Surface Segregation of Components in Poly(vinyl chloride)–Polydimethylsiloxane and Polystyrene–Poly(propylene oxide) Solvent-Cast Blends

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Received 19 March 1997; accepted 15 August 1997

ABSTRACT: X-ray photoelectron spectroscopy and scanning electron microscopy are used to study the surface composition and morphology of poly(vinyl chloride)–polydimethylsiloxane (PVC–PDMS) and polystyrene–poly(propylene oxide) (PS–PPO) solvent-cast blends as a function of the blend composition and constituent molecular weights. The PVC–PDMS blends show a pronounced surface enrichment of PDMS, which is higher the lower the molecular weight of PDMS. The surface behavior of the PPO–PS blends is strongly dependent on the solvent used. Despite the much lower surface tension of PPO compared to that of PS, no surface segregation of PPO is observed in the PPO–PS blends cast from tetrahydrofuran, while the blends cast from chloroform exhibit a high surface enrichment of PPO. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 517–522, 1998

Key words: surface segregation; polymer blends

INTRODUCTION

It has been recognized for a long time that the surface composition of a multicomponent polymer (a copolymer or a polymer blend) may differ substantially from its bulk composition. Roughly, the phenomenon of surface segregation can be associated with two factors (for a comprehensive discussion, see ref. 1). One is the trend of the system to decrease the surface energy by enriching the surface with a lower-surface energy component so as to diminish "missing neighbor effects."[1] The second factor is the trend of the system to reduce the number of energetically unfavorable contacts between unlike components by driving the minority component toward the surface. While the first factor can be measured by the difference in surface energy between the components, $\gamma_B - \gamma_A$, the second factor can be appreciated from the Flory interaction parameter, χ_{AB}.

In most cases, taking into account the two above factors is sufficient to rationalize the equilibrium surface composition of a polymer and the dependence of this composition on the length of the polymer chain and its individual segments (such as blocks and grafts). Thus, block copolymers AB exhibit a growth in the extent of surface segregation with increasing block lengths,[2] which

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Correspondence to: A. J. Pertsin.

Contract grant sponsor: Russian Foundation for Basic Research; contract grant number: 96-03-32412.

Contract grant sponsors: Fund ação de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPRJ); Conselho de Ensino para Graduados e Pesquisa (CEPG-UFRJ).

Journal of Applied Polymer Science, Vol. 68, 517–522 (1998)

CCC 0021-8995/98/040517-06

can be explained by increasing the incompatibility of the components (i.e., increasing χ_{AB}). Blends of compatible homopolymers A–B show an increase in surface segregation with increasing molecular weight (MW) of the higher surface energy component, say B, which is attributed to increasing γ_B and, hence, to increasing the driving force for surface segregation, $\gamma_B - \gamma_A$.[3]

Whereas the equilibrium surface behavior of polymers has been more or less understood, comparatively little is known about the factors responsible for the composition of a polymer surface formed under nonequilibrium conditions. In situations of practical interest, such as solvent casting or injection molding, thermodynamic considerations often prove to be useless in interpreting the observed surface behavior. Thus, we have recently reported[4] that the surface segregation of polydimethylsiloxane (hereafter PDMS or simply siloxane) in dilute PDMS–polychloroprene (PCP) blends cast from a common solution in chloroform decreases substantially with increasing MW of the siloxane additive. In 1% blends, for example, the coverage of the blend surface with siloxane drops from about 100 to 50% when the PDMS MW is increased from 2500 to 625,000. The so significant drop can hardly be attributed to the change in $\gamma_{\mathrm{PCP}} - \gamma_{\mathrm{PDMS}}$ because the variations in γ_{PDMS} on going from MW = 2500 to MW = 625,000 do not exceed several tenths of dyne/cm,[5] two orders of magnitude less than $\gamma_{\mathrm{PCP}} - \gamma_{\mathrm{PDMS}}$ itself. Moreover, an increase in the MW of PDMS formally increases the incompatibility of PDMS and PCP, which should result in a growth (and not reduction) of the extent of surface segregation.

In this article, we present two more examples of how the surface behavior of a polymer blend may differ from what is expected from thermodynamic considerations. Both examples illustrate the importance of kinetic factors in the formation of polymer surfaces. One is concerned with immiscible blends of PDMS in poly(vinyl chloride) (PVC) and the other with partially miscible blends of poly(propylene oxide) (PPO) in polystyrene (PS). The surface tensions of the pure components are $\gamma_{\mathrm{PDMS}} = 20$, $\gamma_{\mathrm{PVC}} = 39$, $\gamma_{\mathrm{PPO}} = 30$, $\gamma_{\mathrm{PS}} = 41$ dyne/cm.[5] The surface composition and morphology were studied by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM).

EXPERIMENTAL

The polymers used were commercially available samples: MW = 2500, 150,000, and 625,000 for PDMS, 190,000 for PVC, 425 and 2470 for PPO, and 200,000 for PS. Specimens for surface analyses were prepared by casting a 2% solution of the blend in tetrahydrofuran (THF) onto a stretched cellophane substrate. PPO–PS blends were also cast, for comparison, from chloroform solutions. After the solvent was allowed to evaporate, the resulting films were dried under ambient conditions for 3 days.

XPS spectra were recorded with a Kratos XSAM-800 spectrometer using a MgKα excitation. The pressure in the sample analysis chamber was 10^{-9}–10^{-10} torr. The X-ray gun was operated at a moderate power (15 kV, 5 mA), which did not produce perceptible radiation damage to the samples. Charge correction in the binding energy scale was made by setting the lowest binding energy feature of the Cl*s* emission to 285 eV. The surface composition of the PDMS–PVC blends was calculated from the integral intensities of the Si2*p* and Cl2*p* signals as described elsewhere.[6] The quantitative surface analysis of the PPO–PS blends was made based on the resolution of the Cl*s* spectra into contributions due to the ether carbon atom of PPO ($E_b = 286.6$ eV) and all other carbon atoms ($E_b = 285.0$ eV). Scanning electron micrographs were obtained with a Hitachi S-2500 electron microscope operating at 15 kV. To ensure surface conductivity, the samples were coated with a thin ($\sim$ 20 nm) gold layer by thermal sputtering.

RESULTS AND DISCUSSION

PDMS–PVC Blends

The results of the quantitative surface analysis of PDMS–PVC blends are summarized in Figure 1, which presents the surface concentration of PDMS, as detected by XPS, plotted versus the known concentration of PDMS in the bulk. The three sets of data refer to three different MWs of PDMS. The concentrations are expressed in atomic percent PDMS, which shows how many atoms of every 100 nonhydrogen atoms belong to PDMS (atomic % PDMS = 4 × atomic % Si). When applied to the surface, this quantity roughly characterizes the fraction of the sample surface covered with PDMS.

The bold solid line at the bottom of Figure 1 corresponds to the equality of the surface and bulk concentrations of PDMS. It is seen that the surface of all samples is greatly enriched in PDMS. Blends of the lowest MW siloxane, PDMS(2500),

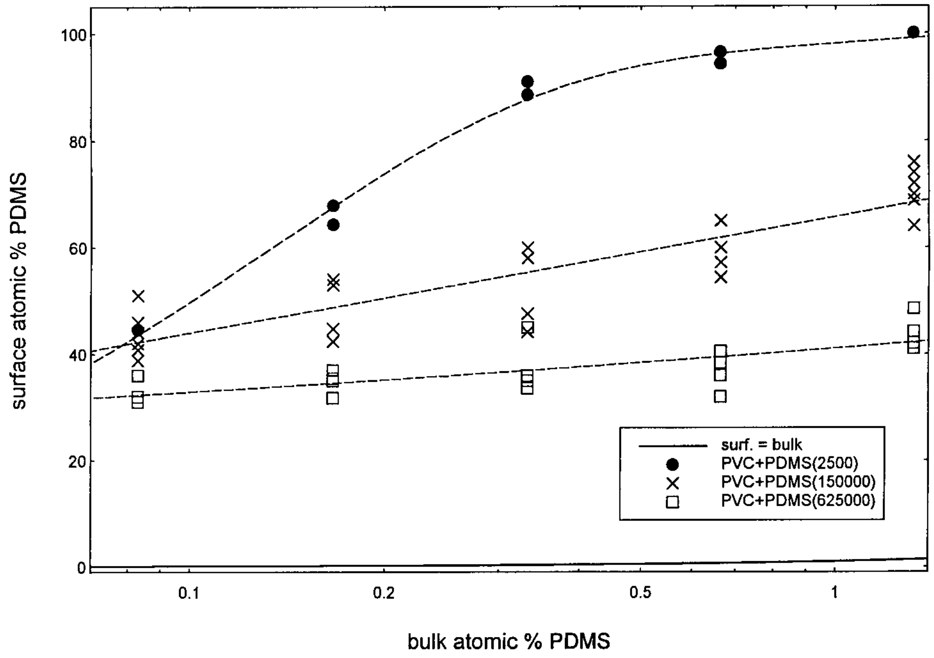

Figure 1 Surface–bulk compositional relationships in PDMS–PVC blends.

show a nearly complete coverage of the surface with PDMS starting with as low as 0.7 atomic % PDMS in the bulk. The nearly complete attenuation of the signal from PVC suggests that the surface of the blend is covered with a continuous siloxane overlayer of thickness $d > 3\ \lambda$, where λ is the photoelectron mean free path ($\sim$ 15 Å). An appropriate structural model of the near-surface region of the blend is schematically depicted in Figure 2(a). From Figure 1, one can see that the extent of siloxane surface segregation decreases dramatically with increasing PDMS MW. At MW = 625,000, the blend surface is covered with PDMS less than by half up to the largest bulk siloxane concentration studied. By and large, the behavior of siloxane in the surface layers of PVC proves to be very similar to what we observed earlier in dilute PDMS–PCP blends.[4]

As in the PDMS–PCP system, the MW dependence of the siloxane surface segregation in PDMS–PVC blends cannot be explained in terms of the MW effect on the PDMS surface tension and the extent of incompatibility between PDMS and PVC. To conceive the factors which may be responsible for the observed surface behavior, let us consider in detail what occurs in the THF solution of the PDMS–PVC blend in the course of solvent evaporation. Initially, the solution represents a homogeneous system containing altogether 2% polymeric components. As is typical of most polymer–solvent systems, the near-surface region of the solution is most likely enriched in the solutes (particularly in PDMS). As the solvent evaporates and the concentration of the polymeric components reaches a certain threshold value, the system demixes into two distinct THF solutions:

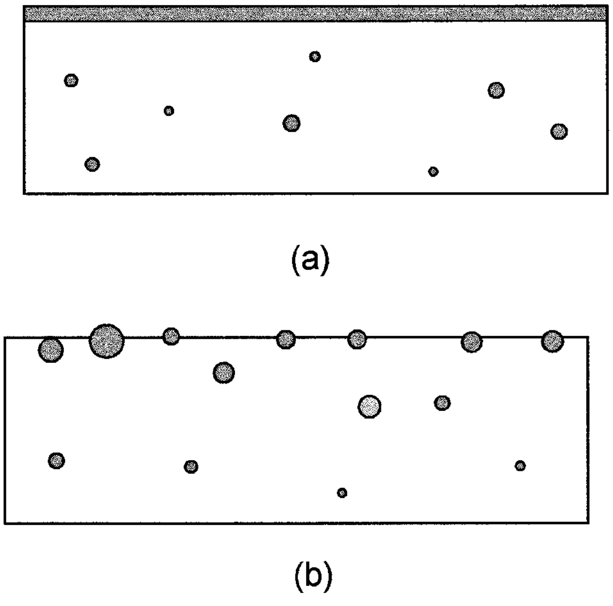

Figure 2 Proposed structure of the near-surface region in (a) PDMS(2500)–PVC and (b) PDMS(625,000)–PVC blends.

one containing predominantly PVC and the other PDMS. Inasmuch as the content of PVC is much greater than that of PDMS, it can be expected that the PVC-rich solution forms a continuous phase, whereas the PDMS-rich one is in the form of dispersed droplets. As the demixing progresses, the droplets grow, coagulate, and float onto the surface, which results in a decrease in the surface energy, as well as in the interface energy between the two liquid phases. The gradual loss of THF is also accompanied by an increase in viscosity of the system. Eventually, at a certain residual concentration of the solvent, the system practically loses mobility, so that the two-phase structure of the system, as it is formed at the given moment, is fixed.

With decreasing MW of PDMS, the mobility of its macromolecules increases, which facilitates demixing and reduces the viscosity of the PDMS-rich phase. As a result, the demixing occurs more completely and the system more closely approaches its equilibrium state, that is, a macroscopically separated two-layer system, with the upper layer formed by PDMS. At MW = 2500, the siloxane droplets that reached the surface are fluid enough to spread completely over the whole surface area to form a continuous siloxane overlayer [Fig. 2(a)], as is observed in the XPS experiment and dictated by the spreading criterion, $\gamma_{\mathrm{PVC}} - \gamma_{\mathrm{PDMS}} > \gamma_{\mathrm{PVC/PDMS}}$, where $\gamma_{\mathrm{PVC/PDMS}}$ is the PVC–PDMS interface tension (<5 dyne/cm).[5] By contrast, at MW = 625,000, the demixing occurs much slower and the system loses its mobility when the content of the PDMS-rich phase is still comparatively low and it is found in the near-surface region in the form of separate droplets. The high viscosity of PDMS(625,000) prevents the emerged droplets from spreading over the surface, so that the latter remains laterally inhomogeneous [Fig. 2(b)].

To support the above speculations, we resorted to SEM and studied the morphology of the interface between the PVC base and surface PDMS. The interface was bared by washing out surface PDMS with a highly selective solvent: hexane. (Control experiments with pure PVC showed that the treatment with hexane did not affect the structure of the PVC surface.) In the case of short-chain siloxane, MW = 2500, the PVC–PDMS interface was found to be absolutely smooth, in accordance with the continuous overlayer model [Fig. 2(a)]. At the same time, the interface formed by long-chain PDMS showed a well-defined relief (Fig. 3) corresponding to the laterally inhomogeneous surface [Fig. 2(b)].

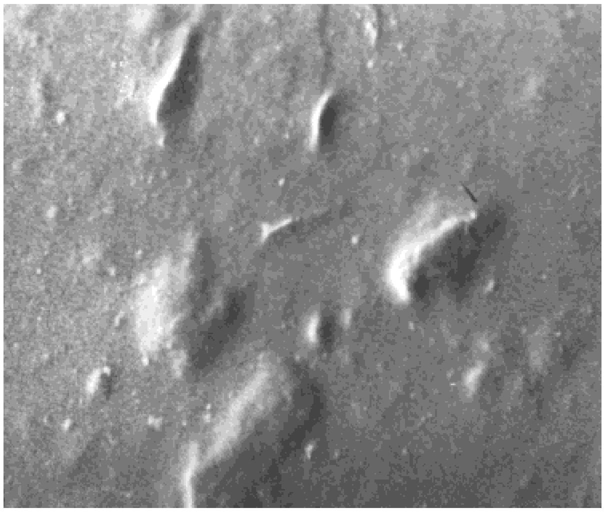

Figure 3 Electron micrographs of the surface of a PDMS(625,000)–PVC blend after treatment with hexane to remove surface PDMS.

PPO–PS Blends

Films of PPO–PS blends cast from the THF solution were transparent up to about 10% PPG, which was in agreement with the miscibility limit inferred from the DSC measurements of the T_g using the same sample preparation procedure and solvent.[7] The surface–bulk compositional relationships found in these blends are shown in Figure 4 as squares. Despite the fact that the surface tension of PPO is much lower than that of PS, no surface enrichment of PPO is observed: The results for the higher MW PPO nearly follow the curve corresponding to the equality of the surface and bulk compositions, while the data for the lower MW PPO even reveal a noticeable surface depletion. No significant change in the surface behavior can be seen in going from transparent to turbid films at bulk PPO concentrations greater than 10%.

To make sure that the surface of the as-cast films is far from equilibrium, two samples were subjected to annealing at a temperature of 170°C, well above the T_g ($\sim$ 90°C). The samples contained 0.56 and 14.3% PPO in the bulk, that is, within and beyond the concentration range of transparency, respectively. To avoid surface oxidation, the samples were annealed in the sample treatment chamber of the XPS spectrometer at a vacuum of 10^{-6} torr. For technical reasons (viz.,

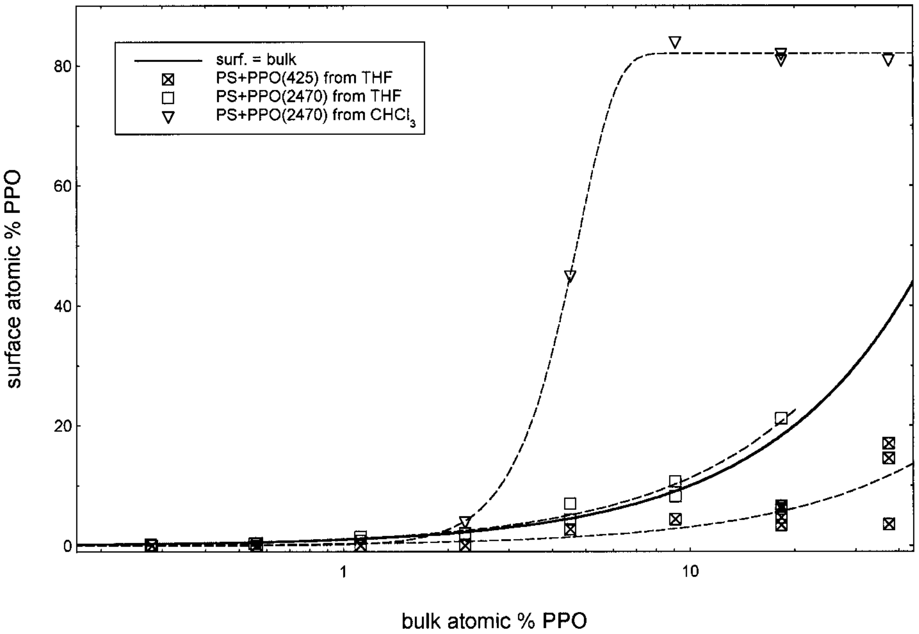

Figure 4 Surface–bulk compositional relationships in PPO–PS blends.

the softening of high-vacuum Teflon seals in the sample insertion lock), the annealing time was limited to 2 h, so that there was no guarantee that the near-surface distribution of the blend components fully attained equilibrium. Nevertheless, both of the annealed samples showed a substantial surface enrichment of PPO: The PPO surface concentration was found to be 23.5 and 55% in the transparent and turbid samples, respectively.

Although it is apparent that the lack of surface segregation of PPO in the PPO–PS blends cast from THF arises from solvent effects, the detailed mechanism of these effects remains unclear. It may well be that the intermolecular interactions in the triple system PPO–PS–THF are such that no enrichment of PPO occurs in the near-surface region of the solution. Then, as the solvent evaporates and the solution viscosity increases, the decreasing mobility of the solute molecules hinders the migration of PPO to the surface, so that the surface composition of the resulting PPO–PS blend remains nearly the same as in the parent solution.

The importance of solvent effects in the formation of the surface of PPO–PS blends is sustained by fact that the replacement of THF by $CHCl_3$ changed dramatically the surface behavior of the blends. In part, this was due to a change in the phase behavior of the system: While the blends cast from THF lost transparency at PPO bulk concentrations greater than 10%, the blends cast from $CHCl_3$ became turbid much earlier, at a concentration of 2.5%. The XPS data relevant to blends cast from $CHCl_3$ are shown in Figure 4 as triangles. It can be seen that the surface composition of miscible (transparent) PPO–PS films follows the bulk composition. The loss of transparency is accompanied by a sharp increase in the PPO surface segregation and then the surface composition levels off at about 80% PPO. The difference in surface behavior between the phase-separated blends cast from THF and from $CHCl_3$ can be associated with the fact that the phase separation of the PPO–PS solutions in THF sets in at late stages of solvent evaporation, when the viscosity of the solution is too high for the droplets of the PPO-rich phase to migrate to the surface. By contrast, the phase separation of the PPO–PS solutions in $CHCl_3$ occurs at comparatively low polymer concentrations and low viscosities, which permits the transfer of the PPO-rich phase to the near-surface region.

In conclusion, the experimental results reported in this article provide further evidence for the importance of kinetic factors in the formation of the surface of solvent-cast polymer blends. The PDMS–PVC immiscible blends show an MW dependence of the PDMS surface segregation, which can be interpreted in terms of the effect of the PDMS MW on the degree of phase separation and on the viscosity of the PDMS–PVC–THF solution in the course of solvent evaporation. Eventually, the extent of the PDMS surface segregation is determined by the extent to which the system approaches equilibrium. The factor of solution viscosity seems also to play an important part in the PPO–PS partially miscible system. In this case, however, many points remain unclear: (1) The effect of the PPO MW on the extent of PPO surface segregation in the blends cast from THF; (2) the cause of the solvent effect on the surface behavior of the blends in going from THF to $CHCl_3$; and (3) the occurrence of a plateau in the surface–bulk compositional relationship observed for blends cast from $CHCl_3$. An understanding of these points requires a detailed characterization of the PPO–PS–THF and PPO–PS–$CHCl_3$ systems, including, at least, determination of their phase diagrams.

This work was funded by a financial grant from the Russian Foundation for Basic Research (Grant No. 96-03-32412) and supported by the Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPRJ) and the Conselho de Ensino para Graduados e Pesquisa (CEPG-UFRJ).

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