Figure 10). The poly(dimethylsiloxane) domains appeared elongated along the stretch direction employed during film production.

Water contact angle measurements showed that the poly(dimethylsiloxane)/polyolefin films which had undergone repetitive annealing/plasma oxidation cycling were as wettable but yet more stable to hydrophobic recovery compared to oxygen plasma treated pure poly(dimethylsiloxane) (Figure 11). Also, the poly(dimethylsiloxane)/polyolefin films became more resilient toward hydrophobic recovery with repetitive annealing/plasma oxidation cycles.

4. Discussion

The bulk miscibility behavior of polymer blends can be explained in terms of thermodynamics (entropic and enthalpic factors), as defined by the Flory–Huggins theory:[19]

$$\frac{\Delta G_m}{kT} = \underset{\text{combinatorial term}}{N_A \ln \phi_A + N_B \ln \phi_B} + \underset{\text{contact dissimilarity}}{N_A \phi_B \chi_{AB}} \quad (1)$$

The first two terms account for the combinatorial entropy of mixing,[19] while the last term relates to the enthalpy of mixing, ΔH_m, and is governed by the specific interaction between the polymer monomers, as represented by the Flory–Huggins interaction parameter, χ_{AB}. This parameter is effectively a measure of the difference in energy (enthalpy of mixing) between a chain of homopolymer A immersed in pure homopolymer A compared to when it is present in pure homopolymer B. This provides an indication of the likelihood for A–A and B–B interactions to be replaced by A–B interactions during mixing of the two homopolymers.[20] Negative values of χ_{AB} predict miscibility, whereas positive values indicate immiscibility, with the magnitude corresponding to the strength of enthalpic interactions between the two homopolymers. For most polymer pairs, the enthalpy of mixing tends to be endothermic (positive), and on this basis the Flory–Huggins interaction parameter, χ_{AB}, can be estimated using solubility parameters:

$$\chi_{AB} = \frac{V_R}{RT}(\delta_A - \delta_B)^2 \quad (2)$$

where V_R is the reference volume. Literature solubility value ranges for the polymers under consideration are reported as[21] δ(PDMS) = 14.9–15.5 MPa$^{1/2}$, δ(PE) = 15.85–18.0 MPa$^{1/2}$, and δ(PP) = 18.8–19.2 MPa$^{1/2}$. On the basis of the high molecular weight polyolefins employed in the current investigation, poly(dimethylsiloxane) would be expected to be more immiscible with polypropylene than polyethylene. Given that polymer–polymer immiscibility can lead to surface enrichment,[3] there should be more PDMS surface segregation for the poly(dimethylsiloxane)/polypropylene blend system. In fact, the opposite trend has been found (Figure 2), thereby indicating that other factors must be taken into consideration, e.g., surface energy, the polymer molec-

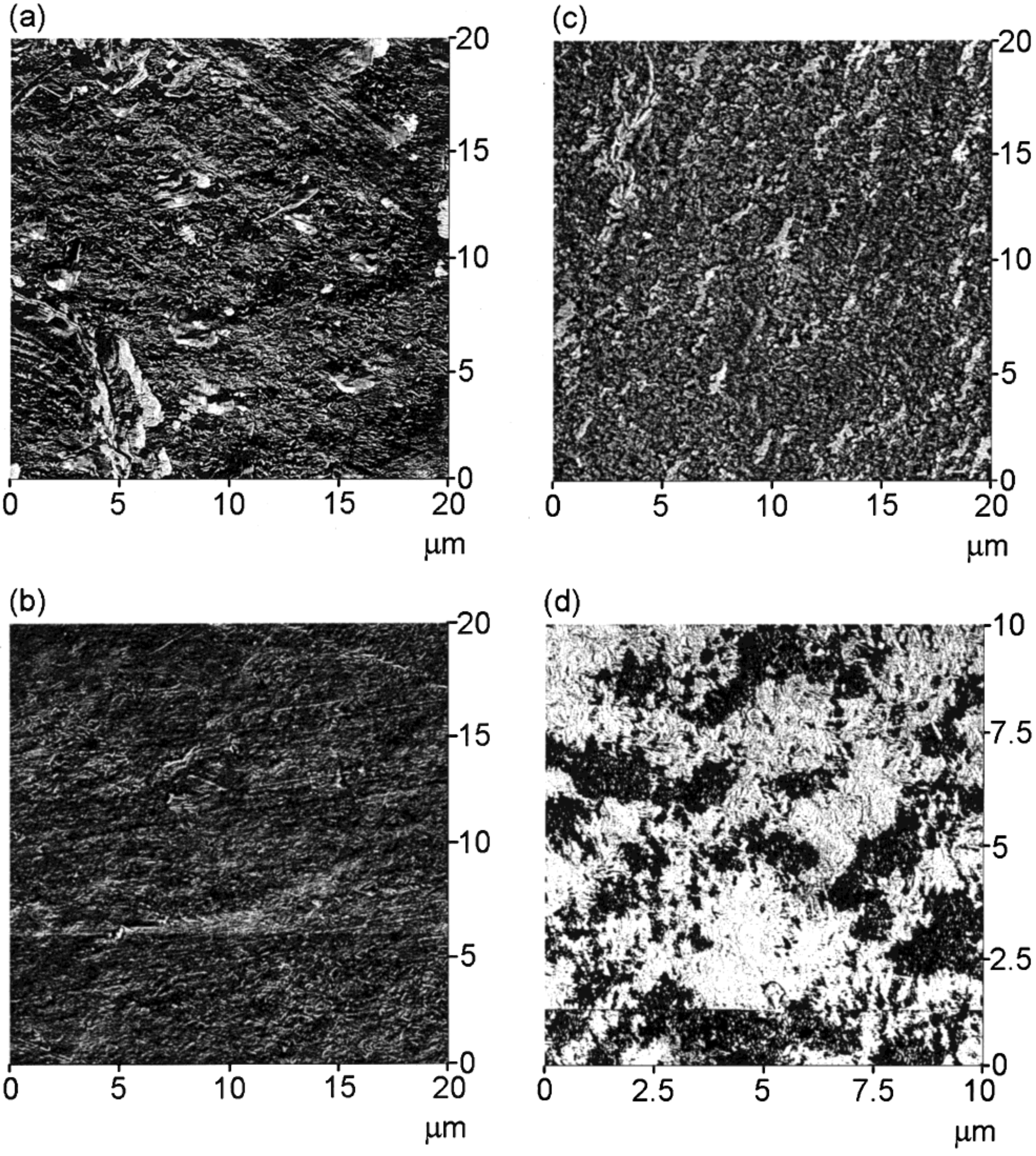

Figure 9. AFM phase images of 2.5 wt % PDMS-doped polyethylene: (a) before washing; (b) after solvent washing; (c) solvent washing followed by annealing at 80 °C for 30 min; and (d) following four heating−plasma cycles.

ular weight,[22−26] film crystallinity,[22] and the kinetics of polymer chain diffusion toward the surface region during film formation.[27]

In the case of surface energy, there is a large difference between poly(dimethylsiloxane) and both types of polyolefin ($\gamma_{\mathrm{PDMS}} = 21$ mJ m^{-2}, $\gamma_{\mathrm{PE}} = 36$ mJ m^{-2}, $\gamma_{\mathrm{PP}} = 29$ mJ m^{-2}).[21] Therefore, the lower surface energy constituent, poly(dimethylsiloxane), can be expected to segregate toward the surface of the PDMS/polyolefin blends under investigation. The larger difference in surface energy between the constituents of the poly(dimethylsiloxane)/polyethylene blend system helps to explain the greater level of PDMS surface enrichment in this case.

Furthermore, polyethylene has a lower average molecular weight, glass transition temperature (T_g), and melting point (T_m) compared to polypropylene (Table 1). On this basis, annealing at 80 °C will produce greater segmental motion of the polyethylene polymeric chains compared to their polypropylene counterparts, which should lead to higher diffusion rates of poly(dimethylsiloxane) toward the air−solid interface in the case of the polyethylene matrix compared to its polypropylene counterpart. The experimental data supports this description up to near the melting point of polyethylene (Figure 2). At higher temperatures, the poly(dimethylsiloxane)/polypropylene system exhibits a drop in PDMS surface segregation, probably as a consequence of

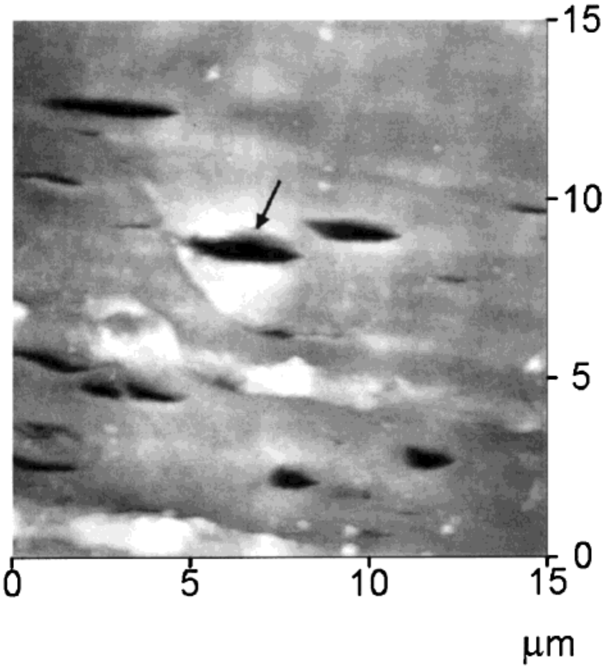

Figure 10. Cross-section AFM height image of microtomed 2.5 wt % PDMS-doped polyethylene film. (Film stretch direction is from left to right, and the arrow indicates the PDMS separated microphases.)

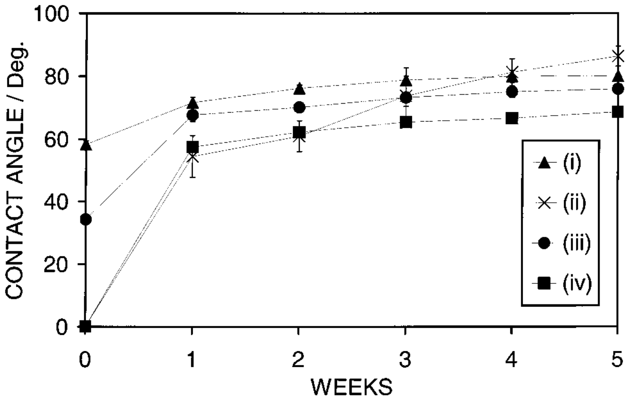

Figure 11. Water contact angle measurements as a function of aging time: (i) 2 W O_2 plasma treatment for 60 s of polyethylene; (ii) 2 W O_2 plasma treatment for 60 s of PDMS; (iii) washed and annealed 2.5 wt % PDMS-doped polyethylene followed by 2 W O_2 plasma treatment for 60 s; and (iv) following four heating−plasma cycles of 2.5 wt % PDMS-doped polyethylene.

thermal desorption of low molecular volatile poly(dimethylsiloxane) moieties away from the polypropylene surface in the vacuum oven[28] or, alternatively, competitive migration of low molecular weight polypropylene chains toward the surface favored by changing kinetic, entropic, and surface energy factors.[3,24−26,29]

Nonisothermal plasma modification of these polymer blends is attractive from a technological perspective in terms of speed, cost, and minimal environmental impact. Although plasma treatment of bulk poly(dimethylsiloxane) has been widely explored in the past for improving wettability[30,31] and adhesion,[31,32] there are associated drawbacks leading to hydrophobic recovery and the formation of microcracks at the surface.[30,33] The current approach comprising heating−plasma treatment cycles leads to wetting behavior which is comparable to that observed for oxygen plasma treated bulk poly(dimethylsiloxane); however, there is the benefit of slower hydrophobic recovery (water contact angle of untreated PDMS = 116 ± 2°) (Figure 11). This can be attributed to the well-adhered SiO_x layer and/or reduced diffusion of low surface energy material from within the bulk.[34]

5. Conclusions

Surface segregation of poly(dimethylsiloxane) from poly(dimethylsiloxane)/polyolefin blend films can be controlled by solvent washing followed by annealing. Plasma oxidation of these surfaces is found to lead to the growth of stable ultrathin layers of SiO_x.

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