

# Effect of Deformation on the Surface Composition of Multicomponent Polymers. III. Behavior of Surface-Active Additive on Elastomer Surface in Stretching–Contraction Cycles

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**ABSTRACT:** The effect of the stretching–contraction cycle on the surface composition and morphology of polychloroprene elastomer blended with small amounts of surface-active polydimethylsiloxane–polysulfone block copolymers was studied using X-ray photoelectron spectroscopy and scanning electron microscopy. Copolymers with a large concentration of rigid polysulfone block showed a substantial drop in the surface concentration of the copolymer additive after the stretching–contraction cycle, while copolymers with a large concentration of flexible siloxane segments retained their surface composition practically unchanged. Wrinkling of surface areas occupied by the additive, which occurred upon contraction of the sample to its initial dimensions, is believed to be the reason for the observed drop in surface concentration of the rigid copolymer additive. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1964–1970, 2000

**Key words:** surface; polymer blends; deformation

## INTRODUCTION

In previous articles<sup>1,2</sup> we reported on studies of the effect of uniaxial stretching on the surface of polychloroprene (PCP) elastomer blended with small amounts of polydimethylsiloxane (PDMS)

and PDMS-containing surface-active additives. Changes in the surface composition and morphology were followed using X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). Prior to stretching, all blends exhibited a high surface enrichment in the additive, which segregated on the PCP surface to form a continuous or discontinuous overlayer. Stretching led to a substantial surface depletion of the additive, with the extent of depletion dependent on the additive's molecular weight and architecture. Thus, short-chain PDMS (MW = 2500) showed a much stronger surface depletion with stretching

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**Table I** Average Composition of Unstretched PCP-PDMS/PSF Blends in Bulk and in Near-Surface Region for  $d_{XPS} = 50$  (25) Å (atom %)

Additive	PCP		PDMS		PSF		PDMS/PSF	
	Bulk	Surface	Bulk	Surface	Bulk	Surface	Bulk	Surface
1% 2500/44,000	98.7	7 (7)	0.05	28 (40)	1.21	67 (55)	0.04	0.42 (0.73)
0.5% 1800/44,000	99.4	27 (18)	0.02	25 (42)	0.61	45 (38)	0.03	0.56 (1.1)
1% 1800/44,000	98.7	22 (17)	0.04	31 (52)	1.23	46 (32)	0.03	0.67 (1.6)
2.5% 1800/44,000	96.9	18 (14)	0.09	37 (57)	3.06	45 (30)	0.03	0.82 (1.9)
1% 2500/3500	98.9	13 (12)	0.39	49 (62)	0.75	38 (28)	0.52	1.29 (2.2)
2.5% 2500/3500	97.1	8 (3.5)	0.98	48 (67)	1.88	46 (29)	0.52	1.04 (2.3)

than long-chain PDMS (MW = 625,000).<sup>1</sup> This occurred because the short-chain PDMS collapsed on stretching into individual droplets, thereby baring the surface of the underlying PCP matrix.

In blends of PCP with PDMS-polysulfone (PSF) block copolymers,<sup>2</sup> the effect of stretching on the surface composition was governed by the copolymer block lengths. In the case of a 2500/3500 block copolymer, the copolymer overlayer strictly followed the stretching of the elastic substrate, while in blends of a more rigid 2500/44,000 copolymer, the deformation of the overlayer lagged noticeably behind the PCP substrate. In addition, the surface regions of the 2500/44,000 copolymer showed a substantial surface depletion of siloxane with stretching, while in blends of the 2500/3500 copolymer the stretching had practically no effect on the distribution of the copolymer components in the near-surface region.

In this article we continue our studies of the effect of deformation on the surface of PCP-PDMS/PSF blends. Here the focus is on changes in the surface composition and morphology after stretching and subsequent contraction of the samples. Our preliminary experiments<sup>1,2</sup> showed that the stretching-contraction cycle may strongly affect the surface composition even when the sample completely restores its initial dimensions.

## EXPERIMENTAL

The elastomer used was commercially available noncrosslinked PCP Neopren® from Du Pont. The surface-active additives were PDMS/PSF multi-block copolymers with the following block lengths: 1800/44,000, 2500/44,000, and 2500/3500.<sup>2</sup> The blends were prepared by mixing chloroform solu-

tions of the blend components in a prescribed proportion. Three different blend compositions were studied: 0.5%, 1%, and 2.5% (Table I). The polymer films were made by casting the solutions of the blends onto stretched cellophane. The samples for deformation experiments were in the form of strips 70 × 10 × 0.3 mm in size. The samples were stretched at a rate of 0.1 mm/s to a given stretching degree, kept for an hour in the stretched state, and then unloaded at the same rate until the sample restored its initial size. The stretching degree was varied from 2 to 7.

XPS spectra were acquired using a Kratos XSAM-800 dual-chamber spectrometer with a Mg anode at a vacuum of 10<sup>-9</sup>-10<sup>-10</sup> Torr. The surface composition was calculated from the integral intensities of the Si2p, S2p, and Cl2p lines as described elsewhere.<sup>3</sup> To judge the presence of a concentration gradient in the near-surface region, the spectra were acquired at both 90° and 30° electron takeoff angles, which corresponded to an XPS sampling depth,  $d_{XPS}$ , of about 50 and 25 Å, respectively. Scanning electron micrographs were obtained on a JEOL JSM-5300LV electron microscope equipped with an accessory for energy dispersive X-ray (EDX) microanalysis (Oxford Instruments). The samples for SEM were coated with a layer of gold 300 Å in thickness using a JFC-1100E sputter coater.

## RESULTS AND DISCUSSION

### XPS Measurements

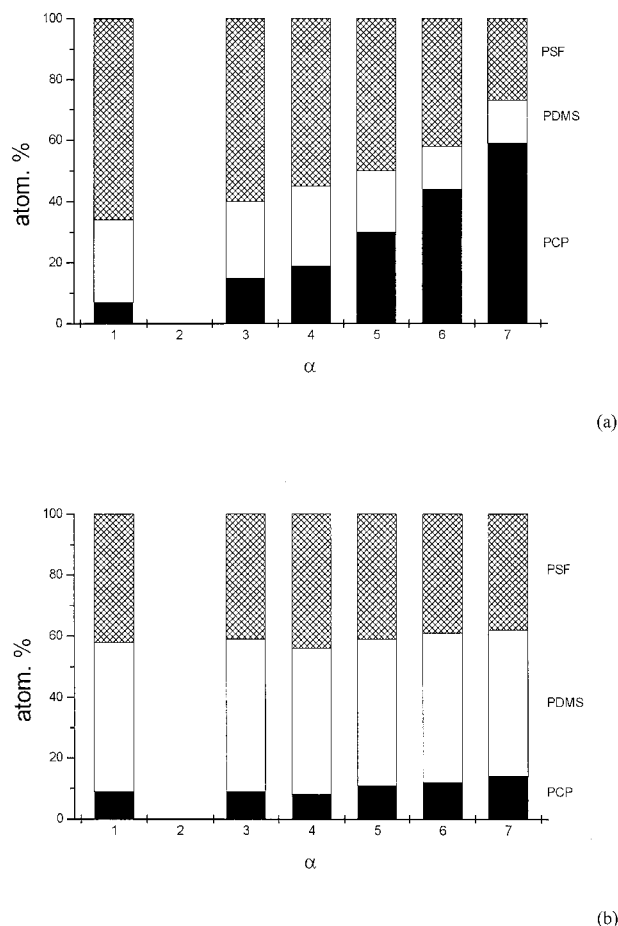
The initial unstretched films showed, as expected, a high surface segregation of the copolymer additive. This can be seen quite well in Table I, which

summarizes the relevant results in terms of the atomic percentage of the blend components (the atomic percent is preferred over the weight percent because the former provides an approximate estimate of the surface area occupied by the given component). The surface areas occupied by the additive are, in their turn, enriched in the siloxane component because of a “local” surface segregation, which can be well appreciated from the ratio PDMS/PSF.

A comparison of the average surface concentration of PCP for  $d_{XPS} = 50 \text{ \AA}$  and  $d_{XPS} = 25 \text{ \AA}$  shows that in most blends a decrease in  $d_{XPS}$  results in a noticeable decrease in the concentration of the elastomer matrix and a respective increase in the concentration of the additive. This suggests that the thickness of the surface areas occupied by the additive is less than  $50 \text{ \AA}$ . The decrease of  $d_{XPS}$  from  $50 \text{ \AA}$  to  $25 \text{ \AA}$  also leads to an increase in the ratio PDMS/PSF, which provides additional evidence for the local segregation of PDMS.

Now we turn to samples subjected to the stretching–contraction cycle. It is convenient to start our discussion with a comparison of samples containing 1% 2500/44,000 copolymer and 2.5% 2500/3500 copolymer (Table I). Prior to deformation, these samples have almost the same total content of surface additive (93% and 92%, respectively) but differ significantly in the length and proportion of the rigid PSF block. The surface composition of the samples after the stretching–contraction cycle is shown schematically in Figure 1 as a function of the stretching degree,  $\alpha$ , with  $\alpha = 1$  corresponding to the initial unstretched samples. As seen from Fig. 1(a), which refers to the copolymer additive with a long rigid block (2500/44,000 copolymer), the stretching–contraction cycle results in a substantial reduction of the surface area occupied by the additive and in the associated exposure of the underlying elastomer matrix. Thus, in the sample stretched to  $\alpha = 7$  and contracted to its initial size, the fraction of bare PCP surface rises from 7% to 60%.

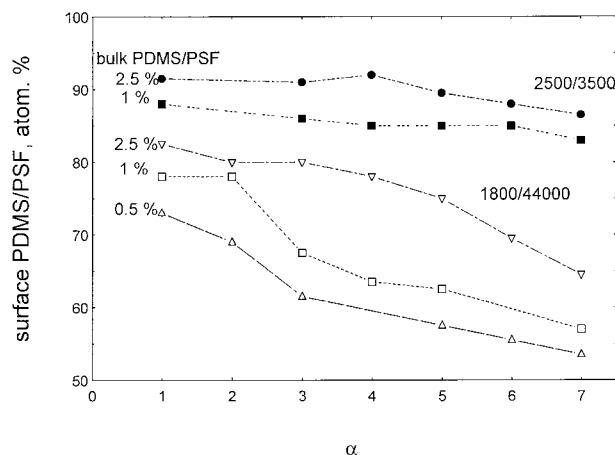
For the 2500/3500 copolymer additive, with a much larger content of the flexible block, the effect of the stretching–contraction cycle on the surface composition of the blend is negligible [Fig. 1(b)]. A statistically significant decrease in the surface concentration of the copolymer is only observed at the largest stretching degree,  $\alpha = 7$ , and does not exceed 5%. Thus, the reversibility of



**Figure 1** The surface composition of (a) PCP + 1% PDMS/PSF (2500/44,000) and (b) PCP + 2.5% PDMS/PSF (2500/3500) blends after the stretching–contraction cycle as a function of the stretching degree,  $\alpha$ .

the surface composition of the blends in the stretching–contraction cycle is governed by the proportion of the flexible and rigid blocks, which determines, in its turn, the mechanical rigidity of the copolymer as material.

The above discussed difference in the surface behavior between the “rigid” (2500/44,000) and “soft” (2500/3500) additives was also observed in the other blends studied in this work. This can be seen from Figure 2, which shows the surface concentration of the additive after the stretching–contraction cycle as a function of the stretching degree for some other blend compositions. Here again, the stretching–contraction cycle has a significant effect on the surface composition only in blends containing the PSF-rich additive (1800/44,000). It can also be seen that the deformation behavior of the surface composition depends on



**Figure 2** The surface concentration of the copolymer additive in the PCP + PDMS/PSF blends after the stretching-contraction cycle as a function of the stretching degree  $\alpha$ .

the additive content in the bulk: The higher the additive content, the greater the stretching degree required for irreversible changes in the surface composition. Similar to the above discussed 2.5% blend of the 2500/3500 additive, the 1% blend retains its surface composition practically unchanged.

The surface behavior of the siloxane component (Fig. 3) is similar to that of the whole copolymer additive: In blends of the "soft" additive, the surface siloxane changes after the stretching-contraction cycle only slightly, while the blends of the "rigid" additive show a substantial drop in the surface concentration of siloxane.

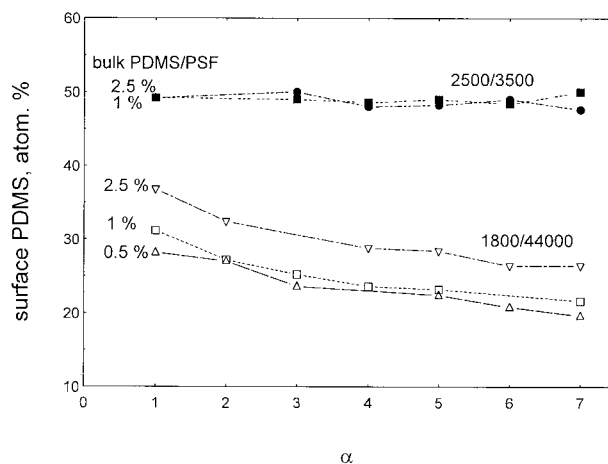
### SEM Results

In the SEM micrographs the surface of the initial unstretched samples looked smooth and structureless. The stretching led to the appearance of strips along the stretching axis,<sup>1</sup> which is characteristic of stretched polymers. After the samples were unloaded and allowed to contract to their initial dimensions, the strips disappeared, and a new, wrinkled structure emerged. Typical micrographs of the sample surface after the stretching-contraction cycle are given in Figure 4. The wrinkled areas are 20–100  $\mu\text{m}$  in size and are slightly elongated along the axis of stretching. Each area contains 20–50 wrinkles. The wrinkles are 2–3  $\mu\text{m}$  in width and are strictly perpendicular to the stretching axis.

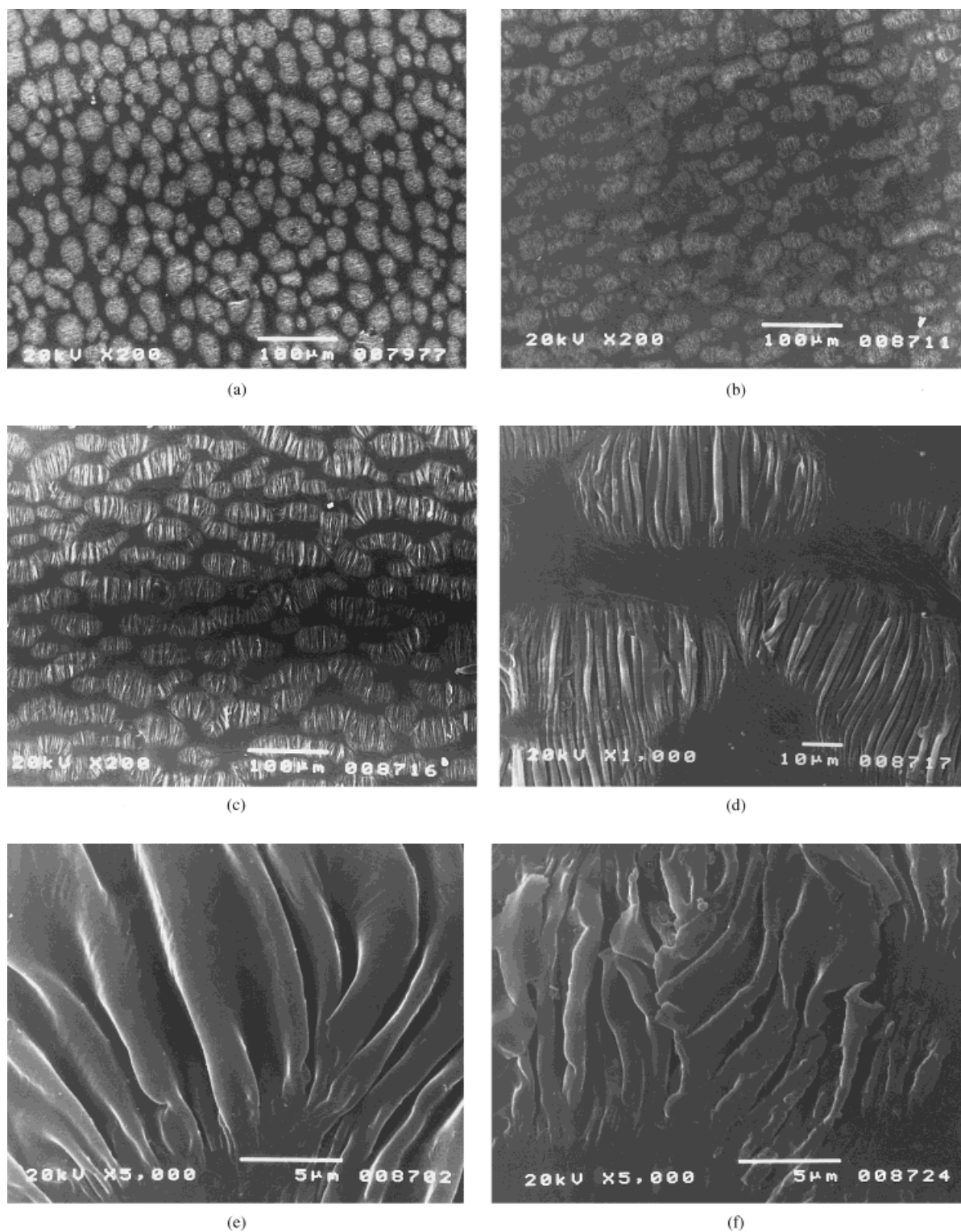
In reference experiments with pure PCP, no wrinkled structures were found. This suggests

that the wrinkled areas seen in Figure 4 are formed by the domains of the surface-segregated copolymer additive. Further evidence in support of this conclusion was provided by EDX microanalysis, which showed a drastic drop in the surface concentration of chlorine when the electron beam struck the wrinkled domains. The wrinkled structures were clear-cut in blends containing the "rigid" copolymers, while the "soft" copolymer either exhibited no wrinkled structures at all or formed vague wrinkles uniformly distributed over the sample surface (Fig. 5).

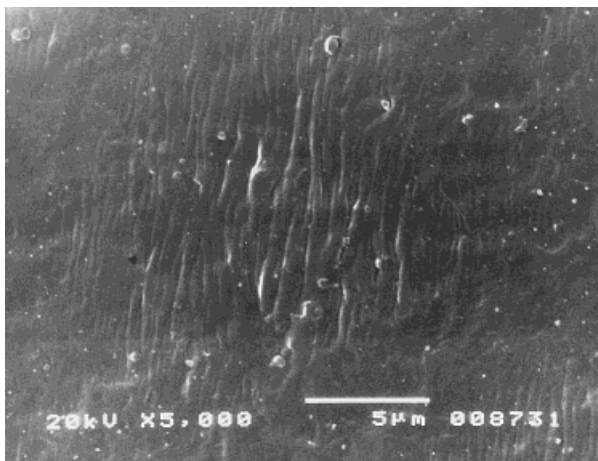
The wrinkling of the copolymer domains was observed even at the smallest stretching degree tried ( $\alpha = 2$ ). For a given blend composition, the average size of the wrinkled domains was independent of  $\alpha$  throughout the range  $2 \leq \alpha \leq 7$  [Fig. 4(b,c)]. However, the domain size was strongly dependent on the total additive content in the blend: For the 0.5%, 1%, and 2.5% blends of the 1800/44,000 copolymer, the average domain size was 20, 50, and 100  $\mu\text{m}$ , respectively. The growth of the domain size with increasing additive content can be visually appreciated from typical micrographs of the 1% and 2.5% blends in Fig. 4a–c. Up to  $\alpha = 4$ –5, the wrinkles were more or less smooth and regular and extended from one domain boundary to the other [Fig. 4(d,e)]. With increasing  $\alpha$ , they became more clear-cut and embossed [Fig. 4(b,c)]. As  $\alpha$  was further increased, the regularity was lost, the wrinkles disrupted and piled up [Fig. 4(f)].



**Figure 3** The surface concentration of PDMS in the PCP + PDMS/PSF blends after the stretching-contraction cycle as a function of the stretching degree  $\alpha$ .



**Figure 4** Electron micrographs of PCP + PDMS/PSF 1800/44,000 blends after the stretching–contraction cycle for: (a) 1% PDMS/PSF,  $\alpha = 5$ , magnification 200 $\times$ , (b) 2.5% PDMS/PSF,  $\alpha = 3$ , magnification 200 $\times$ , (c) 2.5% PDMS/PSF,  $\alpha = 5$ , magnification 200 $\times$ , (d) 2.5% PDMS/PSF,  $\alpha = 5$ , magnification 1,000 $\times$ , (e) 2.5% PDMS/PSF,  $\alpha = 5$ , magnification 5,000 $\times$ , (f) 2.5% PDMS/PSF,  $\alpha = 7$ , magnification 5,000 $\times$ .



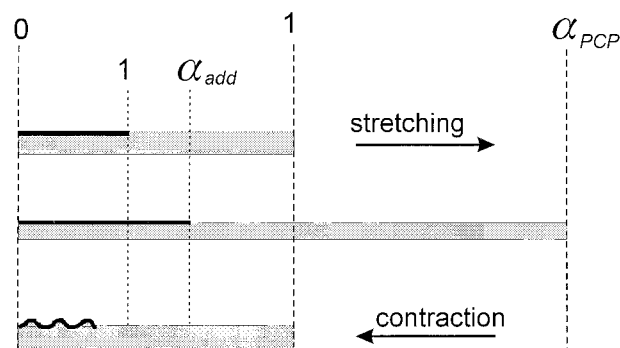
**Figure 5** Electron micrographs of PCP + 2.5% PDMS/PSF 2500/3500 blends after the stretching-contraction cycle,  $\alpha = 6$ .

An idealized mechanism of the formation of wrinkles in the blends of “rigid” copolymer additive is schematically depicted in Figure 6. The light and dark bars represent the PCP elastomer and a domain of the additive on its surface ( $\alpha_{PCP}$  and  $\alpha_{add}$  are the respective stretching degrees). Considering that the thickness of the domain is of the order of 10–100 Å, while its lateral dimensions are of the order of 100  $\mu\text{m}$ , the domain is best visualized as a very thin sheet of a plastic but fairly rigid material attached to the surface of an elastic substrate. On stretching, the sheet also elongates but lags behind the PCP support. As we have shown in the preceding article,<sup>2</sup> this lag can be described by the equation  $\alpha_{add} = (\alpha_{PCP})^\omega$ , where  $0 \leq \omega \leq 1$ . When the elastomer is unloaded and allowed to contract, it proves to be easier for the sheet to wrinkle than to contract reversibly to its initial length (the reason is that the resistance of the thin copolymer sheet to folding is much less than its resistance to compression). In the ideal case, the sheet shrinks together with the elastomer substrate, so that the net deformation degree of the sheet after the stretching-contraction cycle is  $\alpha_{add}/\alpha_{PCP} = \alpha_{PCP}^{\omega-1}$ . Considering that the deformation of the PCP + PDMS/PSF blends along the axes perpendicular to the axis of stretching is well described by the inverse square root dependence of  $\alpha$ ,<sup>2</sup> the area  $S_0$  initially occupied by the additive reduces, after the stretching-contraction cycle, to  $S_0 \alpha_{PCP}^{(\omega-1)} \alpha_{PCP}^{-(\omega-1)/2} = S_0 \alpha_{PCP}^{(\omega-1)/2}$ . The associated rel-

ative change in the area is  $\Delta S/S_0 = 1 - \alpha_{PCP}^{(\omega-1)/2}$ . So, the stretching-contraction cycle may either reduce ( $\Delta S/S_0 < 0$ ) or increase ( $\Delta S/S_0 > 0$ ) the area occupied by the copolymer additive, depending on the magnitudes of  $\alpha_{PCP}$  and  $\omega$ . In as much as the stretching-contraction cycle retains the total surface area of the sample unchanged, a change in  $\Delta S/S_0$  results in a proportional change in the surface concentration of the additive, as detected by XPS. For an infinitely rigid (nonstretchable) additive,  $\omega = 0$  and  $\Delta S/S_0 < 0$  at any  $\alpha_{PCP}$ . If the additive is infinitely soft and strictly follows the deformation of the underlying elastomer,  $\omega = 1$  and  $\Delta S/S_0 = 0$ . Returning to the PDMS/PSF copolymers studied in this work, we can thus conclude that the surface behavior of the “rigid” copolymers containing the long PSF block (44,000 MM) is described by a small  $\omega$ , while the behavior of the “soft” 2500/3500 copolymer corresponds to  $\omega$  close to unity.

## CONCLUSIONS

As an extension of our previous work,<sup>1,2</sup> we studied the effect of stretching-contraction cycles on the surface composition of blends of PCP elastomer with surface-active PDMS/PSF diblock copolymers. The blends showed a depletion in the surface concentration of the additive after the stretching-contraction cycle, with the depletion degree being dependent on the rigidity of the copolymer additive, as determined by the content of the rigid PSF block. The deformation-induced changes in the surface compo-



**Figure 6** A schematic mechanism of the formation of wrinkled structures.

sition were rationalized in terms of the formation of wrinkled structures on the sample surface. The wrinkling of rigid surface areas upon contraction of the underlying substrate seems to be quite a general phenomenon. Similar changes in surface morphology have been observed in polymers coated with thin metallic layers by vacuum deposition.<sup>4</sup> Moreover, a similar mechanism has been invoked in geology to explain the formation of mountains.

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