Effect of Deformation on the Surface Composition of Multicomponent Polymers. II. Blends of Polydimethylsiloxane–Polysulfone Block Copolymers in Polychloroprene

M. M. GORELOVA,[1] A. J. PERTSIN,[2] I. O. VOLKOV,[2] N. B. SANCHES,[1] A. S. GOMES[1]

[1] Institute of Macromolecules, Federal University of Rio de Janeiro, Cx. Postal 68.525, CEP 21945-970, Rio de Janeiro, RJ, Brazil

[2] Institute of Organo-Element Compounds, Russian Academy of Sciences, 28 Vavilov Str., V-334, GSP-1, Moscow 117813, Russia

ABSTRACT: The effect of uniaxial stretching on the surface composition of dilute blends of polydimethylsiloxane/polysulfone 2500/44,000 and 2500/3500 block copolymers in polychloroprene is studied using X-ray photoelectron spectroscopy. The surface of the initial (unstretched) blends is found to be covered by a discontinuous copolymer overlayer with a thickness greater than the XPS sampling depth. The stretching leads to a substantial drop in the extent of the copolymer surface segregation. For the 2500/3500 block copolymer, the dependence of the surface composition of the blends on the stretching degree is well described by a homogeneous deformation model, whereas for blends of the 2500/44,000 copolymer, the stretching of the copolymer overlayer lags noticeably behind that of the polychloroprene matrix. In the blends of the 2500/3500 copolymer, the stretching has practically no effect on the distribution of the copolymer components in the near-surface region. By contrast, the 2500/44,000 copolymer shows a substantial surface depletion of siloxane with stretching. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 2349–2356, 1998

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INTRODUCTION

In the last decade, the surface segregation of the components in copolymers and polymer blends has attracted considerable interest.[1] This interest arises, in particular, from the hopes that the phenomenon of surface segregation can be efficiently used to produce surfaces with controlled chemistry and topography.[2] Along with extensive theoretical and computer simulation work aimed at describing the equilibrium surface composition of multicomponent polymers, a great number of experimental studies have been made using mainly X-ray photoelectron spectroscopy (XPS) and, more recently, the neutron-reflectivity technique.[3] Among the factors whose role in surface segregation has been understood to a greater or lesser extent are the chain architecture, molecular weight characteristics, and preparation variables such as the annealing and casting solvent.

A novel aspect of surface segregation was explored in our recent article,[4] where we used XPS

to follow the surface composition of a multicomponent polymer in the course of uniaxial stretching and subsequent unloading of the polymer film. It was hoped that the measurements of surface segregation as a function of strain, aside from being of immediate practical interest, would provide better insight into the mass-transfer processes and structural transformations involved in deformation. The experiments were carried out with dilute blends of polydimethylsiloxane (PDMS) in polychloroprene (PCP). The stretching was accompanied by a dramatic reduction in the siloxane surface concentration, while the subsequent unloading had the reverse effect. The surface behavior of the blends upon deformation was found to be strongly dependent on the molecular weight of the PDMS. The blends of long-chain PDMS ($MW = 625,000$) showed a much lesser siloxane surface depletion with stretching compared to that observed with blends of short-chain PDMS ($MW = 2500$). Furthermore, the surface behavior of the former was completely reversible in the sample length, whereas the latter showed distinct surface compositions on stretching and contraction.

In this work, we extended our XPS studies[4] to blends of PCP with PDMS/poly(bisphenol A sulfone) (PSF) block copolymers (hereafter, PCP+PDMS/PSF blends). The use of a copolymer as the surface-active additive allows us to gain more information about the deformation-induced transformations in the surface layers by following the changes in the ratio of the copolymer components. Each of the three components of the blends has its own "label" for XPS—Si in PDMS, S in PSF, and Cl in PCP—which makes the quantitative surface analysis quite reliable. Both PDMS and PSF are immiscible with PCP, so that the homopolymer matrix and the copolymer additive can be expected to be phase-separated. The surface tensions of pure PDMS, PSF, and PCP are 20, 36, and 44, respectively.[5] It can therefore be anticipated that the surface of the blends will be enriched in the copolymer phase, while the latter will, in turn, show a high surface segregation of the PDMS component.

Unlike the blends of PCP with homo-PDMS, the surface-active copolymer additive in the PCP+PDMS/PSF blends is much less deformable than in the PCP matrix. So, an interesting question to be answered is this work is whether the surface-segregated copolymer phase stretches together with the PCP matrix or lags behind it or does not stretch at all.

EXPERIMENTAL

The copolymers used were two PDMS/PSF perfectly alternating multiblock copolymers, hereafter designated as 25/440 and 25/35, based on the lengths of their individual blocks. (For example, 25/440 is a copolymer with the PDMS and PSF block lengths of $MW = 2500$ and 44,000, respectively.) The homo-PCP was commercially available noncrosslinked sample, $MW = 200,000$.

The blends of a given composition were prepared by mixing prescribed amounts of dilute solutions of the blend components in a mutual solvent, chloroform. The composition range studied was 0.1–4 wt % copolymer additive. Polymer films for deformation experiments and XPS measurements were made by casting from chloroform solutions onto a stretched cellophane substrate and then allowing the solvent to evaporate. Stretching experiments were conducted with polymer strips $20 \times 70 \times 0.3$ mm in size. The stretching was accomplished at room temperature at a rate of 0.01 mm/s. After stretching to a desired degree, a part of the film was fixed in the stretched form by sticking a rigid metallic strip to the underside of the film. The remaining part of the film was unloaded at a 0.01 mm/s rate until the sample recovered its initial length.

XPS spectra were recorded with a Kratos XSAM-800 spectrometer using a MgKα excitation. Base 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 detectable radiation damage to the samples. Charge correction in the binding energy scale was made by setting the lowest binding energy feature of the C1s emission to 285 eV. The surface composition of the blends was calculated from the integral intensities of the Si2p, S2p, and Cl2p signals as described elsewhere.[6] The surface composition of the copolymer phase was also determined in an independent way based on the resolution of the O1s spectrum into contributions due to the oxygen atoms in the PDMS and PSF blocks: O—Si = 532.6, O=S = 532.0, and O—Ph = 533.6 eV. To judge the presence of a concentration gradient in the near-surface region, the spectra were acquired at both 90° and 30° electron take-off angles, which correspond to a sampling depth of about 50 and 25 Å, respectively.

RESULTS AND DISCUSSION

As expected, all the PCP+PDMS/PSF blends showed a high surface segregation of the copoly-
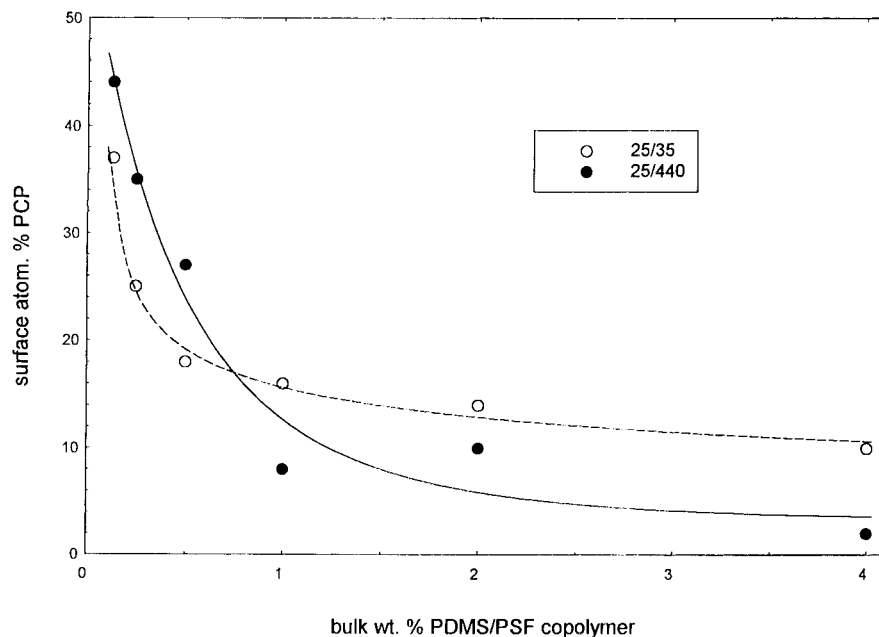
Figure 1 Surface concentration of PCP in its blends with PDMS/PSF copolymers as a function of the bulk concentration of the copolymer additive. The lines are an eye guide.

mer additive. This can be appreciated from Figure 1, which refers to the initial (unstretched) films and illustrates the attenuation of the signal from the PCP matrix due to the surface-segregated PDMS/PSF copolymer. The results of the surface analysis are presented in terms of the average surface concentration of PCP, as detected by XPS, plotted as a function of the overall bulk content of the additive. The surface concentration of PCP is expressed in atomic percent, which shows how many atoms of every 100 nonhydrogen atoms in the surface layers belong to PCP (at. % PCP = 5 × at. % Cl). It can be seen from Figure 1 that the addition of only 1% PDMS/PSF copolymer to PCP leads to replacement of more than 80% of the PCP atoms in the near-surface region by the atoms of the copolymer additive. Nevertheless, the 100% coverage of the sample surface with the additive is not achieved even at the highest copolymer content studied. The latter fact is common with immiscible binary polymer blends. Although equilibrium bulk thermodynamics favors complete demixing of the components of such blends into two separate continuous layers, macroscopic equilibrium is usually not attained, so that both of the components are present at the sample surface.

Important information concerning the surface topography of the unstretched films was provided by the angular-dependent XPS measurements.

The surface concentration of PCP in all unstretched films was practically independent of the sampling depth. This result can only be rationalized by assuming that the copolymer additive forms a discontinuous overlayer with a thickness greater than the XPS sampling depth, that is, all the PCP detected by XPS is seen from breaks in the copolymer overlayer, and no PCP signal comes from under the overlayer. (Otherwise, the signal from the PCP matrix would be sensitive to the electron take-off angle.)

Aside from the surface segregation of the copolymer additive as a whole, the copolymer overlayer on the surface of the initial blends showed, as expected, a high surface enrichment in the PDMS component. This is illustrated in Figure 2 in terms of the atomic ratio of Si to S. Since PCP contains neither Si nor S, the Si/S ratio is unresponsive to the PCP matrix and well characterizes the organization of the copolymer macromolecules on the sample surface. The XPS results for the Si/S ratio in the blends are compared in Figure 2 with the respective data for the surface and bulk of the pure PDMS/PSF copolymers. It can be seen that the Si/S ratio in the copolymer overlayers much exceeds the corresponding bulk values determined by the stoichiometric composition of the copolymers. To within the scatter of the experimental points, the surface composition of the co-
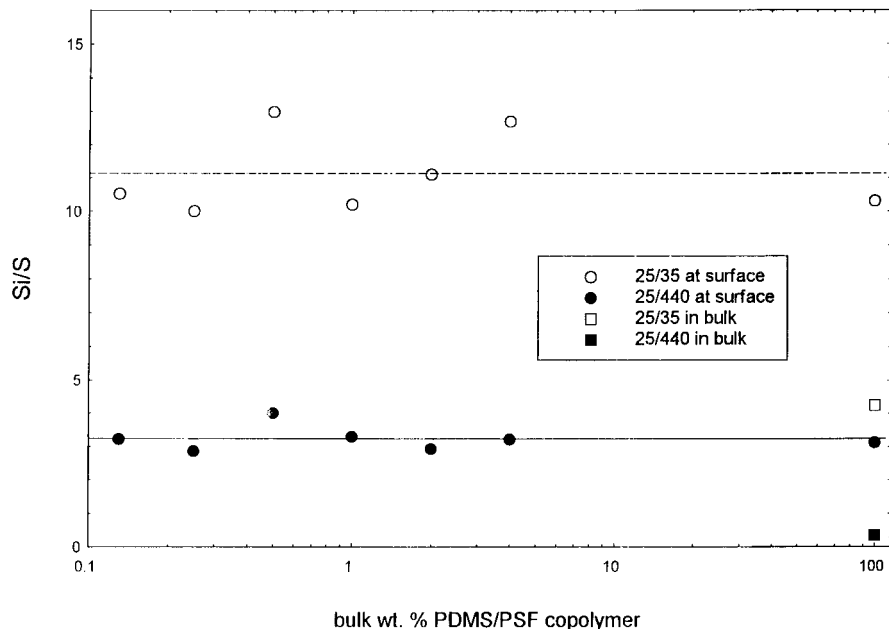
Figure 2 Atomic ratio of Si to S at the surface of PCP+PDMS/PSF blends in comparison with the relevant data for the surface and bulk of pure PDMS/PSF copolymers. The lines are an eye guide.

polymer overlayer does not depend on the content of the copolymer additive and is nearly the same as the surface composition of the pure PDMS/PSF copolymers. (The same conclusion followed from the behavior of the O1s spectrum, where the fraction of the O—Ph feature remained unchanged throughout the composition range studied.) This suggests that the surface segregation of the copolymer additive occurs in the "thick overlayer" regime,[6] when the overlayer is thick enough to ensure, during film casting, the formation of a surface structure similar to that of the pure copolymers.

For deformation experiments, we chose blends containing 1% copolymer additive. As seen from the concentration curves in Figure 1, this corresponds to a point where the near-surface region of the blends is as if saturated with the copolymer additive, so that a further addition of the copolymer changes the surface composition only slightly. The effect of deformation on the surface composition of the blends was described in terms of parameter K defined as the average surface concentration of Cl in the stretched sample, related to that in the initial sample,

$$K(\alpha) = c_{Cl}(\alpha)/c_{Cl}(1) \qquad (1)$$

where α is the stretching degree. The XPS results for $K(\alpha)$ are depicted in Figure 3 as circles. From these results, it is evident that the signal from the PCP matrix rises substantially with stretching. This is particularly true of copolymer 25/440 which shows a nearly fivefold increase in c_{Cl}. An important point is that stretching of the sample leads to the appearance of a noticeable concentration gradient of chlorine over the XPS sampling depth. This can be seen from Table I, which presents the XPS data on $c_{Cl}(\alpha)$ for two sampling depths, 25 and 50 Å. As the stretching degree is increased, the value of c_{Cl} in the 50-Å layer becomes more and more in excess of that in the 25-Å layer. This indicates conclusively that the co-

Table I Average Surface Concentration of Chlorine (atomic %) for 25- and 50-Å Sampling Depths as a Function of Stretching Degree

Copolymer 25/35			Copolymer 25/440		
α	25 Å	50 Å	α	25 Å	50 Å
1.0	2.5	2.4	1.0	1.4	1.4
3.0	3.6	4.5	3.0	4.7	4.9
4.1	4.4	5.1	4.0	5.0	5.3
5.0	4.7	6.8	5.2	5.1	6.0
6.0	4.8	6.8	6.4	5.7	7.2
7.0	5.6	8.0			

polymer overlayer gradually thins with stretching to make the underlying PCP matrix more accessible to XPS.

To get a better idea of the deformation-induced changes in the near-surface region, we compared the experimental data on $K(\alpha)$ with the expected behavior of $K(\alpha)$ calculated for several likely models of deformation. The starting point for the calculations was the familiar expression for the average atomic density as derived from the integral intensity of a photoelectron line:

$$\langle n_i \rangle = \int_0^\infty n_i(z) \exp(-z/\lambda_i) dz/\lambda_i \qquad (2)$$

In this expression, which refers to a take-off angle of 90°, $n_i(z)$ is the local atomic density of element i at depth z and λ_i is the mean free path of photoelectrons emitted by atoms i from the given core level. If the surface is laterally inhomogeneous and the inhomogeneities are much smaller than the XPS sampling area, the averaging over the depth in eq. (2) should be complemented by averaging over the surface area. In the simplest case, the surface comprises laterally homogeneous regions of two kinds, designated as a and b, and the atomic density of element i averaged over the depth and surface is given by

$$\langle n_i \rangle = s\langle n_i^a \rangle + (1 - s)\langle n_i^b \rangle \qquad (3)$$

where s is the fractional surface area of regions a, while $\langle n_i^a \rangle$ and $\langle n_i^b \rangle$ are defined by eq. (2) with $n_i(z)$ replaced by the respective depth profiles, $n_i^a(z)$ and $n_i^b(z)$.

The relation of $\langle n_i \rangle$ to the corresponding signal intensity is usually uncertain to a constant factor. As a consequence, the quantitative XPS analysis yields not $\langle n_i \rangle$ itself but the average atomic percentage, c_i, which appears in eq. (1) and is explicitly defined by the equation

$$c_i = \langle n_i \rangle / \sum_k \langle n_k \rangle \times 100 \ (\%) \qquad (4)$$

where the summation is over all elements present in the material.

Returning to our particular polymeric system, let us refer regions a to the surface areas covered with the copolymer overlayer and regions b to the breaks in the overlayer, that is, to the areas of bare PCP. Then, for all atomic species i entering into PCP, we have

$$\langle n_i^b \rangle = n_i^{PCP}, \qquad (5)$$

where n_i^{PCP} is the atomic density of element i in pure PCP. All the atomic densities $\langle n_i^b \rangle$ related to the copolymer additive vanish.

For regions a, the signal from the PCP matrix is attenuated by the copolymer overlayer so that for atoms i entering into PCP the integration of eq. (2) gives

$$\langle n_i^a \rangle = n_i^{PCP}[1 - \exp(-t/\lambda_i)] \qquad (6)$$

where t is the thickness of the copolymer overlayer. To write down similar equations for the copolymer additive, we have to assume certain depth profiles $n_i^a(z)$ $(0 < z < t)$ for the elements entering into the PDMS and PSF segments in the copolymer overlayer. Fortunately, the concentrations c_{Cl} needed to evaluate parameter K from eq. (1) depend on these profiles only through the sum in the denominator of eq. (4). This sum, in turn, depends on the deformation only slightly and largely cancels out in the calculation of the ratio $c_{Cl}(\alpha)/c_{Cl}(1)$. To check this point, we compared the curves $K(\alpha)$ calculated with three assumed depth distributions of the copolymer components: (1) PDMS and PSF are separated into individual layers, with the PDMS layer above; (2) the same as (1) but with the PDMS layer below; and (3) PDMS and PSF are uniformly distributed throughout the copolymer overlayer. Despite the substantial differences between these distributions, the resulting curves $K(\alpha)$ proved to be practically coincident. Based on this result, all further calculations were made assuming the uniform distribution of PDMS and PSF in the copolymer overlayer. In this case, the densities of the atoms entering into the overlayer are averaged over the depth as

$$\langle n_i^a \rangle = n_i^{BCP} \exp(-t/\lambda_i), \qquad (7)$$

where n_i^{BCP} is the average density of atoms i in the pure PDMS/PSF block copolymer. The values of n_i^{BCP} were calculated assuming additivity of the molar density of the PDMS/PSF block copolymer with respect to those of pure PDMS and PSF.

The expression for c_{Cl}, resulting from substitution of eqs. (3) and (5)–(7) into eq. (4), involves two deformation-dependent parameters, s and t. If the deformation of the whole sample is homogeneous, the stretching of the overlayer exactly follows that of the PCP matrix. In this case, the

fractional area of bare PCP remains unchanged, $s = s_0$, while the overlayer thickness transforms as $t = t_0\gamma$, where the subscript "0" refers to the initial unstretched films and γ denotes the degree of contraction of sample in thickness. To a good approximation, $\gamma = \alpha^{-1/2}$, so that for the model of homogeneous deformation $t = t_0\alpha^{-1/2}$.

The other limiting case, hereafter referred to as the model of rigid overlayer, is based on the assumption that the copolymer phase remains un-affected and all the new surface area formed on stretching is due to the growing patches of bare PCP. The corresponding equations for s and t are $s = 1 - (1 - s_0)\alpha^{-1/2}$, $t = t_0$. All intermediate cases between the homogeneous deformation and rigid overlayer models can be formally described by introducing an "own" deformation degree for the overlayer, which is related to the deformation degree of the PCP matrix as $\alpha^{\omega}(0 \le \omega \le 1)$, where ω specifies how much the stretching of the over-layer lags behind that of the PCP matrix. This results in the following equations for s and t:

$$s = 1 - (1 - s_0)\alpha^{(\omega-1)/2} \qquad (8)$$

$$t = t_0\alpha^{-\omega/2} \qquad (9)$$

The equations for the rigid overlayer and homoge-neous deformation models now represent special cases of eqs. (8) and (9) at $\omega = 0$ and 1, respec-tively.

The final equation for c_{Cl} is readily obtained by combination of eqs. (3)–(9). The resulting ex-plicit formula, however, is cumbersome and will not presented here for reasons of space. So, in further discussion, we content ourselves to an im-plicit expression

$$c_{Cl} = c_{Cl}(s_0, t_0, \alpha, \omega) \qquad (10)$$

In this expression, α is known from experiment, while one of the other three parameters can be found from the constraint that at $\alpha = 1$ c_{Cl} should be equal to the experimentally observed concen-tration of chlorine in the unstretched film. In our calculations of $K(\alpha)$ from eq. (1), this latter con-straint was used to determine s_0, whereas t_0 and ω were treated as variable parameters of the model. One more constraint followed from the fact that stretching led to the appearance of a pronounced gradient of c_{Cl} over the sampling depth, which was originally absent in the unstretched films (see Ta-ble I). This suggests that the initial overlayer thickness, t_0, is close to or only slightly higher

than the XPS sampling depth at a 90° take-off angle (~ 50 Å).

The calculated dependences $K(\alpha)$ are shown in Figure 3 in comparison to the relevant experimen-tal data. The solid curves refer to the two limiting values of ω: the upper curve to $\omega = 0$ and the lower one to $\omega = 1$. In both cases, the initial overlayer thickness, t_0, is assumed equal to 50 Å. It is evi-dent that the rigid overlayer model fails to de-scribe the observed deformation dependence of the surface segregation. This supports the conclu-sion made from the data of Table I that the copoly-mer overlayer is indeed involved in stretching and gradually thins with increasing α.

A surprising result is that the experimental data for copolymer 25/35 are well described by the simple model of homogeneous deformation ($\omega = 1$). This is not, however, the case with copoly-mer 25/440 whose $K(\alpha)$ is noticeably underesti-mated by the homogeneous deformation model. It is important that the use of $t_0 \ge 50$ Å gives an even lower $K(\alpha)$, which increases the discrepan-cies between the predicted and experimental val-ues. The agreement can only be improved by de-creasing ω, that is, by assuming that the stretch-ing degree of the overlayer is less than that of the PCP matrix. The best least-squares fit of the theoretical curve to the experimental data was obtained at $\omega = 0.82$. At $\alpha = 3$, for example, this gives an overlayer stretching degree of 2.5.

Further information about the deformation-in-duced changes in the copolymer overlayer was provided by the measurements of the surface com-position of the PDMS and PSF blocks. Here, again, copolymers 25/440 and 25/35 showed quite different surface behavior with stretching. The former exhibited a strong surface depletion in PDMS, which manifested itself in a nearly twofold decrease of the Si/S ratio [Fig. 4(a)] and also in the growth of the relative contribution of the O—Ph feature to the O1s line profile [Fig. 4(b)]. The latter did not reveal perceptible changes in the Si/S ratio and in the profile of the O1s line.

The observed differences in the surface behav-ior of the 25/440 and 25/35 copolymers on stretch-ing can be explained in terms of the composition of the soft (PDMS) and hard (PSF) segments. The relative fraction of the soft segments in copolymer 25/35 is much larger than that in copolymer 25/440. As a consequence, the overlayer of copolymer 25/35 is more easily deformable and able to follow the deformation of the underlying PCP matrix on stretching. A reflection of this is the higher value of ω. Another consequence of the large content of
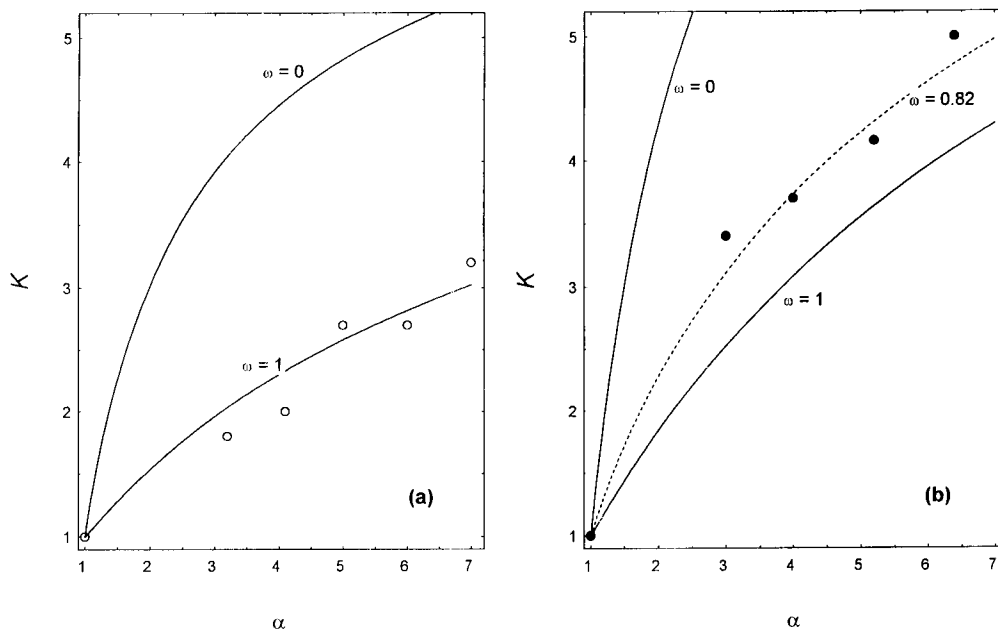
Figure 3 Attenuation of the signal from the PCP matrix as a function of the stretching degree for blends of PCP with (a) copolymer 25/35 and (b) copolymer 25/440. The lines show theoretical results for the indicated values of ω.

the soft segments is that the near-surface region of copolymer 25/35 is more capable of reorganizing its structure on stretching so as to restore the

PDMS surface segregation favored by the surface thermodynamics. That is why the overlayer of copolymer 25/35 retains its surface composition on
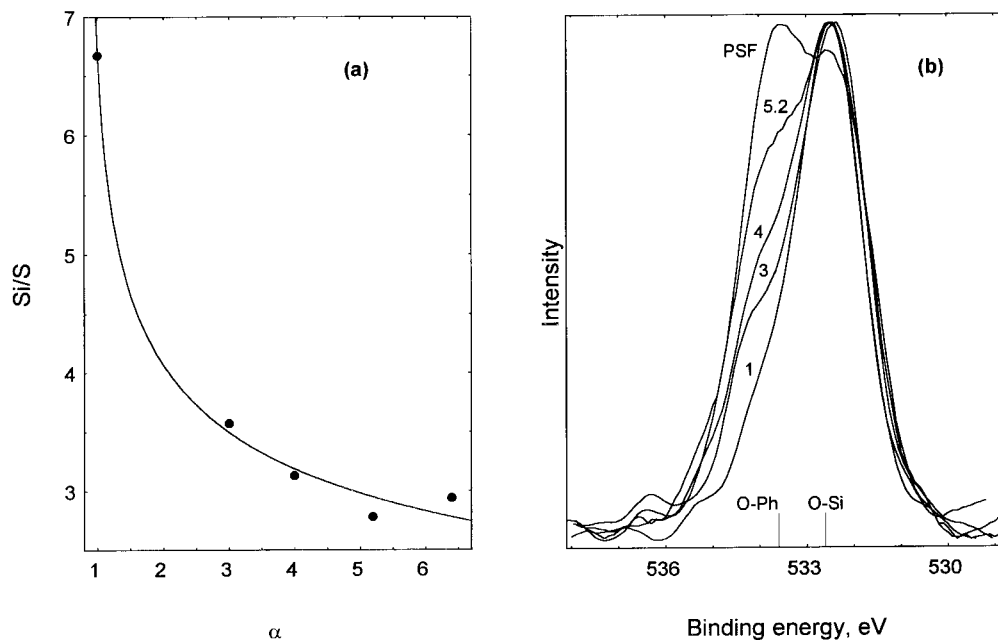

Figure 4 Effect of stretching on (a) the Si/S ratio and (b) the O1s line profile in blends of PCP with copolymer 25/440. The numbers in the O1s spectra indicate the stretching degree. To appreciate the growth of the O—Ph component due to PSF, the O1s line of pure PSF is also shown.
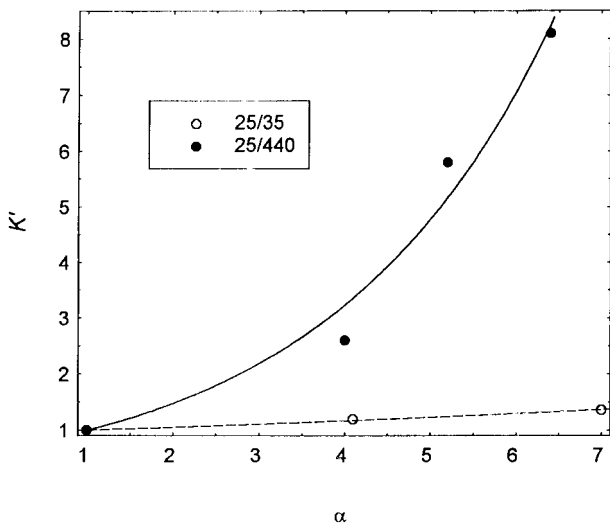
Figure 5 Relative changes in the percentage of surface chlorine in samples stretched to a given α and then allowed to contract to their initial lengths. The lines are an eye guide.

stretching, whereas that of copolymer 25/440 shows surface depletion in PDMS.

To conclude the discussion, we turn to Figure 5, which illustrates the changes in the surface composition after stretching and subsequent unloading of the polymer films. The XPS results are presented in terms of parameter K', which is defined similarly to K in eq. (1) except that $c_{Cl}(\alpha)$ now refers to a sample stretched to a given α and then allowed to contract to its initial size ($\alpha = 1$). One can see that the surface behavior of the blends in the "stretching–contraction" cycle is irreversible. This is particularly true of copolymer 25/440, which shows an eightfold increase in the percentage of surface chlorine after stretching to $\alpha = 6.4$ and subsequent contraction to $\alpha = 1$. What is even more surprising is that the resulting surface concentration of chlorine is substantially higher than that in the stretched sample ($K = 5.1$ at $\alpha = 6.4$, see Fig. 3). This means that the copolymer overlayer shrinks, during film contraction, to a greater extent compared to the PCP matrix, which can formally be described by eqs. (8) and (9) with $\omega > 1$. The reason for the observed exposure of the PCP matrix in the course of contraction remains to be understood. Inasmuch as the contraction of the PCP matrix necessarily involves mass transfer from the surface to the bulk, it is not unlikely that the contracting matrix captures individual fragments of the overlying copolymer phase and carries them into the polymer bulk, thus removing the copolymer from the near-surface region sampled by XPS. A more definite conclusion will hopefully be made from the electron microscopic studies of the surface topography, which are now in progress.

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