

Effect of Deformation on the Surface Composition of Multicomponent Polymers: Blends of Poly(dimethyl siloxane) in Polychloroprene

M. M. GORELOVA,¹ A. J. PERTSIN,^{2*} I. O. VOLKOV,² L. V. FILIMONOVA,² and E. S. OBOLONKOVA¹

¹Institute of Synthetic Polymeric Materials, Russian Academy of Sciences, 70 Profsoyuznaya Str., Moscow 117393, Russia; ²Institute of Organo-Element Compounds, Russian Academy of Sciences, 28 Vavilov Str., V-334, GSP-1, Moscow 117813, Russia

SYNOPSIS

X-ray photoelectron spectroscopy and scanning electron microscopy are used to follow the effect of uniaxial stretching on the surface composition and morphology of poly(dimethyl siloxane)/poly(chloroprene) blends. Before stretching, the blends exhibit a high surface segregation of siloxane due to an extremely low surface energy of the latter. The stretching gives rise to a substantial drop in the siloxane surface enrichment, whereas the subsequent unloading has the reverse effect. The surface behavior of the blends upon deformation strongly depends on the molecular weight of the siloxane component. Oligomeric siloxane (MW = 2500) shows a much stronger surface depletion with stretching, compared to that observed with a siloxane polymer (MW = 625,000). Furthermore, the surface behavior of the blends of the polymeric siloxane is completely reversible in sample length, whereas the blends of the oligomeric siloxane have different surface compositions on stretching and contraction. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The surface segregation of components of lower surface energy is a phenomenon typical of multicomponent polymer systems (both copolymers and polymer blends).¹ It can even be stated that a difference between the bulk and surface compositions of a multicomponent polymer is rather a rule than an exclusion. In the last years, the number of publications concerned with surface segregation in polymers has considerably grown. This results, first, from the wide distribution of powerful nondestructive techniques for surface analysis, such as X-ray photoelectron spectroscopy (XPS) and ion scattering spectroscopy (ISS). Second, the interest in the surface behavior of polymers stems from the understanding of the fact that many important properties of polymers, such as adhesion, biocompatibility, friction characteristics, and wettability, are

governed by the composition and structure of the topmost surface layers. The knowledge of the factors responsible for surface segregation allows one to design the surface composition of a polymer so as to obtain desired surface properties.

Systematic studies of the surface segregation in polymers using the methods of electron and ion spectroscopy began in the 1980s.²⁻⁵ Most attention was paid to the dependence of the surface composition on the molecular architecture of the multicomponent system, i.e., on the way in which the components are linked together by covalent bonds.⁶⁻¹⁰ Also studied was the influence of a film-casting solvent and annealing on the surface behavior of copolymers and blends.^{2,6,11}

An important question which has not been yet investigated is the question of what occurs in the surface layers of a multicomponent polymer when it is subjected to mechanical deformation. There are many factors which can affect the structure and composition of the polymer surface as the polymer is deformed. In the case of stretching, e.g., an obvious factor is the increase in the polymer surface area,

* To whom correspondence should be addressed.

which implies the occurrence of mass transfer in the direction from the bulk to the surface. As a result, the near-surface region, originally enriched with the lower surface energy component, will be "diluted" with deeper polymer layers, so that the extent of surface segregation will be reduced. Another factor capable of changing the surface composition is the extension and orientation of the polymer chains along the stretching axis. This factor can be expected to be particularly important in block copolymers, where the segregation occurs within the same polymer chain, through preferential surface exposure of the blocks of the lower surface energy component. On stretching, the different blocks of the copolymer chains will be leveled off in depth, with the result that the extent of surface segregation will be decreased.

In essence, all phenomena attendant on deformation, such as recrystallization, crazing, the increase in free volume, the local growth of molecular mobility, and the orientation of supermolecular structural elements, can have an effect upon the distribution of components in the near-surface region. Measurements of the extent of surface segregation as a function of strain can therefore serve as a probe in studies of the mass transfer and structural transformations involved in deformation.

This work represents a first attempt to follow the effect of deformation on the surface composition and morphology of a multicomponent polymer. The experiments were carried out with dilute blends of poly(dimethyl siloxane) (hereafter PDMS or simply siloxane) in polychloroprene (PCP) using XPS and scanning electron microscopy (SEM). (Some preliminary results of the XPS measurements have been reported in our recent article.¹²) PDMS was taken as a surface-active additive because of its extremely low surface energy and the resulting strong trend to surface segregation. PCP was chosen as a polymer base mainly because it allowed us to reach high stretching degrees and it could be easily blended with PDMS via a common solution in chloroform. An advantage of the PDMS/PCP system was that each of the components had its own "characteristic" element, Si in PDMS and Cl in PCP, which made the quantitative surface analysis more reliable.

EXPERIMENTAL

The polymers used were commercially available PDMS, MW = 2500 and 625,000, and noncross-linked PCP, MW = 200,000, crystallinity = 30%. The polymer blends were prepared via a common

solution of the blend components in chloroform. The samples were in the form of films cast from a 1% solution onto a stretched cellophane substrate. The stretching experiments were conducted with strips $60 \times 20 \times 0.1$ mm in size. (Unfortunately, the use of samples with a better initial ratio of length to width involved difficulties because of constraints imposed by XPS measurements upon the smallest sample width.) The stretching was conducted at room temperature at a rate of 0.1 mm/s. After stretching to a desired degree, a part of the film was fixed in the stretched form by sticking a rigid metallic substrate to the underside of the film. The remaining part of the film was unloaded at a 0.1 mm/s rate to a fixed length or until the length no longer decreased.

The stretching of the PCP/PDMS films involved necking. The neck spread over the full length of the sample at a stretching degree $\alpha \approx 3$. Further stretching occurred uniformly up to the rupture of the sample at $\alpha = 7-8$. Samples stretched to $\alpha > 3$ and then unloaded at room temperature showed a residual elongation, α_r , which was well described by a linear function of α , $\alpha_r = 0.62\alpha + 0.05$. The complete recovery required the heating of the samples to 35–40°C.

XPS spectra were acquired using a Kratos XSAM-800 dual-chamber spectrometer with a Mg anode at a vacuum of 10^{-9} – 10^{-10} Torr. The surface composition was calculated from the intergal intensities of the XPS lines as described elsewhere.⁷ Scanning electron micrographs were obtained on a JEOL JSM-5300LV electron microscope operating at 20 kV. The samples were coated with gold (300 Å) using a JFC-1100E sputter coater.

RESULTS AND DISCUSSION

The use of XPS in quantitative surface analysis is based on the fact that the intensity of an XPS signal from a core level of an element i is proportional to the average atomic density of this element in the near-surface region, $\langle n_i \rangle$. The density is averaged over depth so that the contribution of a thin near-surface layer at depth z to the signal intensity decays exponentially with z :

$$\langle n_i \rangle = \int_0^{\infty} n_i(z) \exp(-z/\lambda_i) dz / \lambda_i \quad (1)$$

In this equation, $n_i(z)$ is the local atomic density of element i at depth z , and λ_i , the mean free path of photoelectrons emitted by atoms i from the given

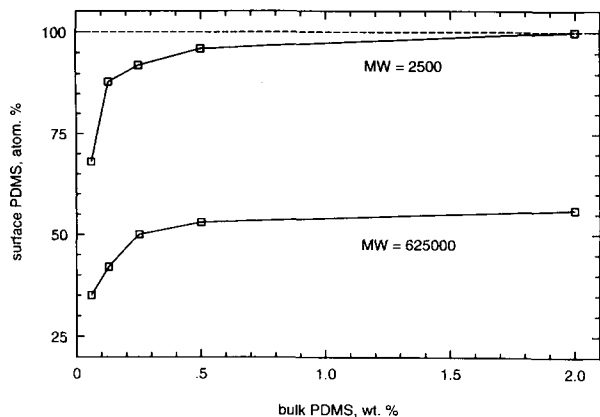


Figure 1 Surface vs. bulk concentrations of PDMS in PDMS/PCP blends for short-chain (MW = 2500) and long-chain (MW = 625,000) PDMS.

core level. The major contribution to the integral in eq. (1) is due to atoms at depths less than $3\lambda_i$, which is typically equal to several tens of angstroms. The relation of $\langle n_i \rangle$ to the relevant line intensity is usually uncertain to a constant factor. As a consequence, the quantitative XPS analysis provides not $\langle n_i \rangle$ itself but the atomic surface concentration of element i , c_i , defined by the equation

$$c_i = 100 \langle n_i \rangle / \sum_k \langle n_k \rangle \quad (2)$$

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

As could be expected from the surface energies of pure PDMS and PCP, their blends exhibited a high surface enrichment in siloxane. This can be seen from Figure 1, which refers to the initial (unstretched) films and shows the surface concentration of siloxane, as determined by XPS, plotted against the known siloxane concentration in the bulk. The siloxane surface segregation is particularly high in the blends of PCP with the short-chain PDMS (MW = 2500). In this case, it is sufficient to add as low as 0.25% PDMS to PCP to make the surface of the latter covered with an overlayer of practically pure siloxane. The long-chain PDMS (MW = 625,000) shows a much lower surface segregation: Even at 2% PDMS in the bulk (the highest PDMS bulk concentration studied in this work), the siloxane surface concentration does not exceed 60%. The observed MW dependence of the siloxane surface segregation in the PCP/PDMS blends is quite the reverse of what is theoretically predicted and experimentally observed for diblock copolymers.¹⁰ A discussion of this point and some additional experimental data will be presented in a separate article.

Now we turn to stretched samples. The extent of siloxane surface segregation as a function of the stretching degree α can conveniently be described in terms of parameter K defined as the surface concentration of Si in the stretched sample, related to that in the initial sample, $K(\alpha) = c_{Si}(\alpha)/c_{Si}(1)$. The XPS results for $K(\alpha)$ in 0.25% blends are shown in Figure 2 as full circles. It can be seen that the extent of surface segregation of siloxane drops substantially with stretching. Thus, a fivefold stretching of the sample reduces the surface concentration of siloxane about three times. To rationalize the observed changes in surface segregation, we compared the experimental data with two theoretical curves derived from two different models. Both the models utilize the experimental fact that the surface of the samples containing 0.25% siloxane is covered with an overlayer of practically pure siloxane, with a thickness greater than $3\lambda_{Si}$ [Fig. 3(a)]. The first model [Fig. 3(b)] involves the assumption that the sample deformation is homogeneous, so that the concentration depth profile of Si, $n_{Si}(z)$, undergoes an affine transformation,

$$n_{Si}(\gamma z, \alpha) = n_{Si}(z, 1) \quad (3)$$

where the second argument of n_{Si} specifies the stretching degree and γ denotes the degree of contraction of sample in thickness ($\gamma < 1$). The upper curve in Figure 2 was calculated for a stepwise dis-

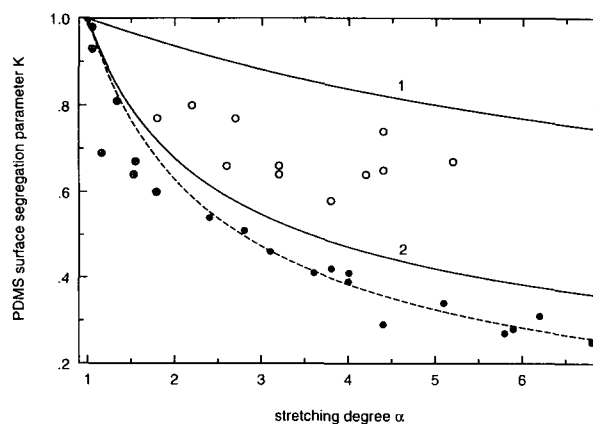


Figure 2 The dependence of the PDMS surface segregation parameter K on the stretching degree α for 0.25% blends of PDMS (MW = 2500) in PCP. The experimental results are for (●) stretched samples, (○) unloaded samples, and (⊕) data on stretched samples with reference to $\alpha = 3.8$. The dashed curve is an eye guide for the experimental data on stretched samples. The theoretical results are for (1) the homogeneous deformation model and (2) the ruptured overlayer model.

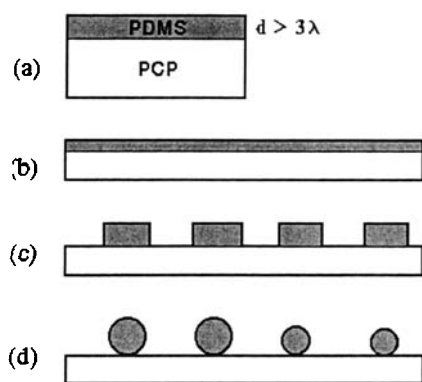


Figure 3 Surface morphology models of PCP/PDMS (MW = 2500) blends: (a) initial sample, (b–d) stretched samples, as described by (b) homogeneous deformation model, (c) ruptured overlayer model, and (d) same as (c) but followed by contraction of the overlayer remains into droplets.

tribution corresponding to a pure siloxane overlayer $3\lambda_{Si}$ thick,

$$n_{Si}(z, 1) = \begin{cases} n_{Si}^0, & z \leq 3\lambda_{Si} \\ 0 & z > 3\lambda_{Si} \end{cases} \quad (4)$$

where n_{Si}^0 is the atomic density of Si in pure PDMS.

It can be readily shown that the theoretical curve $K(\alpha)$ calculated with $n_{Si}(z, 1)$ given by eq. (4) provides the lowest possible K within the framework of the homogeneous deformation model: Both an increase in the overlayer thickness in eq. (4) and the replacement of the stepwise concentration depth profile by a function smoothly falling at $z > 3\lambda_{Si}$ result in a slower decrease of K with α . (If the thickness of the siloxane overlayer in the initial sample is greater than $3\lambda_{Si}/\lambda$, the overlayer thickness in the stretched sample will exceed $3\lambda_{Si}$, so that K will not practically depend on α at all.)

As seen from Figure 2, the experimental results for K lie much below the upper theoretical curve, i.e., the homogeneous deformation model fails to describe the observed drop in siloxane surface concentration even in the most favorable case, when the theoretical values of $K(\alpha)$ are as low as possible. Considering this result, we tried an alternative model, which was certain to predict a very strong siloxane surface depletion with stretching. This second model is based on the assumption that all the new surface area formed upon stretching is composed of the pure PCP component. In this case, the theoretical $K(\alpha)$ can be shown to be given by

$$K(\alpha) = 100/[\omega + \alpha\beta(100 - \omega)] \quad (5)$$

In this equation, β is the degree of contraction of sample in width ($\alpha\beta\gamma \approx 1$); the parameter ω is related to the initial siloxane surface concentration, c_{PDMS}^0 , and the atomic densities of the pure components, n_i , by the formula

$$\omega = c_{PDMS}^0 (1 - n_{PCP}/n_{PDMS}) \quad (6)$$

A possible realization of this model is depicted in Figure 3(c). It is assumed that the stretching does not affect the thickness and total area of the siloxane overlayer but brings about numerous ruptures in it to expose the underlying PCP base. In this case, all the increase in the surface area will solely be due to the PCP component, as required. As can be seen from Figure 2, the predictions of the “ruptured overlayer model” are, as expected, much below the theoretical curve derived from the homogeneous deformation model. Nevertheless, they still lie above the experimental points, so that the ruptured overlayer model also does not explain the stretching-induced escape of surface siloxane into the bulk.

To examine whether the unusually strong surface depletion of siloxane with stretching is associated with necking, we excluded the region of necking from consideration and evaluated the behavior of K separately in the region of uniform stretching ($\alpha > 3$). To this end, the sample stretched to $\alpha = 3.8$ was taken as the initial one and its stretching degree α was assumed to be unity. The experimental results transformed in such a way are shown in Figure 2 as crossed circles. It is seen that in the region of uniform stretching the surface depletion of siloxane is also much stronger than is predicted by the ruptured overlayer model. Moreover, the transformed data well complement the original experimental points, which suggests that the mechanism of siloxane surface depletion with stretching is most likely the same throughout the deformation range studied.

In the discussion of our preliminary XPS results,¹² we proposed two possible explanations for the unusually strong surface depletion of siloxane with stretching. The first is associated with crazing in the PCP matrix. It is not unlikely that siloxane drains down into the crazes, thus escaping from the near-surface region sampled by XPS. The second explanation is related to a spherulite–fibrilla transformation, which is known to take place upon stretching of PCP films.¹³ It can be speculated that the rotation of crystallites, involved in this transformation, leads to intensive stirring of the near-surface layers and the resulting escape of the surface siloxane into the bulk. In other words, the rotating crystallites play the role of numerous stirrers which

mix the siloxane-enriched near-surface region with deeper polymer layers composed of practically pure PCP.

The SEM study made in this work revealed one more factor which could be responsible for the anomalous surface depletion of siloxane on stretching. Figure 4 presents typical electron micrographs of pure PCP and a PCP/PDMS blend before and after stretching to $\alpha = 4$. The stretching of pure PCP led to a clearly seen morphological transformation of the initial spherulitic structure [Fig. 4(a)] to a structure of the fibrillar type [Fig. 4(b)]. Compared to the initial pure PCP sample, the surface of the initial PCP/PDMS blend [Fig. 4(c)] showed a much more smoothed relief due to the presence of a siloxane overlayer on the sample surface. After stretching, the surface of most samples appeared as shown in Figure 4(d): The siloxane overlayer broke into small droplets to expose the underlying PCP.

The relevant model can be derived from the one shown in Figure 3(c) by introducing the additional assumption that the disruption of the siloxane overlayer into individual islands of the same total area is followed by the contraction of the islands into droplets [Fig. 3(d)]. As a result, the exposed surface of PVC further increases, so that the siloxane concentration seen by XPS sinks below the theoretical curve predicted by the ruptured overlayer model and eq. (4).

The electron micrograph shown in Figure 4(d) brings up an obvious question: Why does the surface siloxane gather up into droplets and not spread over the whole surface, as can be expected from the inequality $\sigma_{\text{PCP/air}} - \sigma_{\text{PDMS/air}} - \sigma_{\text{PDMS/PCP}} > 0$ ($\sigma_{\text{PCP/air}} = 44$, $\sigma_{\text{PDMS/air}} = 20$, $\sigma_{\text{PDMS/PCP}} \approx 6.5$ dyne/cm [Ref. 14]). The only plausible answer is that the stretching affects the magnitudes of the surface energies, so that the above inequality is no longer valid. It can be spec-

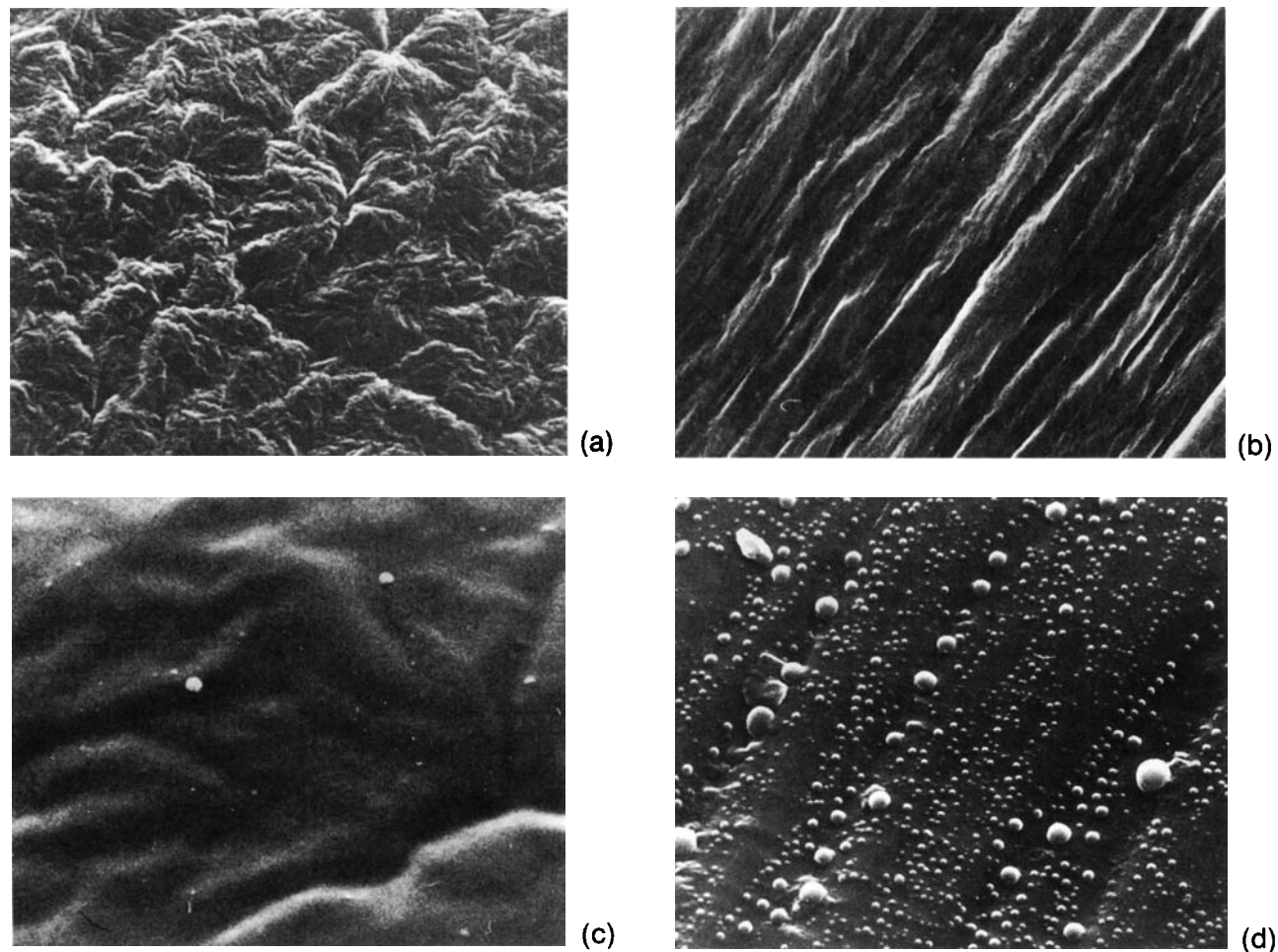


Figure 4 Scanning electron micrographs of (a) initial and (b) stretched PCP films, in comparison with micrographs of (c) initial, (b) stretched, and (e) unloaded films of PCP/PDMS (MW = 2500) blends ($\times 5000$).

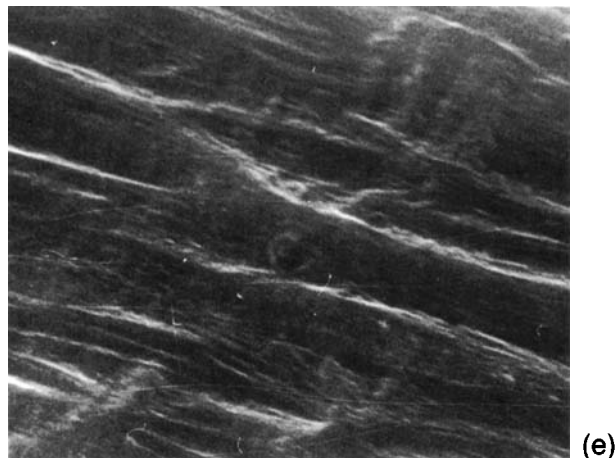


Figure 4 (Continued from the previous page)

ulated that the transformation of the siloxane overlayer in the course of stretching proceeds in two steps. At low stretching degrees, the overlayer remains continuous and its thickness steadily decreases with increasing α [just as it occurs in the homogeneous deformation model shown in Fig. 3(b)]. As the overlayer thickness becomes comparable to the molecular dimensions and the range of the intermolecular interactions, microscopic effects in the surface tension come into force and change the magnitudes of the interface energies involving PDMS. From general considerations, it follows that both $\sigma_{\text{PDMS/air}}$ and $\sigma_{\text{PDMS/PCP}}$ will increase with decreasing thickness of the siloxane overlayer, so that the difference $\sigma_{\text{PCP/air}} - \sigma_{\text{PDMS/air}} - \sigma_{\text{PDMS/PCP}}$ may well change its sign. At this point, the overlayer would break into droplets to reduce the area of the PDMS/air and PDMS/PCP interfaces.

The existence of a certain critical thickness for the overlayer disruption is confirmed by the surface behavior of a 2% PDMS/PCP blend. The relevant experimental results are shown in Figure 5 as full circles. One can see that the drop in the siloxane surface segregation parameter K occurs with an appreciable delay, viz., not earlier than the stretching degree attains a value of 3. The observed delay can be explained based on a reasonable assumption that the siloxane overlayer formed on the surface of the 2% blend is much thicker than that occurring in the 0.25% blend. As a result, the thinning of the former overlayer to the critical thickness requires a much higher stretching degree to be attained.

To appreciate the rate of siloxane surface depletion with stretching after the overlayer disruption, the experimental results for the 2% blends were also compared with the theoretical predictions based on the uniform deformation and overlayer rupture

models. Unlike the comparison made in Figure 3, the model curves were calculated with reference to $\alpha = 3$ (and not 1), i.e., the threefold stretched sample was assumed to be the initial one and both the model curves were scaled by the factor 3 along the abscissa axis. As seen from Figure 5, the 2% blends, too, show a much stronger surface depletion of siloxane with stretching than it is predicted by the model calculations.

So far nothing has been said as to what happens to the surface of stretched samples after the stress is removed and the samples are allowed to contract to a given α . The relevant experimental data are shown in Figures 3 and 5 as open circles. An unexpected result is that in most cases the surface concentration of siloxane in an unloaded sample is higher than that in a stretched sample with the same α . This refers to the whole range of α for the 0.25% blends (Fig. 3) and to $\alpha > 5$ for the 2% blends (Fig. 5). The increase in the surface segregation of siloxane in the unloaded samples suggests that along with the above-discussed processes, which may be responsible for the apparent siloxane surface depletion on stretching, there is a reverse process involving the transfer of bulk siloxane to the surface. (For example, siloxane can simply squeeze out to the surface from various microcavities in the polymer bulk, just as water from a squeezed sponge.) When the sample is stretched, this outward flux of siloxane is masked by the siloxane overlayer disruption seen by XPS as surface depletion of PDMS. However, the outward flux makes itself evident when the sample is contracted and the siloxane droplets on the sample surface merge back into a continuous overlayer [Fig. 4(e)].

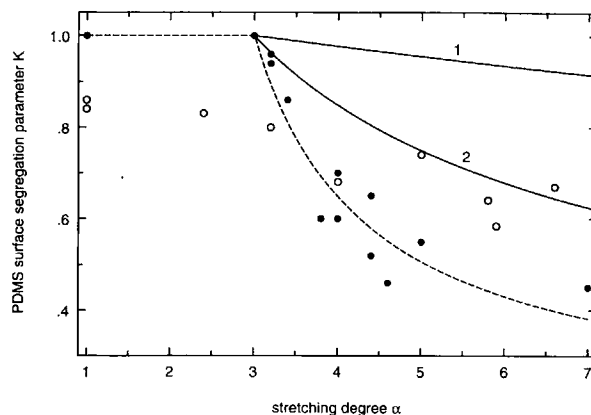


Figure 5 The dependence of the PDMS surface segregation parameter K on the stretching degree α for 2% blends of PDMS (MW = 2500) in PCP. The designations are the same as in Figure 2.

The occurrence of siloxane transfer to the surface upon stretching and subsequent contraction of the sample was revealed more explicitly in a special experiment, in which the parallel processes leading to the apparent surface depletion of siloxane were suppressed. To this end, a sample prepared in the usual way was washed in diethyl ether (a solvent selective to PDMS) to remove the siloxane overlayer. According to XPS, this reduced the surface concentration of siloxane, c_{PDMS} , from 95 to 20 atom %. (The surface composition of the washed sample showed no detectable changes both on keeping for several days at room temperature and on heating to 40°C.) The sample was then stretched to $\alpha = 5$ and then unloaded at room temperature until its length no longer decreased. The resulting α was 2.8. Despite the fact that the surface area of the sample remained $\sqrt{2.8} \approx 1.7$ times larger than that of the initial sample, the surface concentration of siloxane proved to be 26 atom %, i.e., the segregation parameter K exceeded unity ($K = 26/20 = 1.3$). After the heating to 40°, the sample completely recovered its dimensions and the siloxane surface concentration rose to 38 atom % ($K = 1.9$).

To complete the discussion, we turn to blends of PCP with the long-chain PDMS (MW = 625,000). The results of XPS measurements for 0.25% blends are summarized in Figure 6. Two differences from the data depicted in Figure 2 stand out. First, the long-chain PDMS shows a much weaker surface depletion on stretching. The experimental points fall between the two model curves, which can perhaps be interpreted as evidence that the effect of stretching on the near-surface region can be described as a combination of thinning and rupture of the siloxane-rich surface layers. (Importantly, no droplets on the surface of stretched samples were observed in the electron micrographs of the PCP/PDMS [625,000] blends.) The second difference between the XPS data in Figures 2 and 6 is that the surface behavior of the long-chain PDMS on stretching and subsequent contraction is completely reversible: At a fixed α , the stretched and unloaded samples show practically the same surface segregation of siloxane.

The influence of the PDMS chain length on the surface behavior of PCP/PDMS blends on stretching is hardly surprising. First, it should be remembered that the PCP/PDMS (2500) and PCP/PDMS (625,000) blends of the same bulk composition have from the outset (before stretching) quite different surface compositions (Fig. 1), which should result in different surface morphologies. Whereas the short-chain PDMS gives a surface composition close to 100%, which corresponds to a nearly continuous

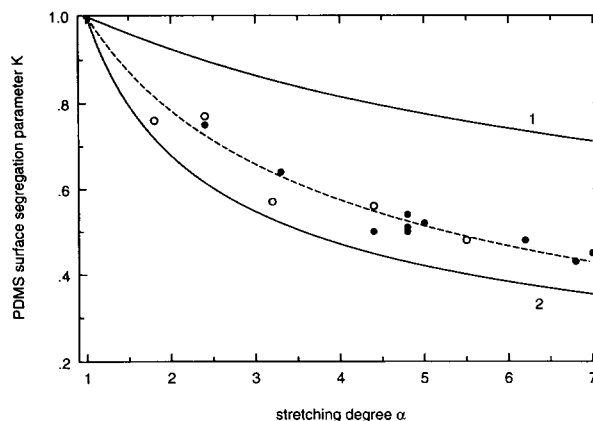


Figure 6 The dependence of the PDMS surface segregation parameter K on the stretching degree α for 0.25% blends of PDMS (MW = 625,000) in PCP. The designations are the same as in Figure 2.

overlayer on the PVC surface, the long-chain PDMS covers only half the surface area, so that the surface morphology should indubitably be different. Second, the chain length affects many of the physical properties of PDMS, which can govern the surface behavior of PDMS on stretching. The most important of these properties seems to be viscosity. It appears that the long-chain PDMS does not follow the pattern observed with the short-chain PDMS mainly because the former has no time to drain down into crazes, to gather up into droplets, to squeeze out to the surface from microcavities, etc. As a result, only some selected (fast and reversible) processes, such as the thinning and rupture of the siloxane-rich surface layers, are realized.

CONCLUSIONS

The XPS and SEM results of this work show that mechanical deformation can strongly affect the surface composition of a multicomponent polymer. In the PDMS/PCP blends, the stretching gives rise to a substantial reduction in the surface segregation of siloxane. The course of the surface depletion of siloxane with stretching depends on the molecular weight and initial surface concentration of siloxane. In the case of oligomeric siloxane additive (MW = 2500), the surface depletion of siloxane starts at a certain stretching degree α dependent on the initial siloxane surface concentration. As the latter is increased, the siloxane surface depletion commences at a higher α . A remarkable feature of the PCP/PDMS (2500) blends is the irreversibility of their surface compositions in α : The surface siloxane

concentration in a sample stretched to a given α_1 is different from (typically, lower than) that in a sample stretched to a certain $\alpha_2 > \alpha_1$ and then unloaded to α_1 . The blends of polymeric siloxane (MW = 625,000) show a comparatively weaker surface depletion of siloxane on stretching and, in addition, a completely reversible surface behavior on subsequent contraction.

In this work, we have suggested several possible explanations for the observed effect of mechanical deformation on the surface composition. At this stage, it is hardly possible to give a more unambiguous interpretation of the experimental data. We hope that further studies will provide a better understanding of the processes responsible for the observed changes in surface composition and morphology.

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