

An XPS Study of the Surface–Bulk Compositional Differences in Siloxane-Containing Block Copolymers and Polymer Blends

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SYNOPSIS

X-ray photoelectron spectroscopy (XPS) is used to compare the surface behavior in various binary systems of poly(dimethylsiloxane) with poly(bisphenol A sulfone) and poly(bisphenol A carbonate). All the systems studied show a pronounced surface enrichment in siloxane. At a fixed siloxane concentration in the bulk the lowest extent of surface enrichment is observed in the neat copolymers, next go the blends of copolymers in homopolymers, and the highest extent of surface enrichment is characteristic of the blends of homopolymers. The blends of two copolymers show an unexpected surface behavior: The addition of minor amounts of a siloxane-rich copolymer to another copolymer possessing a much lower siloxane content decreases (rather than increases) the surface siloxane concentration of the latter. A microscopic model is suggested to explain the observed surface behavior. The model involves the formation of a “quasi-two-dimensional” overlayer of additive's macromolecules on the blend surface, with the macromolecules oriented preferentially parallel to the sample surface.

INTRODUCTION

It has been recognized for a long time that many important properties of a polymer are determined by the composition and structure of its surface.¹ Among the surface-sensitive properties are adhesion, wettability, friction characteristics, biocompatibility, weathering, and many others. In multicomponent polymer systems (copolymers and polymer blends) the surface composition may differ greatly from the composition in the bulk since components of lower surface energy always tend to enrich the surface to minimize the free energy of the system. The surface segregation occurs at very low concentrations,^{2–5} which allows an efficient modification of the surface-sensitive properties to be accomplished without significant change in the bulk properties.

In the case of solvent-cast polymer films the surface–bulk compositional differences depend on the

difference in the surface energies of the components, on casting solvent, on the rate of solvent evaporation, on temperature, and some other factors.^{2,6} Also, at a given bulk composition the extent of surface segregation should depend on what particular type of polymer system is dealt with: a block copolymer, a blend of homopolymers, a blend of homopolymer and copolymer, or a blend of copolymers. A dependence of this kind should indeed occur because the presence or absence of chemical links between the components of a system affects the migration of the lower surface energy species toward the surface during the film casting.

Despite the obvious significance of the surface–bulk compositional relationships in polymers, relatively few systematic studies have been done on this subject. For the most part, these are X-ray photoelectron spectroscopy (XPS) studies of block copolymers (see a review in Ref. 2) performed on a very limited number of bulk compositions (usually, on three distinct compositions). Even less studied are blends of homopolymers³ and blends of homopolymers with copolymers,^{2,4,5} while blends of copolymers have not been yet investigated at all.

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For the development of efficient methods of surface modification, of great importance would also be a comparison of the surface segregation in different types of polymer systems with similar bulk compositions. Unfortunately, almost no work of this kind has been reported.

In this work we present the results of a comparative XPS study on various binary systems of poly(dimethylsiloxane) (PDMS) with poly(sulfone) (PSF) and poly(carbonate) (PC). PDMS-containing systems represent a very convenient object to follow the surface-bulk compositional differences since the surface energy of PDMS is at least 10 dyn/cm lower than that for other polymers ($\sigma = 22, 36,$ and 34.5 dyn/cm for PDMS, PSF, and PC, respectively). There is also a practical interest to PDMS-containing systems, stimulated by the remarkable surface properties of siloxane (low wettability, high biocompatibility and thromboresistivity, the ability to form, under the action of some oxidizing agents, ultra-thin quartzlike overlayers with excellent protective and gas separation properties).⁷⁻⁹ Some preliminary results of this work have been discussed in our previous papers.^{10,11}

EXPERIMENTAL

Materials and Sample Preparation

The homopolymers used in this study were commercially available samples, MW = 40,000 for PSF, 36,000 for PC, and 600,000 for PDMS. The block copolymers studied were poly(bisphenol A sulfone)/

PDMS and poly(bisphenol A carbonate)/PDMS copolymers with block lengths listed in Table I. It is worth noting that the PSF/PDMS copolymers used cover a much wider range of bulk siloxane content than the range investigated previously by other authors.^{2,12} This particularly refers to the low-concentration part of the range, which extends to as low as 3.9% PDMS and overlaps with the concentration range studied for blends.

Aside from the usual poly(bisphenol A carbonate)/PDMS block copolymers (samples 20 to 22 in Table I), use was also made of copolymers containing diurethane segments— $[\text{CH}_2\text{O}(\text{CH}_2)_2\text{OC}(\text{O})\text{NH}-\text{C}_6\text{H}_4]_2\text{CH}_2$ —between the siloxane and carbonate blocks (samples 23 and 24, hereinafter PC/PU/PDMS copolymers). The nitrogen-containing diurethane segments served as labels to make the two kinds of copolymers distinguishable by XPS in studies of their blends.

In surface studies of polymer blends the following samples were used: blends of homopolymers PSF + PDMS and PC + PDMS; blends of homopolymer and copolymer PSF + PSF/PDMS(9), PC + PC/PDMS(20), PC + PC/PDMS(22), PC + PC/PU/PDMS(23), and PC + PC/PU/PDMS(24); blends of copolymers PC/PU/PDMS(23) + PC/PDMS(22).

The symbols “+” and “/” are here used to delimit the components of the blends and copolymers, respectively; in all notations of the blends the abbreviation of the base is first, followed by the abbreviation of the additive; the number in parentheses refers to the number of copolymer in Table I.

Table I Characterization Data for Block Copolymers

No.	Block Length		wt % PDMS	No.	Block Length		wt % PDMS
	PDMS	PSF or PC			PDMS	PSF or PC	
<i>PSF/PDMS</i>							
1	1800	1500	55	14	10000	4500	69
2	2500	1500	63	15	2500	9000	22
3	7000	1500	82	16	2500	13000	16
4	10000	1500	87	17	10000	13000	44
5	1800	2500	42	18	1800	44000	3.9
6	2500	2500	50	19	2500	44000	5.4
7	7000	2500	74	<i>PC/PDMS</i>			
8	10000	2500	80	20	1030	2500	29
9	1800	3500	34	21	2400	2500	49
10	2500	3500	41	22	5400	2500	68
11	3500	3500	66	<i>PC/PU/PDMS</i>			
12	10000	3500	74	23	1030	2800	27
13	2500	4500	36	24	1790	2000	47

The samples of homopolymers and copolymers were prepared by casting from 2% chloroform solutions on stretched cellophane films. The solutions of blends were prepared by mixing prescribed amounts of dilute chloroform solutions of the base and additive. The highest content of the additive was governed by the incompatibility of the components: Only those films were studied that showed no apparent indications of phase separation (such as the appearance of islands of individual phases, cracking, or fragility). All the samples were dried in atmosphere for a day and then in vacuum for 5 h.

XPS Instrumentation and Line Shape Analysis

XPS spectra were taken on a Kratos Analytical Instruments XSAM-800 dual-chamber spectrometer equipped with a hemispherical electron energy analyzer and a quad-anode X-ray source. The energy resolution of the spectrometer was 1.1 eV as determined on the Ag3*d* core level using MgK α radiation. The analyzer was operated in the fixed retardation ratio (FRR) mode. The energy scale of the instrument was calibrated by setting Cu2*p* = 932.7, CuLMM = 918.7, Ag3*d* = 368.3, Au4*f* = 84.0, and Ni(E_{Fermi}) = 0 eV. Charge correction in the binding energy scale was made by setting the CH $_x$ feature of the C1s emission to 285 eV. The pressure in the analysis chamber was maintained at 1×10^{-10} torr during spectra collection. Typical operating conditions for the X-ray gun were as follows: 150 W, 15 kV, 10 mA. No radiation damage of samples was observed during the data acquisition time. Angular-dependent studies were done by rotating the sample holder.

All data manipulations were accomplished with the standard DS800 software of the XSAM-800 spectrometer. Overlapping peaks were resolved into their individual components by a least-squares fitting procedure using Gaussian functions for the peak components.

Quantitative analysis of the sample surfaces was based on the relation

$$(\text{wt } \%)_X \sim \frac{\text{MW}_X I_X}{A(E_X)\lambda(E_X)f_X\sigma_X}$$

where the subscript *X* refers to a particular element; E_X is the kinetic energy of photoelectrons emitted from the relevant inner shell of atom *X*, I_X is the associated integral peak intensity; *A* is the inherent efficiency of electron detection by the spectrometer; f_X and σ_X are the asymmetry parameter and pho-

toionization cross section for the given inner shell; and λ is the photoelectron mean free path. The functions $A(E_X)$ and $\lambda(E_X)$ were taken to be proportional to $E_X^{3/2}$ and $E_X^{1/2}$, respectively. The numerical values for f_X and σ_X were borrowed from Ref. 13.

RESULTS AND DISCUSSION

Homopolymers

In order to interpret the XPS data for the copolymers and blends, it is first necessary to analyze the spectra of their individual constituents. Figure 1 depicts the C1s and O1s spectra from the neat PDMS, PSF, PC, and also from a diphenylmethane diisocyanate-ethanol adduct (DU) modeling the diurethane segments of the PC/PU/PDMS copolymers. The spectra are normalized to constant intensity and offset vertically. The vertical bars show the position and intensity of the peak components. The results of a quantitative analysis of the C1s and O1s spectra are presented in Table II together with assignments of the components and the quantitative results for the other elements.

Inspection of Table II shows that the XPS data agrees well with the stoichiometric composition of the homopolymers and DU. Hence the quantification procedure used is quite adequate for the objects under study. Another conclusion that can be drawn from Table I and Figure 1 is that the XPS spectra from PDMS, PSF, PC, and DU contain particular peaks and particular peak components that are strictly characteristic of each individual compound. These are, first of all, the Si2*p*, S2*p*, and N1s peaks, which allow an easy evaluation of the surface content of the siloxane, sulfone, and diurethane blocks, respectively. Also, the surface concentration of the DU blocks can be independently evaluated from the integral intensity of the OC(O)N component at 290.0 eV, the concentration of the PC blocks from the O—C component at 534.4 eV, and the concentration of the PSF blocks from the O=S component at 533.7 eV. All this provides a reliable means for analyzing the surface composition of the copolymers and blends.

Copolymers, Blends of Homopolymers, and Blends of Copolymers in Homopolymers

We start the discussion of the surface behavior of the binary systems with the copolymers and blends of PSF and PDMS. The quantitative results in Fig-

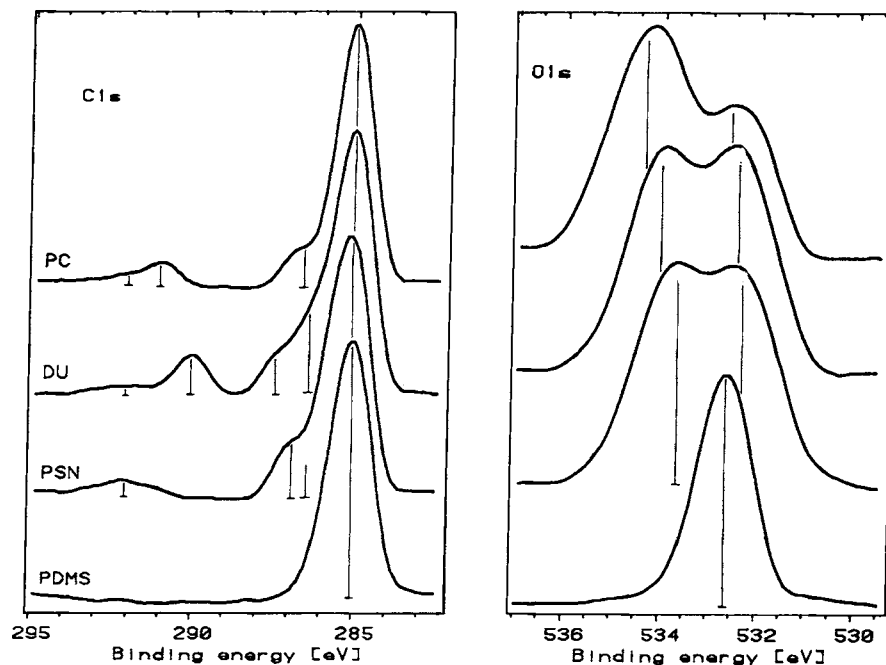


Figure 1 C1s and O1s core level spectra for the homopolymers and DU.

ure 2 on the PSF/PDMS, PSF + PDMS, and PSF + PSF/PDMS(9) systems show the weight percent surface siloxane, as detected by XPS, plotted against the known weight percent siloxane in the bulk. One can note an appreciable scatter in the experimental data for the copolymers. This scatter can be attributed to the fact that the surface composition of a block copolymer depends not only on the bulk composition but also on the absolute block lengths. A study of the dependence on the absolute block lengths is currently under way, and the results will be published in a separate paper.

The dashed line in Figure 2 corresponds to equality of the surface and bulk concentrations of siloxane. It is seen that all experimental points lie well above the dashed line, i.e., the surface of all samples is highly enriched in siloxane. The three different types of binary systems can be compared in the bulk concentration range 3.9–16%, which is common to all the three system types. As expected, at a fixed bulk concentration the lowest extent of surface segregation is observed with block copolymers. This is not surprising in view of the presence of chemical links between the siloxane and sulfone segments. The highest surface segregation is characteristic of the PSF + PDMS blends, while the PSF + PSF/PDMS(9) blends take an intermediate position.

If we define the extent of surface segregation, s , as the ratio of the surface siloxane content to the bulk siloxane content, we find that s increases with

decreasing siloxane content in the bulk. For instance, for copolymers 16 and 18 containing 12 and 2.8% bulk siloxane the extent of surface segregation is equal to 4 and 15, respectively.

In both types of the blends studied the surface versus bulk concentration dependence shows an asymptotic behavior with increasing siloxane concentration. In the PSF + PDMS blends the surface concentration of siloxane tends to 100%. That is the surface of the PSF + PDMS blends becomes covered with an overlayer of essentially pure PDMS, with a thickness larger than the XPS sampling depth (~ 50 Å). The surface layers of the PSF + PSF/PDMS(9) blends prove to be composed of a practically pure PSF/PDMS(9) copolymer with its inherent surface siloxane content (80%).

As seen from Figure 2, at bulk siloxane contents above 0.1% the pure PDMS is a more efficient modifying additive than the PSF/PDMS copolymer, in the sense that at a given bulk siloxane content the former provides a higher extent of surface enrichment than does the latter. It is to be noted, however, that in the films modified by the pure PDMS the apparent incompatibility sets in at a much lower bulk siloxane content, compared to the films modified by the PSF/PDMS(9) copolymer.

In the low concentration range ($<0.1\%$) a more efficient modifying additive is, quite the reverse, the PSF/PDMS(9) copolymer, which allows a huge extent of surface segregation to be reached

Table II Peak Assignments and Quantification Data for the Homopolymers and DU

Core Level	Component	E_{bind}	Concentration, at %	
			Stoich.	XPS
<i>PDMS</i>				
C1s		285.0	50	50
O1s		532.6	25	25
Si2p		102.6	25	25
<i>PSF</i>				
C1s	CH	285.0	66	70
	CS	286.3	6	6
	CO	286.7	13	12
	Shake-up ^a	292.0	5	4
O1s	O-C	532.1	6	5
	O=S	533.7	6	5
S2p		167.6	3	4
<i>PC</i>				
C1s	CH	285.0	71	71
	CO	286.5	11	12
	OC(O)O	291.0	6	6
	Shake-up ^a	292.0	7	5
O1s	O=C	532.6	3	5
	O-C	534.4	9	8
<i>DU</i>				
C1s	CH	285.0	44	45
	CN, CCO	286.3	16	14
	CO	287.3	8	6
	OC(O)N	290.0	8	7
	Shake-up ^a	292.0	4	2
O1s	O=C	532.3	8	9
	O-C	534.0	8	8
N1s		400.7	8	8

^a A shake-up satellite due to $\pi-\pi^*$ transition.

($s \approx 2000$). Such a high surface segregation results from the appearance of a plateau in the surface versus bulk concentration dependence where the surface composition of the blends is practically independent of the bulk composition. A similar plateau has been found by us in the blends of PSF with other PSF/PDMS copolymers¹⁰ and has also been observed by other authors.^{2,4,5}

In the binary systems based on PC and PDMS the relationships between the surface and bulk compositions are very similar. This is seen from Figure 3, which presents our XPS data on the PC/PDMS

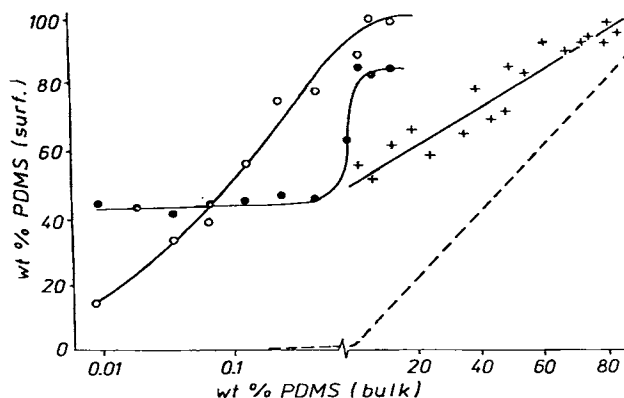


Figure 2 Surface vs. bulk compositions for PSF/PDMS copolymers (+), PSF + PDMS blends (O) and PSF + PSF/PDMS (9) blends (●).

copolymers and the PC + PDMS and PC + PC/PDMS(22) blends. The only difference observed refers to the blends of the type homopolymer + copolymer, which exhibit no low-concentration plateau down to 0.013% siloxane in the bulk. No plateau was also found by us in the blends of the PC/PDMS(20), PC/PU/PDMS(23), and PC/PU/PDMS(24) copolymers in PC. This finding is at variance with an early XPS study of Dwight et al.⁴ who did observe a low-concentration plateau in PC + PC/PDMS blends.

Blends of Copolymers: The Model of a "Quasi-two-dimensional Overlayer"

As follows from the results discussed in the previous section, the surface of a homopolymer can be highly enriched in siloxane via addition of minor amounts of pure PDMS or a copolymer of PDMS and the

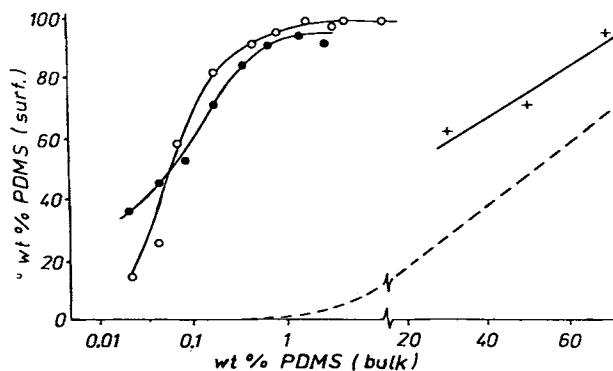


Figure 3 Surface vs. bulk compositions for PC/PDMS copolymers (+), PC + PDMS blends (O) and PC + PC/PDMS(22) blends (●).

given polymer. Surprisingly, the addition of a siloxane-rich copolymer to another copolymer with a lower siloxane content does not necessarily enhance the surface siloxane composition of the latter.

Figure 4 shows our XPS results for the blends of the PC/PDMS(22) copolymer (the additive) in the PC/PU/PDMS(23) copolymer (the base). When neat, the base shows 67% siloxane at the surface and 27% siloxane in the bulk. In the neat additive the surface and bulk siloxane concentrations are 96 and 68%, respectively. So, one can expect that the surface siloxane content in the blends will be higher than 67% at all compositions of the blends. Actually, on addition of the additive the surface siloxane concentration first drops to 55%, then slowly increases, reaches the starting concentration of 67%, and then jumps to a value fairly close to the surface siloxane concentration in the neat additive.

As this takes place, the signal from the DU segments, which enter solely into the composition of the base, gradually reduces, vanishing at the point corresponding to the "jump" of the surface siloxane content. The observed attenuation of the DU signal suggests that despite the occurring decrease in the surface siloxane concentration, the topmost surface layers of the blends consist preferentially of the siloxane-rich macromolecules of the additive. Such a conclusion has been supported by angular-dependent XPS: When the XPS sampling depth was halved (by decreasing the electron take-off angle from 90° to 30°), the signal from the DU segments drastically dropped or disappeared at all.

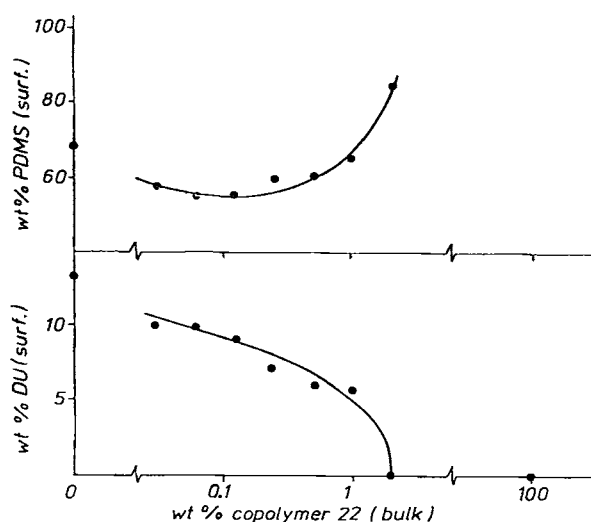


Figure 4 Surface concentration of PDMS and DU in the PC/PU/PDMS(23) + PC/PDMS(22) blends as a function of bulk content of PC/PDMS(22).

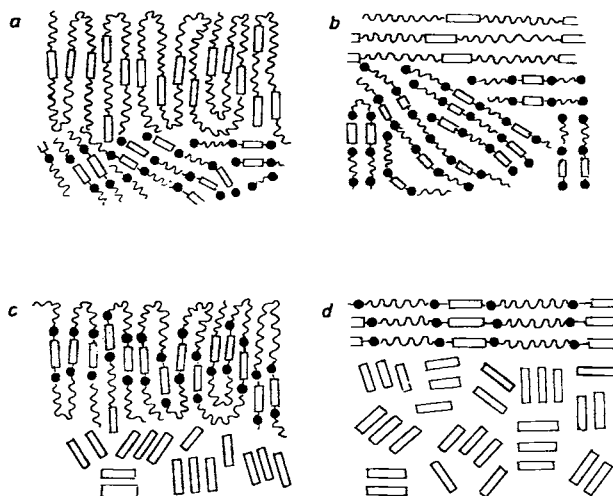


Figure 5 A schematic representation of the surface structure in the PC/PU/PDMS(23) + PC/PDMS(22) blends at high (a) and low (b) bulk contents of PC/PDMS(22); and in the PC + PC/PU/PDMS(24) blends at high (c) and low (d) bulk contents of PC/PU/PDMS(24) (wavy line, rectangle, and circle stand for PDMS, PC, and DU segments, respectively).

To summarize, on the addition of small amounts of a high-siloxane-content copolymer to a low-siloxane-content copolymer the additive macromolecules do segregate to the surface, but, nevertheless, the surface siloxane concentration reduces. Such an unusual surface behavior can be explained by the following model. Let us assume that due to incompatibility of the blend components the polymer film consists of an overlayer, composed preferentially of the additive macromolecules, covering the polymer bulk composed of essentially pure base. At high contents of the additive ($> 2\%$) the overlayer is thick enough to ensure, during film casting, three-dimensional displacements of the macromolecules and the formation of a surface structure similar to that of the neat additive: The near-surface region is dominated by the siloxane segments [see Fig. 5(a)]. The observed surface composition of such a system should tend to the surface composition of the pure additive.

At low contents of the additive ($< 0.5\%$) the overlayer becomes so thin that the macromolecules of the additive are as if compressed between the base-additive interface and the sample surface to form a quasi-two-dimensional ensemble. In this ensemble the macromolecules are oriented preferentially parallel to the surface, so that the different blocks of a macromolecule are almost equally accessible to XPS [Fig. 5(b)]. If the thickness of the overlayer is

greater than the XPS sampling depth, the observed surface composition of the blend should tend to the bulk (stoichiometric) composition of the additive. Otherwise, there may be some deviation from this value due to the contribution to the XPS signal intensities from the underlying layers of the base.

At low contents of the additive the surface siloxane concentration, as detected by XPS, falls to 55%, a value lower than both the bulk siloxane concentration in the neat additive (68%) and the surface siloxane concentration in the neat base (67%). This result suggests, first, that the thickness of the quasi-two-dimensional overlayer is less than the XPS sampling depth and, second, that the adjacent subsurface regions composed mainly of the base macromolecules are less enriched in siloxane than the free surface of the neat base. (This is quite understandable because these subsurface regions are not in contact with air.)

These speculations were supported by angular-dependent XPS. When the XPS sampling depth was decreased (by decreasing the electron take-off angle), the signal from diurethane dropped and the observed siloxane concentration became close to the bulk value for the pure additive. Thus, a 60° rotation of the sample with 0.03% additive from its initial normal position produced a decrease in the surface percent diurethane from 10 to 6% and an increase in the surface percent siloxane from 59 to 69%.

Since the formation of a quasi-two-dimensional layered structure is governed by a pure geometrical factor, it can be expected that such a structure will be common to all types of dilute blends of incompatible polymers. To check this point, we have studied the blends of the PC/PU/PDMS(24) copolymer in homo-PC. (Note that unlike the previous case of two copolymers, now the DU segments label the additive, not the base.) The results are presented in Figure 6, which shows the surface concentration of diurethane and siloxane as a function of the bulk content of the copolymer additive. Also shown is the ratio of the diurethane and siloxane blocks, as determined from the integral intensities of the N1s and Si2p signals. Since the PC base contains neither N nor Si atoms, the diurethane-siloxane ratio is unresponsive to the base and well characterizes the organization of the additive macromolecules at the sample surface.

As expected, with increasing content of the additive the surface concentration of the siloxane segments rises. The surface concentration of the diurethane blocks also rises to reach a value of 15%, which perceptibly exceeds the surface diurethane concentration in the neat additive (11%). This re-

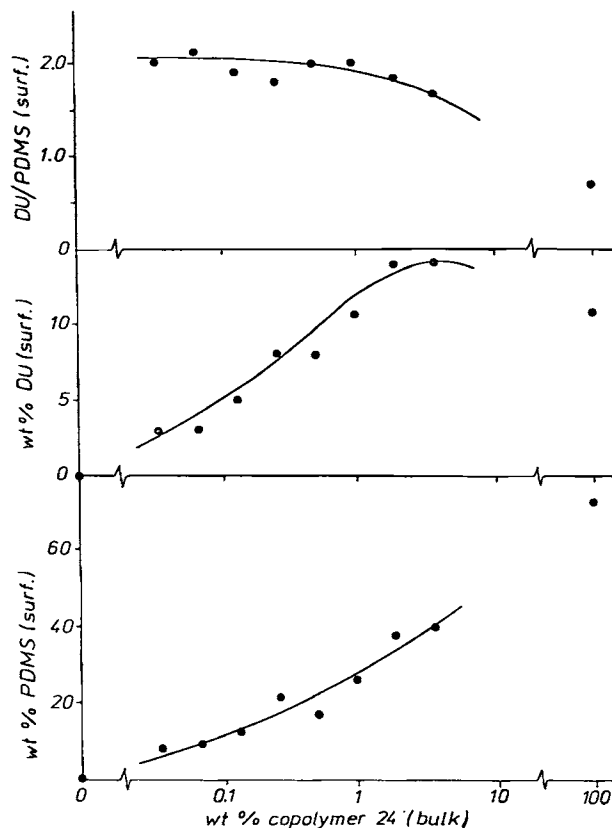


Figure 6 Surface concentration of PDMS and DU and the ratio of the DU and PDMS blocks in the PC + PC/PU/PDMS(24) blends as a function of the bulk content of PC/PU/PDMS(24).

sult indicates conclusively that in the relevant blends the diurethane segments of the additive macromolecules become more accessible to XPS than in the neat additive.

A more weighty argument in favor of the formation of a quasi-two-dimensional overlayer is provided by the behavior of the diurethane-siloxane ratio. In the neat additive this ratio is equal to 0.75 and falls with decreasing the XPS sampling depth. In the blends the diurethane-siloxane ratio proves to be independent of the electron take-off angle and tends to a value of 2 corresponding to the stoichiometric value for the PC/PU/PDMS(24) copolymer. This important result can be only rationalized in terms of preferential orientation of the additive macromolecules parallel to the sample surface [see Fig. 5(c,d)].

CONCLUSIONS

The XPS results reported in this work cover all the most important types of binary polymer systems.

For the copolymers and the blends of homo- and copolymers in homopolymers our data is in qualitative agreement with previous work on other compositions.^{2,3,12} As to the blends of copolymers, these were studied, to our knowledge, for the first time. In these blends an unusual surface behavior has been observed and a microscopic model has been suggested to explain this behavior.

The model suggested appears to be applicable to all blends of incompatible polymers. The basic assumptions of the model are, first, the formation of an overlayer on the sample surface, composed predominantly of the additive macromolecules, and, second, a transition from a "thick" overlayer, with a surface structure typical of the neat additive, to a quasi-two-dimensional overlayer, with preferentially parallel orientation of the macromolecules relative to the sample surface.

An interesting consequence from this model is that at high contents of the additive the surface composition of a blend should tend to the surface composition of the neat additive, while at low contents it should approach the bulk (stoichiometric) composition of the additive. (The latter trend should be observed in XPS at small electron take-off angles.) Not only our own results support this conclusion but also an analysis of the angular-dependent XPS data reported by other authors.²

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