# Surface Modification of Poly(vinyl chloride) with Poly(methyl methacrylate)/Poly(dimethyl siloxane) Graft Copolymers

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## SYNOPSIS

X-ray photoelectron spectroscopy is used to study the surface segregation of siloxane in dilute blends of poly(methyl methacrylate)/poly(dimethyl siloxane) graft copolymers in poly(vinyl chloride) (PVC). The graft copolymers are found to be extremely efficient surface modifiers, which form, when added in amounts of 0.5% or more, a continuous siloxane overlayer on the surface of PVC. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

It is a general knowledge that the surface of a multicomponent polymer (a copolymer or a blend) may substantially differ in structure and composition from its bulk. This is particularly true of siloxane-containing polymers because the surface energy of siloxane is much lower than that for most other polymers. Extensive studies of the surface/bulk compositional differences in siloxane-containing polymers have shown that the concentration of siloxane in the uppermost surface layers may be two to three orders of magnitude higher than its concentration in the bulk.[1,2] This phenomenon can be well used in polymer technology to endow a polymer with the specific surface properties of siloxane. The relevant modification procedure consists in simple blending of the polymer with small amounts of poly(dimethyl siloxane) (PDMS) or a siloxane-containing copolymer via the melt or a common solution. The polymer surface enriched with siloxane in this way may be subjected to further modification by an oxygen plasma treatment to give an ultrathin quartzlike overlayer with outstanding resistive and gas-separation properties.[3]

In our earlier work,[4] we used X-ray photoelectron spectroscopy (XPS) to study the surface behavior of siloxane in binary and ternary blends of PDMS and PDMS/poly(bisphenol A carbonate) (PC) block copolymers in poly(vinyl chloride) (PVC). It was found that pure PDMS was not an efficient surface modifier of PVC. The highest siloxane coverage that could be attained in the PVC + PDMS blends without apparent indications of phase separation was as low as 25% (at 0.015 wt % bulk PDMS). The modification of PVC with the PDMS/PC block copolymers allowed a 100% coverage of the PVC surface with the modifier to be achieved. The resulting siloxane coverage remained, however, rather low (50–60%) and was limited by the value characteristic of the surface of the pure copolymer additive. The highest siloxane coverage (60–70%) was achieved in triple blends of PVC + PDMS/PC + PDMS.

In this work, we continued our attempts to introduce siloxane to PVC so as to attain 100% surface siloxane without phase separation. The basic idea is to use PDMS in the form of a long-chain graft to another polymer that is partially compatible with PVC. Poly(methyl methacrylate) (PMMA) is well suited for this purpose. It can be expected that the PMMA component will offer a sufficient compatibility of the modifier with PVC to avoid phase separation, whereas the long-chain siloxane graft will form the desired overlayer.

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## EXPERIMENTAL

The polymers used were commercial PVC, MW = 82,000, and the four PMMA/PDMS graft copolymers characterized in Table I. The graft copolymers were synthesized through radical copolymerization of methyl methacrylate and a (methacryloxipropyldimethylsiloxy)poly(dimethyl siloxane).[5] The copolymer composition was determined by ¹H-NMR spectroscopy from the intensities of signals relevant to the PMMA and PDMS components. The absence of homopolymer impurities in the resulting graft copolymers was checked by GPL.

As seen from Table I, the four copolymers used in the preparation of blends differ substantially in the length of the siloxane graft (50 monomer units for copolymers A and C, and 250 monomer units for copolymers B and D). The amount of grafting, which can easily be evaluated from the data of Table I, varies from one PDMS graft per 2000 PMMA units in copolymer D to one PDMS graft per 30 PMMA units in copolymer A.

The blends of PVC with the graft copolymers were prepared via a common solution of the blend components in tetrahydrofuran. The samples of the blends and pure copolymer additives used in the surface analysis were in the form of ~ 100 μm-thick films cast from 2% tetrahydrofuran solutions on a stretched cellophane substrate. The concentration of the copolymer additive in the blends was varied from 0.06 to 2%. For additive concentrations up to 0.5%, the films were absolutely transparent, whereas at concentrations above 1%, they showed a slight opalescence.

The surface composition of the films was studied by X-ray photoelectron spectroscopy (XPS) using a Kratos XSAM-800 instrument. MgKα X-rays were used as the source, operated at 15 kV and 5 mA. Base pressure in the analysis chamber was maintained at $5 \cdot 10^{-10}$ Torr. The samples were mounted on the sample holder using adhesive tape.

The quantitative analysis was made based on integral peak intensities as described elsewhere.[1] To assess the compositional gradient in the surface layers, the XPS spectra were taken at two different electron take-off angles, 0° and 50°, to give an average composition in the topmost surface layers about 50 and 30 Å thick, respectively.

As has been observed with other siloxane-containing blends,[4] the spectral lines of the blend components (PVC, PMMA, and PDMS) showed a slight relative shift (up to 0.4 eV). This shift appeared at high concentrations of the additive and was due to microphase separation at the sample surface and the associated differential charging of the blend components. No charge neutralization procedure was used to avoid differential charging because it created no difficulties: The magnitude of differential charging could be exactly determined from the position of the Si2p and Cl2p core levels and then taken into account on decomposition of the XPS spectra into individual spectral features.

## RESULTS AND DISCUSSION

Typical XPS spectra of the pure graft copolymers are shown in Figure 1. The C1s and O1s core levels represent an exact superposition of the signals due to the PMMA and PDMS components (PMMA: $\underline{C}H_3$ = 285.0, $\underline{C}CO$ = 285.8, $\underline{C}O$ = 287.0, $\underline{C}(O)O$ = 289.3, $\underline{O}=C-O$ = 532.5, $\underline{O}-C=O$ = 534.0 eV; PDMS: $\underline{C}H_3$ = 285.0; $\underline{O}-Si$ = 532.5 eV). The surface composition can be independently determined from the Si2p signal due to the PDMS component (102.5 eV) or from the well-resolved $\underline{C}(O)O$ and $\underline{O}-C=O$ spectral features due to the PMMA component. For all of the copolymers used, the re-

## Table I    Characterization Data for PMMA/PDMS Graft Copolymers

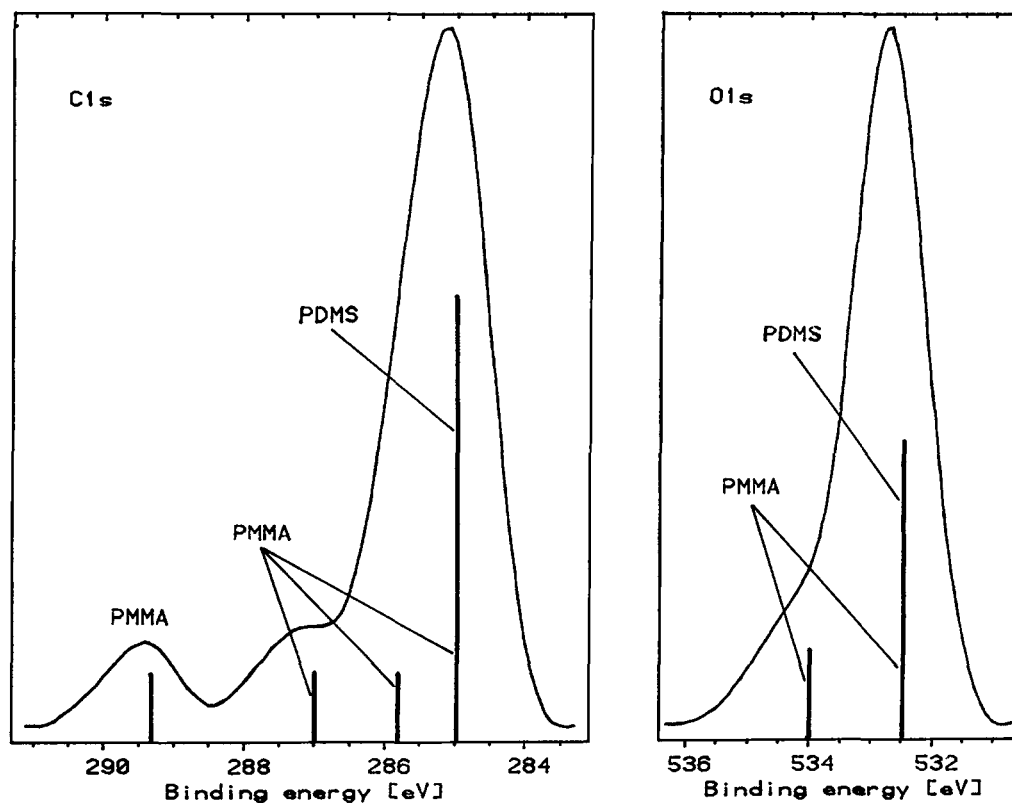| Copolymer | PMMA : PDMS (Monomer Units) | Length of PDMS Graft (Monomer Units) | PDMS Concentration (at. %) | | |
|---|---|---|---|---|---|
| | | | | Surface | |
| | | | Bulk | 50 Å Layer | 30 Å Layer |
| A | 1 : 1.6 | 50 | 48 | 97 | 100 |
| B | 1 : 1.27 | 250 | 42 | 100 | 100 |
| C | 1 : 0.24 | 50 | 12 | 89 | 94 |
| D | 1 : 0.125 | 250 | 6 | 51 | 64 |

**Figure 1**    C1s and O1s core level emission for copolymer D.

sults calculated from the Si2p and $\underline{C}(O)O$ peaks were practically coincident, whereas the use of the $\underline{O}$—C==O feature slightly overestimated the content of the PDMS component in the surface layers. The latter fact is not surprising because the electron mean free path for the O1s core level is noticeably shorter than that for the C1s and Si2p core levels. As a result, the quantitative analysis based on the O1s core level referred, in fact, to a thinner surface layer, which had a higher concentration of siloxane because of a perceptible concentration gradient.

The surface/bulk compositional relationships in the graft copolymers and their blends with PVC are convenient to discuss in terms of the atomic concentration of siloxane, atom % PDMS = 4 × atom % Si, which shows how many atoms of every 100 nonhydrogen atoms belong to siloxane. When applied to the topmost surface layers, this quantity provides a good practical measure for the fraction of the sample surface that is covered with siloxane.

The measured surface concentrations of siloxane in the 30 and 50 Å surface layers of the pure graft copolymers are presented in Table I, together with the relevant bulk values. The highest siloxane coverage is observed in copolymer B, whose surface lay-

ers are composed of pure PDMS at least to a depth of 50 Å. The 30 Å-thick surface layer of copolymer A is also composed of pure PDMS. In the 50 Å layer, however, there appear small amounts of the PMMA component. The observed difference between copolymers A and B can obviously be associated with the shorter length of the siloxane graft in copolymer A.

A comparison of the surface concentrations of siloxane in Table I with the previously reported values for siloxane-containing block copolymers[4] reveals that the graft copolymers show, at similar bulk concentrations of siloxane, a much higher siloxane coverage. For example, in a PDMS/PC block copolymer, containing 17 atom % siloxane in the bulk, the surface siloxane was found to be 52 atom %.[4] This value can be compared with that for the graft copolymer C, whose surface consists of siloxane to the extent of 89%, despite a lower content of siloxane in the bulk (12 atom %).

Now we turn to the XPS results for the blends of the graft copolymers in PVC. A C1s core level typical of the blends is shown in Figure 2. The presence of PVC leads to the appearance of two new spectral features, $\underline{C}$—Cl = 287.2 and $\underline{C}$—C—Cl
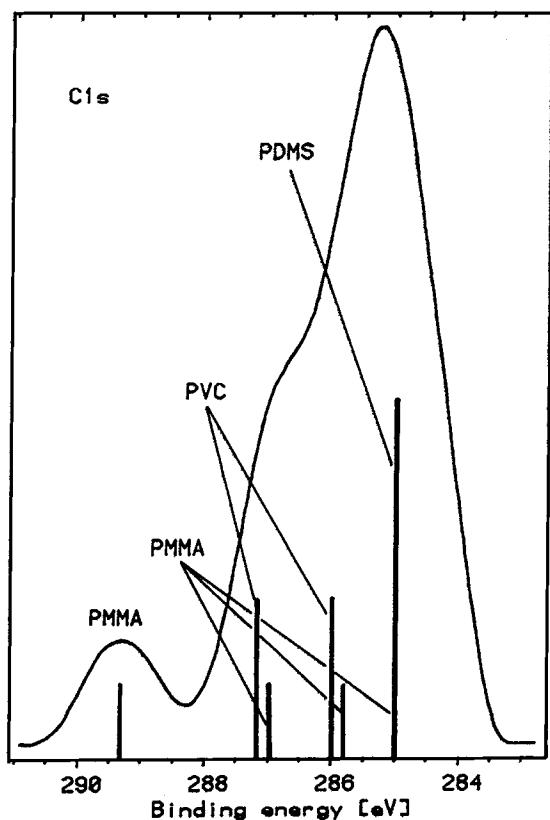
**Figure 2** C1s core level emission for a blend of 1% copolymer D in PVC.

= 286.0 eV, which can both be used to evaluate the surface concentration of the PVC component. An independent (and more reliable) evaluation of the surface concentration of PVC can be done using the integral peak intensity of the Cl2$p$ line (200.7 eV). As with the pure graft copolymers, the quantitative surface analyses of the blends, based on the different spectral lines and different spectral features, gave nearly coincident results.

The surface behavior of siloxane in the blends of PMMA/PDMS graft copolymers in PVC is illustrated in Table II, which lists the atomic percent siloxane in the 50 and 30 Å surface layers, as detected by XPS, as a function of the known content of modifier in the bulk. Comparing the results for the four different copolymer additives, one can conclude that the surface segregation of siloxane is governed mainly by the length of the siloxane graft: The segregation is highest for copolymers B and D having long graft chains. It is remarkable that copolymer D proves to be a more efficient surface modifier even than copolymer A, despite the fact that the siloxane content of the former is eight times as low as that of the latter (Table I).

Another remarkable property of copolymer D is that the surface siloxane in its blends with PVC may attain concentrations substantially higher than that observed in pure copolymer D (Table II). This results from the fact that the appearance of PVC greatly enhances the surface segregation of siloxane relative to PMMA, compared to that in pure copolymer D: Whereas the surface layers of pure copolymer D contain only 1.8 PDMS monomer units per PMMA unit, the PDMS:PMMA ratio on the surface of the PVC + D blends ranges from 3.3 (at 0.06 wt % bulk D) to 11 (at 2 wt % bulk D).

An encouraging result is that the graft copolymers used allow one to attain high siloxane coverages at very low contents of the modifying additive. Thus, it is sufficient to add as low as 0.13 wt % copolymer B to PVC to cover 90% of its surface with siloxane. A 100% siloxane coverage can be achieved starting from 0.5 wt % copolymer B in the bulk.

Thus, the results of this work show that the PMMA/PDMS graft copolymers are very efficient surface modifiers of PVC. Their high efficiency seems to be due to two factors: The first factor is the comparatively good compatibility of the PMMA

**Table II   Concentration of Siloxane (atom %) in 50 and 30 Å Surface Layers for Blends of PVC with PMMA/PDMS Graft Copolymers A–D, as a Function of the Bulk Concentration of the Copolymer Additive**

| Wt % Bulk Additive | A | | B | | C | | D | |
|---|---|---|---|---|---|---|---|---|
| | 50 Å | 30 Å | 50 Å | 30 Å | 50 Å | 30 Å | 50 Å | 30 Å |
| 0.06 | | | 68 | 81 | 25 | 42 | 36 | 46 |
| 0.13 | 16 | 21 | 81 | 91 | 33 | 52 | 52 | 62 |
| 0.25 | 25 | 34 | 81 | 96 | 42 | 67 | 57 | 72 |
| 0.50 | | | 90 | 100 | 55 | 69 | 64 | 85 |
| 1.00 | 32 | 40 | 93 | 100 | 69 | 81 | 71 | 88 |
| 2.00 | | | 97 | 100 | 73 | 81 | 80 | 89 |

component with PVC, which allows perceptible amounts of the modifier to be introduced into PVC without phase separation. The second factor is the appropriate molecular structure of the modifier. Unlike the case of block copolymers,[4] the PDMS grafts are long and linked to the PMMA support by only one end. This facilitates the migration of the siloxane component to the surface and favors the formation of a continuous siloxane overlayer.

To test the protective properties of the siloxane overlayer on PVC, we conducted experiments in which the sample was bombarded by high-energy oxygen atoms (beam energy 5 eV, beam density 4 · $10^{19}$ m$^{-2}$ s$^{-1}$, exposition time 2 h). The results of these experiments will be described in a separate article, and here we only note that the surface modification of PVC with copolymer B reduced the loss in the sample weight upon bombardment by more than an order of magnitude (from 13% in the initial PVC to 0.9% in the modified PVC). An XPS analysis of the modified PVC after the treatment with atomic oxygen showed that the modifying overlayer remained continuous: No signal from Cl atoms of the underlying PVC was detected. Another finding was that about 90% of the surface siloxane was converted to a quartzlike compound, similar to that formed on the surface of siloxane under the action of low-temperature afterglow discharge oxygen plasma.[3]

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