

Surface Behavior of Blends of Siloxane and Siloxane-Containing Copolymers in Poly(vinyl chloride)

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SYNOPSIS

X-ray photoelectron spectroscopy is used to reveal surface/bulk compositional relationships in blends of polydimethylsiloxane (PDMS) and PDMS/polycarbonate block copolymers in poly(vinyl chloride) (PVC). It is shown that the surface of PVC can be enriched in siloxane up to 60 at. % PDMS without visible indications of phase separation.

INTRODUCTION

It is well known that the surface composition of a multicomponent polymer (a copolymer or a blend) may differ greatly from its composition in the bulk, as a result of the difference in the surface energies of the components. Surface/bulk compositional differences are particularly pronounced in polymers containing polydimethylsiloxane (hereafter PDMS or, simply, siloxane) due to its extremely low surface energy ($\sigma = 22$ dyne/cm). Thus, in dilute blends of PDMS/polysulfone (PSF) copolymers in homo-PSF, the surface and bulk concentrations of siloxane may differ by a factor of 2000.¹

The high extent of surface segregation typical of siloxane-containing polymers can be used in practice to endow a polymer with the remarkable surface properties of siloxane, without significant change in the polymer's bulk properties. The range of useful surface properties of siloxane includes low wettability, good biocompatibility and thromboresistivity, and a satisfactory flame resistance. Of great utility may also be the ability of siloxane to form, under the action of some oxidizing agents, ultrathin quartzlike overlayers with excellent protective and gas-separation properties.²⁻⁴

The use of siloxane as a modifier of the surface properties of a polymer calls for a knowledge of the dependence of the surface concentration of siloxane

on its bulk concentration in the relevant blends. Unfortunately, the number of polymers whose blends with siloxane or siloxane-containing copolymers have been studied by surface-sensitive methods is very limited. Actually, quite reliable and comprehensive data, which allow controllable variation of the surface concentration of siloxane, are available only for two polymers: PSF and polycarbonate (PC).⁵⁻¹⁰

In this paper, we use X-ray photoelectron spectroscopy (XPS) to reveal the surface behavior of siloxane in its blends with poly(vinyl chloride) (PVC). The goal of this work was to estimate the upper level of surface concentration of siloxane that can be attained in PVC without apparent indications of phase separation (such as the loss of transparency or the appearance of visible islands of the individual phases on the sample surface). Aside from binary blends of pure PDMS in PVC, we investigated binary and ternary blends of the type PVC + PDMS/PC and PVC + PDMS/PC + PDMS, respectively. (In these abbreviations, "+" is used to delimit the components of a blend, in contrast to "/" used to delimit the components of a block copolymer).

EXPERIMENTAL

The homopolymers used in this study were commercially available samples, MW = 82,000 for PVC and 600,000 for PDMS. The PDMS/PC block copolymers were, first, a usual PDMS/poly(bisphenol A carbonate) block copolymer (block lengths 1790/

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2500, 17.2 at. % PDMS, hereafter BCP-1) and, second, a similar block copolymer but containing diurethane segments $-\text{[CH}_2\text{O}-(\text{CH}_2)_2\text{OC(O)-NH-C}_6\text{H}_4\text{]}_2\text{CH}_2-$ between the siloxane and carbonate blocks (block lengths 1790/250/2000, 15.6 at. % PDMS, hereafter BCP-2). The films for XPS analysis were prepared by casting from tetrahydrofuran solutions on a glass substrate.

XPS spectra were recorded by a Kratos Analytical Instruments XSAM-800 spectrometer using a hemispherical electron energy analyzer. $\text{MgK}\alpha$ X-rays were used as the source, operated at 15 kV and 5 mA. Base pressure in the analysis chamber was maintained at 1×10^{-10} Torr. Quantitative analysis of the sample surfaces was carried out as described in Ref. 1.

Some of the samples studied showed differential charging of the surface: The surface regions composed preferentially of PVC were usually charged more positively (by 0.2–0.5 eV) than those composed preferentially of a siloxane-containing modifier. In such cases, charge correction in the binding energy was accomplished for PVC and the modifier separately, by setting the $\text{Cl}2p$ core level of PVC at 200.7 eV and the $\text{Si}2p$ core level of the modifier at 102.6 eV. The differential charging was higher when the

phase separation was more pronounced on the sample surface.

RESULTS

The XPS spectra of the PDMS, PC, and diurethane components of the multicomponent systems studied have been described in detail elsewhere.¹ The $\text{C}1s$ core level of PVC was composed of two main features, $\text{C}_1 = 287.0$ and $\text{C}_2 = 285.9$ eV, reflecting carbon atoms bonded to Cl directly and through another carbon atom, respectively. There was also a slight spectral feature at 285.0 eV due to small amounts of siloxane contaminants present in the initial PVC. (The corresponding $\text{O}1s$ and $\text{Si}2p$ signals were observed at 532.6 and 102.6 eV, respectively.) The quantitative analysis based on the relations presented in Ref. 1 gave $\text{C}_1 : \text{C}_2 : \text{Cl} = 0.94 : 0.93 : 1$, in good agreement with the stoichiometric values for pure PVC. The surface concentration of siloxane contaminants was about 8 at. %.

In the blends of PVC with PDMS and BCPs, the XPS spectra represented an ideal superposition of the spectra due to the individual components. This is illustrated in Figure 1, which shows the $\text{C}1s$ and

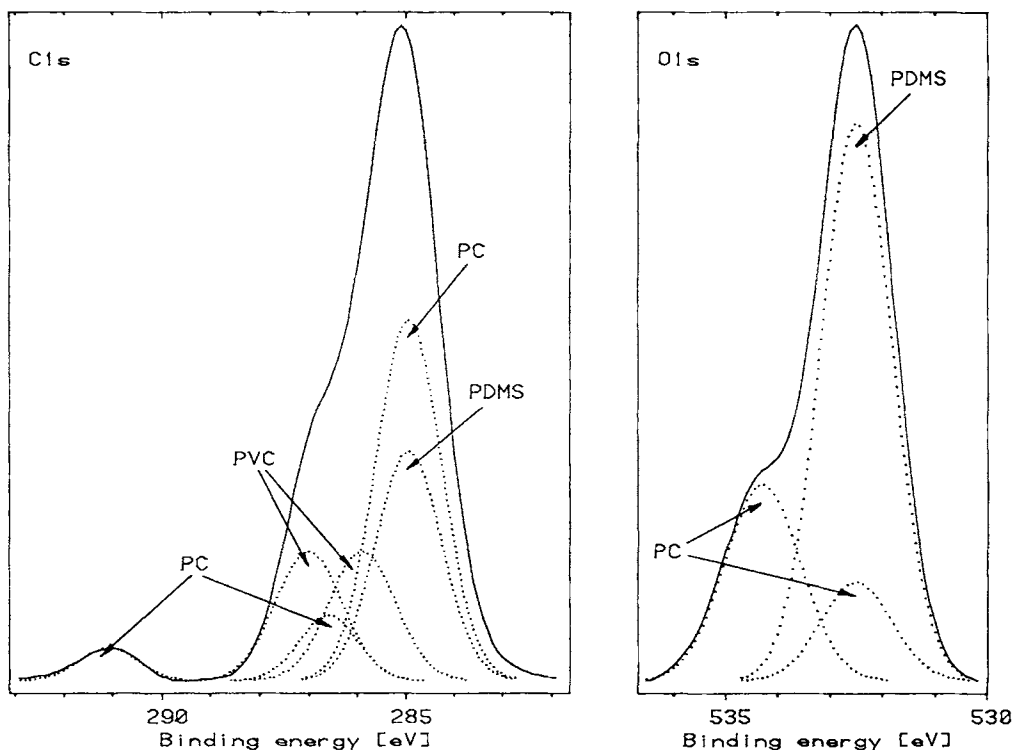


Figure 1 $\text{C}1s$ and $\text{O}1s$ core level emission for a PVC-based blend containing 0.25 wt % BCP-1.

O1s core level emission from the blend of PVC and 0.25% BCP-1. In all cases, the relative contributions of the individual spectral features to the C1s and O1s lines correlated well with the surface composition determined from the integral intensities of the Cl2p, Si2p, and C1s lines, i.e., the results of a quantitative analysis based on the observed surface concentrations of the individual elements could be verified independently based on the decomposition of the C1s and O1s lines.

The surface/bulk compositional relationships in the blends studied are summarized in Figure 2. The quantitative results show the atomic percent surface siloxane, as detected by XPS, plotted against the known weight percent modifier in the bulk. The squares, triangles, and rhombs refer to the PVC + PDMS, PVC + BCP, and PVC + BCP-2 + PDMS blends, respectively. Open symbols correspond to blends that showed no visible indications of phase separation, while full symbols refer to blends whose films lost their transparency or showed macroscopic islands of individual phases on their surfaces.

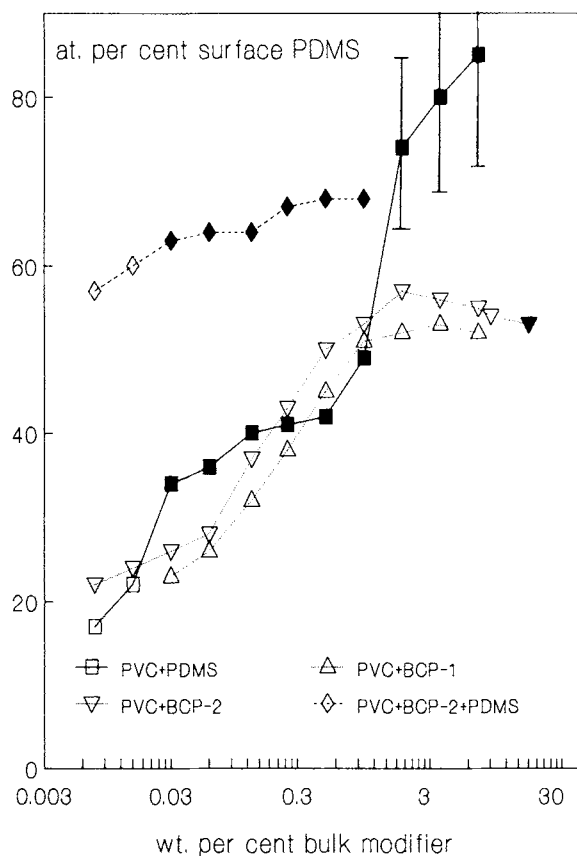


Figure 2 Surface/bulk concentration relationships in blends of PVC with PDMS and PDMS/PC block copolymers.

In the blends of homopolymers, PVC + PDMS, the highest amount of siloxane that could be added to PVC without observing apparent indications of phase separation was 0.015 wt %. The corresponding surface concentration was 25 at. %, i.e., roughly speaking, 75% of the sample surface remained uncovered with siloxane. At bulk siloxane concentrations above 0.03 wt %, the films lost their transparency, while at concentrations above 1 wt %, the inhomogeneity of the samples was so high that the results of the XPS measurements were dependent on what particular area of the sample surface was analyzed. As a result, the quantitative data in the high-concentration region showed a large scatter.

Quite unexpected results showed the behavior of the PVC + BCP blends: The films remained transparent up to 16–20 wt % BCP. This indeed seemed unusual because pure PC, when added to PVC, showed nearly the same limit of compatibility with PVC as did pure PDMS (0.06 wt %). (Realizing that transparency is not a sufficient indication of the absence of phase separation, we are currently studying the mechanical and thermodynamic properties of the PVC + BCP blends. The results of this study will be published in a separate paper.)

As seen from Figure 2, the surface/bulk concentration curves for the PVC + BCP blends are S-shaped, which is rather typical of blends of block copolymers in homopolymers.^{1,9} At BCP concentrations above 1 wt %, the signals from PVC vanished, thus indicating that the sample surface was completely covered with a continuous overlayer of BCP with a thickness larger than the XPS sampling depth (30–50 Å). At the same time, the surface concentration of siloxane approached 50 at. %, a value close to the surface concentration of siloxane observed in pure BCPs (52 and 48 at. % for BCP-1 and BCP-2, respectively).

As compared to pure PDMS, the BCPs are more efficient surface modifiers of PVC, allowing one-half of the sample surface to be covered with siloxane without apparent phase separation. An obvious way to further increase the surface concentration of siloxane is to add pure PDMS to a PVC + BCP blend. With such a modifier, one can expect the formation of a three-layered structure whose uppermost layer is preferentially composed of pure PDMS covering the siloxane-enriched (outer) side of the BCP layer.

The XPS results for PVC blends containing, as modifier, BCP-2 + 1 wt % PDMS are shown in Figure 2 as rhombs. In this case, the addition of only a 0.015 wt % modifier to PVC led to formation of a continuous overlayer containing 60 at. % surface siloxane. No visible indications of phase separation

were observed up to 0.03 wt % modifier. Very similar results were obtained with the BCP-1 copolymer and with binary modifiers containing 5 wt % PDMS.

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