Combined Time-of-Flight Secondary Ion Mass Spectrometry and X-ray Photoelectron Spectroscopy Study of the Surface Segregation of Poly(methyl methacrylate) (PMMA) in Bisphenol A Polycarbonate/PMMA Blends

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Received December 8, 1994; Revised Manuscript Received March 29, 1995®

ABSTRACT: Phase segregation at the surface of Bisphenol A polycarbonate (PC) and poly(methyl methacrylate) (PMMA) blends is studied by X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF SIMS). Blends with different compositions were solution-casted onto silicon wafers with dichloromethane (CH_2Cl_2) as the mutual solvent. A sharp PMMA segregation is observed at the surface of the blends. In fact, the quantitative analysis of the XPS data shows that the PMMA surface molar concentration increases first steeply with the PMMA bulk concentration (the surface concentration reaches 70% of PMMA for a 2.5% bulk concentration), and then it continues to increase slowly and saturates for a 38.8% bulk concentration. The ToF SIMS results show that PC remains detected even for high PMMA surface concentration. A semiquantitative ToF SIMS analysis is also presented, which correlated with the XPS results and confirmed the segregation even if matrix effects are detected when the surface concentration of each polymer is comparable. The segregation is explained by the difference of surface tension between the two polymers. The surface morphology is also sampled by the ToF SIMS imaging mode, but no contrast is detected although optical images reveal a two-phase system in the bulk.

Introduction

Immiscible polymer blends are known to combine the properties of both components. Changing their concentrations modifies the size and shape of the dispersed phase, and this can be used to improve the material properties.

For noncompatible polymers, the bulk morphology and the miscibility of their blends can be modified by different factors such as the temperature[1] and the processing method.[2,3] If the blends are prepared in a solution, the solvent can play an important role known as the "solvent effect". [2] As an example, a Bisphenol A polycarbonate (PC)/poly(methyl methacrylate) (PMMA) blend has been shown to form an immiscible system if dichloromethane (CH_2Cl_2) is used as the solvent. On the contrary, the blend is found miscible when tetrahydrofuran (THF) is used as the solvent.

Concerning the temperature effect, for PC/PMMA blends prepared by casting from a solution in THF, the existence of an immiscibility loop in the phase diagram has been reported.[1,4,5] The coexistence of a lower critical solution temperature (LCST) and an upper critical solution temperature (UCST) is proposed. However, there is still a controversy due to the fact that chemical reactions between the two polymers cannot be excluded to occur at temperatures close to the UCST (around 200 °C).[6]

Another important issue for the applications of the polymer blends is the control of the surface morphology. The critical point is to know if the two phases are present at the surface with the same concentration and morphology as in the bulk or if there is a surface segregation. In the last case, it is important to know the surface morphology. The answer seems to differ for each blend system. In poly(vinylidene chloride) (PVC)/PMMA blends, for example, it has been reported that the surface presents the same two-phase morphology as in the bulk for a wide range of concentrations.[7] In PC/PDMS (poly(dimethylsiloxane)), the surface segregation of the PDMS is very large and the surface morphology differs from that of the bulk.[8] One of the driving forces for the surface phase segregation is the difference of the surface tensions of the constituents.[7] The polymer with the lower surface tension tends to come to the surface to minimize the air–polymer interface energy. But this segregation can be hindered by kinetic factors.

In this work, we will focus on PC/PMMA blends prepared by casting from a solution at a temperature around 50 °C and with CH_2Cl_2 as the mutual solvent. This will ensure the presence of two phases in the bulk. For this system, the two polymers are partially miscible in each phase. This partial miscibility could be due to an interaction between the phenyl ring of PC and the ester group of PMMA.[9,10]

The surface composition of PC/PMMA blends will be studied using surface spectrometries. The combination of XPS and ToF SIMS has already been proven to be very fruitful. Indeed, the topmost surface sensitivity of the molecular ToF SIMS information is very complementary to the quantitative results obtained by XPS.[11] It is to be noticed that other techniques have also been applied to the surface characterization of polymer blends (FTIR, ISS, ...).[12,13]

Experimental Section

(1) Sample Preparation. Only commercial polymers (LEXAN 141 PC from General Electric and OROGLAS V825 PMMA from Rohm & Haas) were used in this study. The repeat units of the two polymers are shown in Figure 1.

They were purified by dissolution in dichloromethane (CH_2Cl_2) followed by precipitation into methanol and filtration. They were further cleaned by washing in *n*-hexane in order to remove any possible PDMS contamination. Indeed, this

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® Abstract published in *Advance ACS Abstracts,* May 15, 1995.

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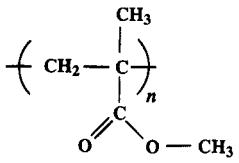
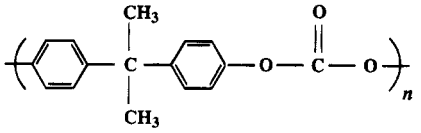


PMMA



PC

Figure 1. Repeat units of the two polymers.

contamination is often detected on commercial polymers.[14] The M_w (34 600 for PC and 55 700 for PMMA) and M_n (23 700 for PC and 44 100 for PMMA) values were determined by gel permeation chromatography (GPC) with tetrahydrofuran (THF) as the carrier solvent. The calibration has been made with polystyrene standards. No low molecular weight material has been detected by this method.

The blends were prepared by dissolving the two polymers into CH_2Cl_2 under light ultrasonic agitation. Blends of different compositions were obtained by varying the respective PC and PMMA weight fraction. Thin films (a few microns thick) of the blends were obtained by casting the solution (5% in weight) onto silicon wafers at a temperature close to 50 °C in order to get a fast evaporation of the solvent. The complete evaporation of the solvent was checked by the lack of Cl^- peaks in the negative SIMS spectra. By this method the pure polymers and the blends were obtained with the following PMMA weight percentages (0, 1, 3, 5, 10, 15, 20, 25, 50, 70, 80, and 100). From each solution two samples were casted, one for the XPS analysis and another for the ToF SIMS analysis. The corresponding bulk molar PMMA concentrations were calculated by taking into account the molar masses of the PC and PMMA repeat units (0, 2.5, 7.3, 11.8, 22, 30.9, 38.8, 45.8, 71.7, 85.6, 91, and 100). Two different solutions were prepared for the pure polymers and the blends with 11.8% and 38.8% PMMA in order to check the reproducibility of the results.

Only molar concentration will be considered in the following text.

(2) Instrumentation. I. XPS (ESCA). The surface composition of the blends was determined by XPS using a SSX 100 spectrometer (Model 206, SSI, Surface Science Instruments)[15,16] equipped with an aluminum anode (10 kV, 11.5 mA) and a quartz monochromator. The surface charge compensation was achieved by using a low-energy (6 or 10 eV) electron flood gun and by covering the sample with a grounded nickel grid 3 mm above the surface.

For each sample, a detailed scan of the O 1s and C 1s lines was performed with a 600 μm spot and a pass energy of 50 eV. The calibration of the binding energy (BE) scale was made by setting the C 1s BE of the neutral carbon (C−C and C−H bonds) peak at 284.8 eV. A Shirley type nonlinear background subtraction[17] was used, and the peaks were decomposed by using a least-squares routine assuming a Gaussian/Lorentzian (85/15) function. Intensity ratios were converted into atomic concentration ratios by using the sensitivity factors proposed by SSI. In our case, the sensitivity factors are 1 for carbon and 2.492 for oxygen.

II. ToF SIMS. Positive and negative ToF SIMS spectra and images were obtained with a Charles Evans time-of-flight SIMS spectrometer[18,19] with the following standard operating conditions. A pulsed 15 keV gallium ion beam (400 pA dc current; 20 ns pulse width further bunched up to 1.5 ns; 5 kHz repetition rate) was rastered over a 97 × 97 μm^2 area for a maximum acquisition time of 600 s. The secondary ions were extracted at a 10.5 keV acceleration voltage and then 270° deflected in three electrostatic hemispherical condensers in order to compensate for the initial energy distribution of ions with the same mass. They were mass-analyzed by measuring their time of flight distributions from the sample surface to the position-sensitive detector. The spectral acquisition time for a mass range of 0−5000 amu was 600 s, corresponding to a total ion dose of 1.6×10^{12} ions/cm^2 per spectrum, ensuring static conditions.[20] The charge compensation of the sample was achieved with a pulsed electron gun (24 eV) and a grounded stainless steel grid covering the sample. For image acquisition the beam energy was raised to 25 keV and the ion pulse width was unbunched at 20 ns. Molecular ion images were recorded on 512 × 512 pixels by scanning the beam on a 97 × 97 μm^2 area during 1800 s, corresponding to a total ion dose per image of 4.8×10^{12} ions/cm^2.

Results and Discussion

(1) XPS. Typical C 1s and O 1s spectra obtained with the two pure polymer samples and for the blends having 2.5% and 11.8% PMMA are shown in Figure 2a,b. The deconvolution results of the C 1s and O 1s peaks obtained without applying any constraints for the two pure polymers are presented in Table 1. As proposed in the literature,[21,22] four contributions were used to fit the C 1s spectrum of PMMA: *C*−C(H), *C*−C(O)−O, *C*−O, and O=*C*−O. Note that a distinction is made here between the neutral carbon *C*−C(H) and the carbon directly attached to the −$COOCH_3$ group. The variations observed within the fwhm values of those four contributions seem surprising. However, similar variations have already been reported by other authors over a large number of different PMMA samples[21] and even when a high-resolution spectrometer is used.[23] Four contributions were also used to fit the C 1s peak of pure PC: *C*−C(H), *C*−O, O=*C*(O_2), and shake-up. As indicated in Table 1, the percentages of the different contributions are very close to the expected stoichiometric values for the two polymers (in most cases, the agreement is within 2%). On the other hand, the C/O values obtained with pure PMMA and pure PC are respectively 2.46 and 5.05, which are also close to the stoichiometric values.

In XPS spectra of the blends, the ester (O=*C*−O) peak of PMMA at 288.9 eV is intense even for the sample with 2.5% PMMA (see Figure 2a). The contribution of the PC characteristic peaks (carbonate *C*O_3 at 290.6 eV and shake-up at 291.7 eV) vanishes for PMMA concentrations greater than 38.8%. The ratio of the two contributions of the O 1s varies from 1:1 in pure PMMA to 1:2 in pure PC.

For the quantitative analysis of the blend surface composition, two methods were used by considering either the C/O ratio or the ester contribution in the total C 1s peak. Note that for the samples made two times we will only present the average value.

The experimental C/O ratio ($(C/O)_{exp}$) contains the contribution of each polymer to the total C 1s and O 1s, which can be expressed by

$$\left(\frac{C}{O}\right)_{exp} = \frac{XC_{pmma} + (1 - X)C_{pc}}{XO_{pmma} + (1 - X)O_{pc}} \quad (1)$$

where X is the molar PMMA surface concentration in the blend and C_{pmma}, O_{pmma}, C_{pc}, and O_{pc} are respectively the stoichiometric carbon and oxygen atomic concentrations in pure PMMA and pure PC.

To check the coherence of the procedure, an alternative way for the XPS quantitative analysis is also

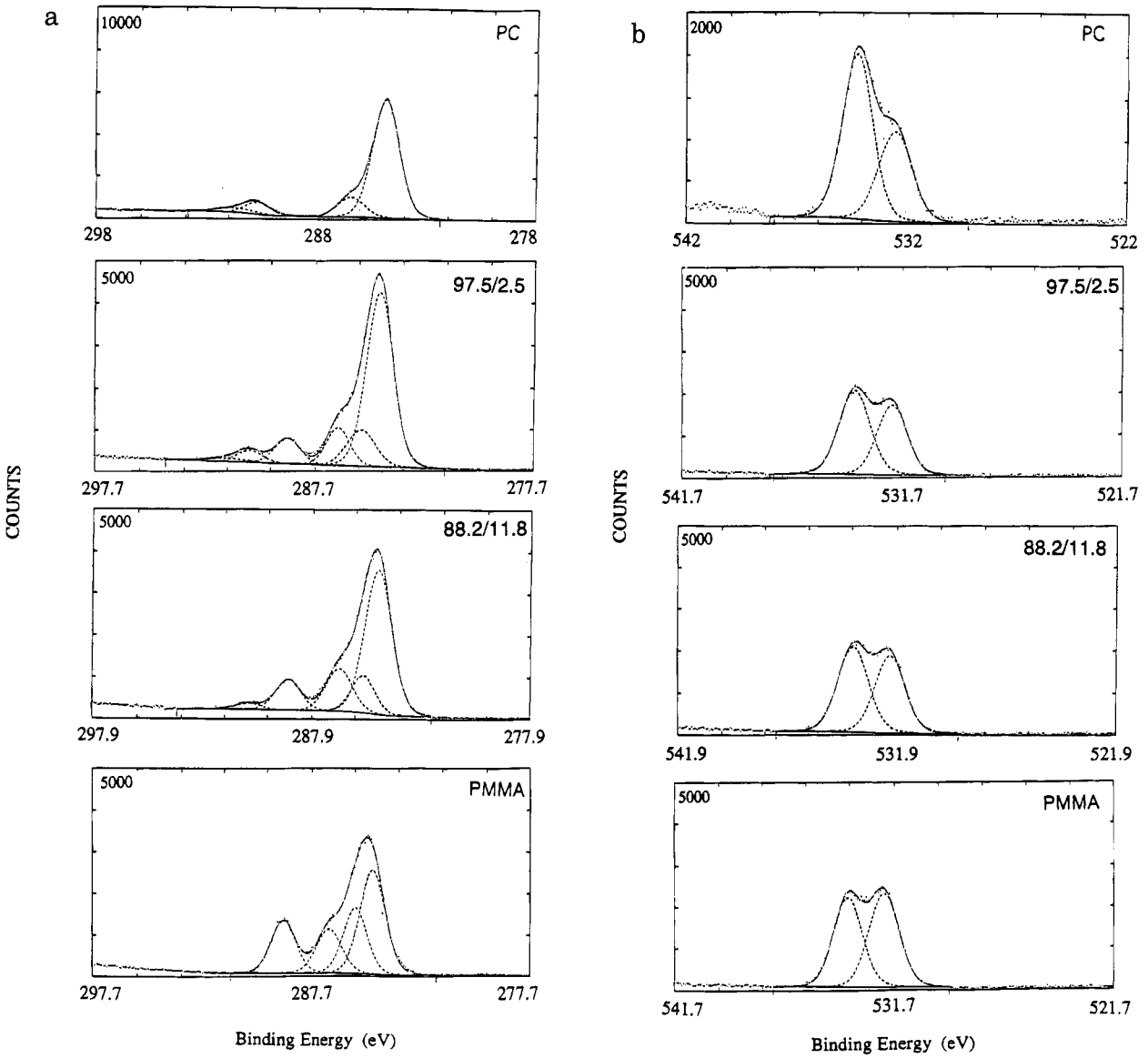


Figure 2. (a) C 1s XPS spectra of (from top to bottom) pure PC, 2.5% PMMA, 11.8% PMMA, and pure PMMA. (b) O 1s XPS spectra of (from top to bottom) pure PC, 2.5% PMMA, 11.8% PMMA, and pure PMMA.

Table 1. XPS Parameters for Two Pure Polymers

	PMMA					PC		
	peak	BE	fwhm	%	peak	BE	fwhm	%
C 1s	*C*–C, *C*–H	284.8	1.30	40.4	*C*–C, *C*–H	284.8	1.27	75.5
	C–C(O)–O	285.6	1.17	19.7	*C*–O	286.4	1.25	13.0
	C–O	286.7	1.37	20.0	O=*C*(O_2)	290.6	1.29	7.5
	O=*C*–O	288.9	1.18	19.8	shake-up	291.7	1.95	4.0
O 1s	C–*O*–C	532.0	1.41	47.8	C–*O*–C	532.5	1.41	32.0
	C=*O*	533.6	1.52	52.2	C=*O*	534.2	1.48	68.0

performed with the O=*C*–O contribution in the C 1s total intensity. For this purpose, the energy position and the fwhm values obtained for the pure PMMA were used as a constraint for the fitting of the PMMA ester peak of the different blends. For the evaluation of the PMMA molar concentration Y at the surface, we consider $(I_{O=C-O})_{exp}$, the percentage of the ester group in the total C 1s. Since in the blend the relative contribution of PMMA in the C 1s total intensity is $5Y$ (5 C atoms per PMMA repeat unit) and that of PC is $16(1 - Y)$ (16 C atoms per PC repeat unit), we have

$$(I_{O=C-O})_{exp} = \frac{Y}{[5Y + 16(1 - Y)]}$$

or

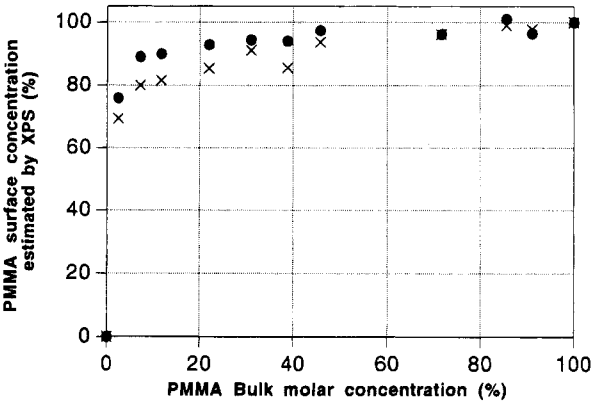


Figure 3. PMMA surface concentration of the blends estimated by means of C/O ratio (circles) and ester peak intensity (crosses) as a function of the PMMA bulk concentration.

$$Y = \frac{16(I_{O=C-O})_{exp}}{[1 + 11(I_{O=C-O})_{exp}]} \quad (2)$$

The surface PMMA concentrations calculated with the above methods are presented in Figure 3 as a function of the PMMA bulk concentration. It can be observed

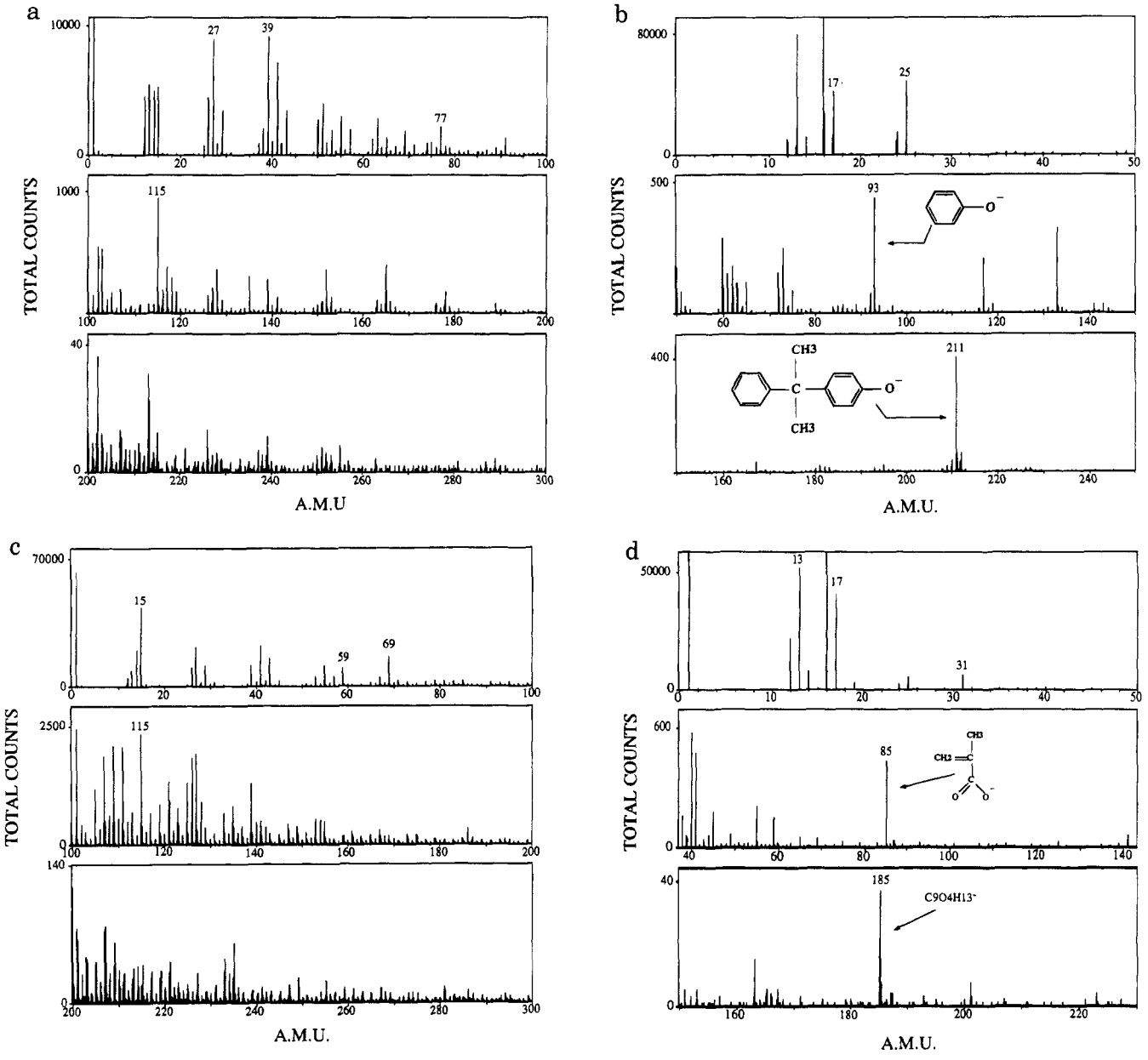


Figure 4. (a) Positive ToF SIMS spectrum of pure PC. (b) Negative ToF SIMS spectrum of pure PC with probable chemical structure of some characteristic peaks. (c) Positive ToF SIMS spectrum of pure PMMA. (d) Negative ToF SIMS spectrum of pure PMMA with probable chemical structure of some characteristic peaks.

that the agreement between the two methods is relatively good.

When increasing the PMMA bulk concentration of the blend, a sharp increase in the PMMA surface concentration is observed. Indeed for the samples with 2.5% and 7.3% bulk PMMA, the surface PMMA concentrations are 70% and 80%, respectively, according to the quantification using the ester group. The PMMA surface concentration continues to increase slowly and finally reaches a plateau when the bulk PMMA concentration is greater than 38.8%. In the plateau, the PMMA surface concentration is around 95%. These results show clearly a segregation of PMMA at the surface of the blends. However, in the plateau, it is difficult to conclude from these results whether PC is still present at the surface of the blends.

(2) ToF SIMS. For each sample, at least two positive and two negative spectra were recorded. Positive and negative ToF SIMS spectra of the pure polymers are shown in Figure 4a–d. The assignments of some characteristic peaks are given in Table 2. For the interpretation of other characteristic peaks, see ref 24. The positive spectra of the pure polymers show a large number of hydrocarbon peaks coming mainly from the polymer backbone in the case of PMMA and from the benzene rings in the case of PC. For PMMA, the

Table 2. Molecular Interpretation of Some of the Characteristic ToF SIMS Peaks for Pure Polymers

negative ions		positive ions	
		PMMA	
−31	CH_3O^-	+15	CH_3^+
−55	$C_3H_3O^-$	+59	$C_2H_3O_2^+$
−85	$C_4H_5O_2^-$	+69	$C_4H_5O^+ + C_5H_9^+$
−141	$C_8H_{13}O_2^-$	+115	$C_6H_{11}O_2^+$
−185	$C_9H_{13}O_4^-$	+121	$C_9H_{13}^+$
		PC	
−93	$C_6H_5O^-$	+63	$C_5H_3^+$
−117	$C_8H_5O^-$	+77	$C_6H_5^+$
−133	$C_9H_9O^-$	+91	$C_7H_7^+$
−211	$C_{15}H_{15}O^-$	+115	$C_9H_7^+$

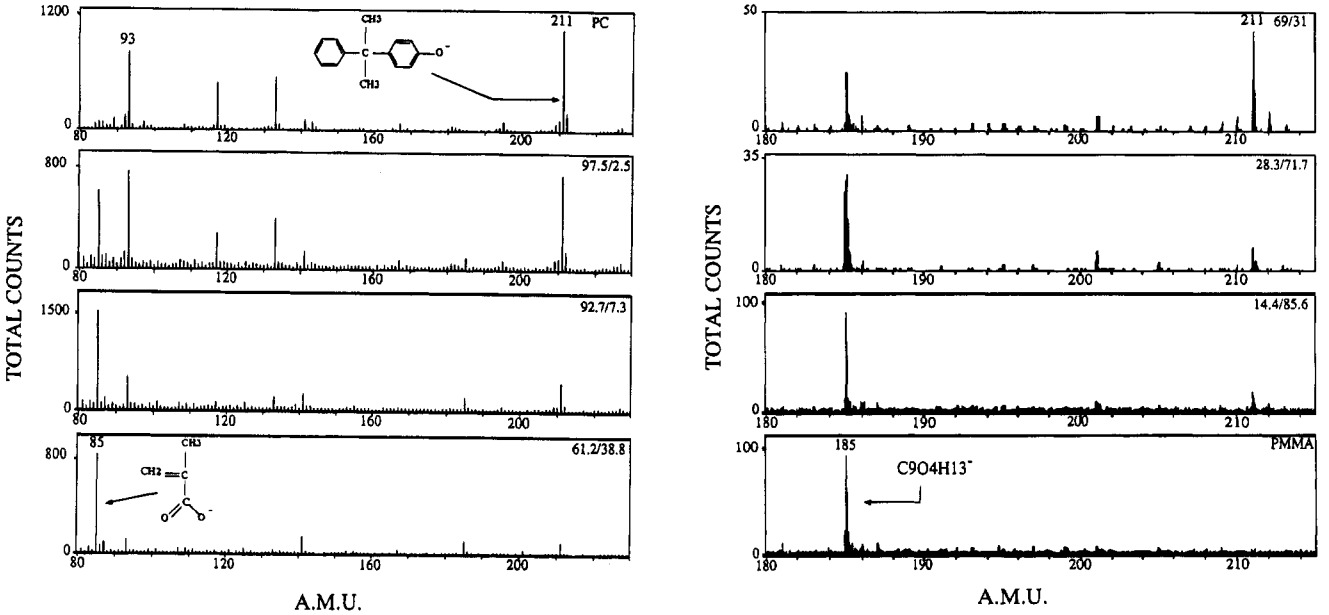


Figure 5. Negative ToF SIMS spectra of the pure polymers and some of the blends showing the evolution of some characteristic peaks (93 and 211 amu for PC and 85 and 185 amu for PMMA). Note that the considered mass range is different in the left column compared to the right one. This is to illustrate the presence of PC for the sample with 85.6% PMMA.

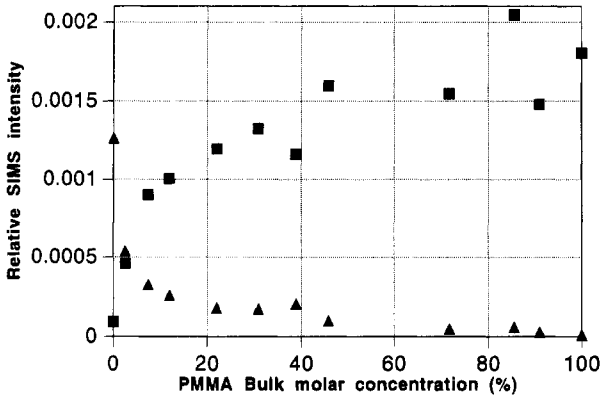


Figure 6. Evolution of the relative intensities (peak area versus total intensity in the spectrum) of the negative peaks at 85 (squares) and 211 (triangles) amu as a function of the PMMA bulk concentration.

presence of the methyl methacrylate pendant group is mainly detected by the intense oxygenated peaks at +59 and +69 amu. However, the discrimination between the two polymers is easier in the negative spectra where the most characteristic peaks are 93 and 211 amu for PC and 85 and 185 amu for PMMA.

Figure 5 shows the evolution of these peaks in the spectra obtained from the blends of different compositions. It can be seen that the peaks associated with the PMMA are significant up to the 2.5% PMMA. Their intensities dominate the spectra when the PMMA concentration is greater than 7.3%. However, the PC contribution, as revealed by the peak at 211 amu did not disappear totally even for the sample with 85.6% PMMA. These results show that both polymers always coexist at the surface of the blends. Since the peaks at 85 and 211 amu are the most characteristic ones of each polymer, the evolution of their relative intensity (peak intensity versus total ion intensity in the spectrum) is presented in Figure 6 as a function of the PMMA bulk concentration. Only average value obtained over the different samples and/or the different spectra of the same sample are presented. The shape of the curve indicates a PMMA surface segregation. This behavior is confirmed by the similar evolution observed for the other characteristic peaks in the negative (−) and positive (+) modes (peaks at −55, −141, −185, +15, and +59 amu for PMMA and peaks at −93, −117, −133, +77, and +91 amu for PC).

Recent results in literature[25,26] have shown that static SIMS can be used as a semiquantitative (or even quantitative) technique for certain polymer systems and that the matrix effect is not a major problem in such cases. Therefore, it would be interesting to check if this is also the case for our blends. For this purpose, the PMMA surface concentration is estimated from the relative intensities of the peaks at 85 and 211 amu as these peaks are intense and largely contributed from one polymer. If the matrix effect is neglected, the PMMA surface concentration X can be estimated using:

$$\frac{I_{85}}{I_{85}+I_{211}} = \frac{X{I_{85}}^{\mathrm{PMMA}} + (1-X){I_{85}}^{\mathrm{PC}}}{X{I_{85}}^{\mathrm{PMMA}} + (1-X){I_{85}}^{\mathrm{PC}} + (1-X){I_{211}}^{\mathrm{PC}} + X{I_{211}}^{\mathrm{PMMA}}}$$

where I_{85} and I_{211} are respectively the relative intensities of the peaks at 85 and 211 amu obtained with a specific blend while I_i^x is the relative intensity of the peak i obtained with pure polymer x. The PMMA surface concentrations calculated using this equation are compared (Figure 7) with those calculated by XPS. A good agreement is found for the PMMA bulk concentration greater than 7.3%, especially for the XPS results obtained with the ester group. However, a large deviation is observed for the sample with 2.5% PMMA bulk concentration. Indeed the PMMA surface concentration estimated by ToF SIMS is lower than that estimated by XPS. This deviation may be explained by different factors: (1) difference in the depth information of the two techniques (first monolayer for SIMS large molecular ions and ≅100 Å for XPS),[27] (2) surface hydrocarbon contamination, and (3) matrix effect. However, the deviation cannot be interpreted by the first factor for our blends where a PMMA surface segregation occurs. Indeed, in such a case, we should have detected more

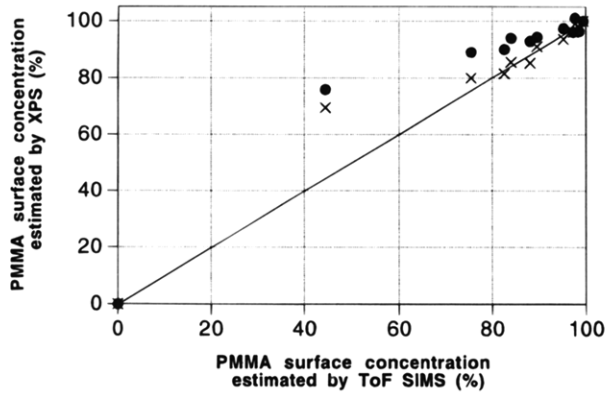


Figure 7. PMMA surface concentration estimated by XPS (circles for the C/O ratio and crosses for the ester peak intensity) as a function of that estimated by ToF SIMS.

PMMA by ToF SIMS than by XPS. Therefore, the composition is assumed to be approximately homogeneous over the two information depths. On the other hand, if hydrocarbon contamination is particularly present in this sample, the ester group percentage in the total C 1s will be decreased and thus the PMMA surface concentration will be underestimated by XPS. This is not what we observe. Indeed the PMMA surface concentration estimated by XPS is much higher than that estimated by ToF SIMS (Figure 7). The influence of hydrocarbon contamination on the SIMS intensity ratio is difficult to estimate, but it could not be great as the intensities of the peaks used in quantification would normally be affected in a similar way. Thus, the influence of hydrocarbon contamination could not explain alone the large deviation observed for the sample with 2.5% PMMA bulk concentration in Figure 7. Therefore, it may be reasonably assumed that the predominant contribution to this deviation is due to the matrix effect. This effect is important only for the PMMA surface concentrations inferior to 80% (PMMA bulk concentrations inferior to 7.3%) regarding the ToF SIMS results. For all the other blends, the surface composition estimated by ToF SIMS is reasonably reliable. These results suggest that, in the case of partially miscible polymer blends, static SIMS can be used as a quantitative technique when the concentration of one polymer in the blend is relatively low and that matrix effects appear to be important when the concentrations of both polymers are comparable. The SIMS matrix effect could be related to the interaction between the polymers. This interaction is weak[7,8] and will play a major role only when the two polymers are present in comparable concentrations at the surface.

In agreement with our results, the PMMA segregation at the surface is expected if we consider the surface tensions of the two polymers (i.e., 42.9 dyn/cm for PC and 41.1 dyn/cm for PMMA).[28] Indeed, the polymer with the lower surface tension tends to come to the surface to minimize the air-polymer interface energy.

(3) Morphology. Up to now, we did not discuss the bulk and surface morphology of the blends. The bulk morphology was investigated by optical microscopy. For this purpose the blends were casted from solution onto glass slices. Two phases were observed for all blends with a PMMA bulk concentration greater than 7.3%. When increasing the PMMA bulk concentration, we observe first a PMMA-dispersed phase in a PC matrix, then the coexistence of two continuous phases (see the image obtained for the blend with 71.7% PMMA bulk concentration in Figure 8), and finally a PC-dispersed

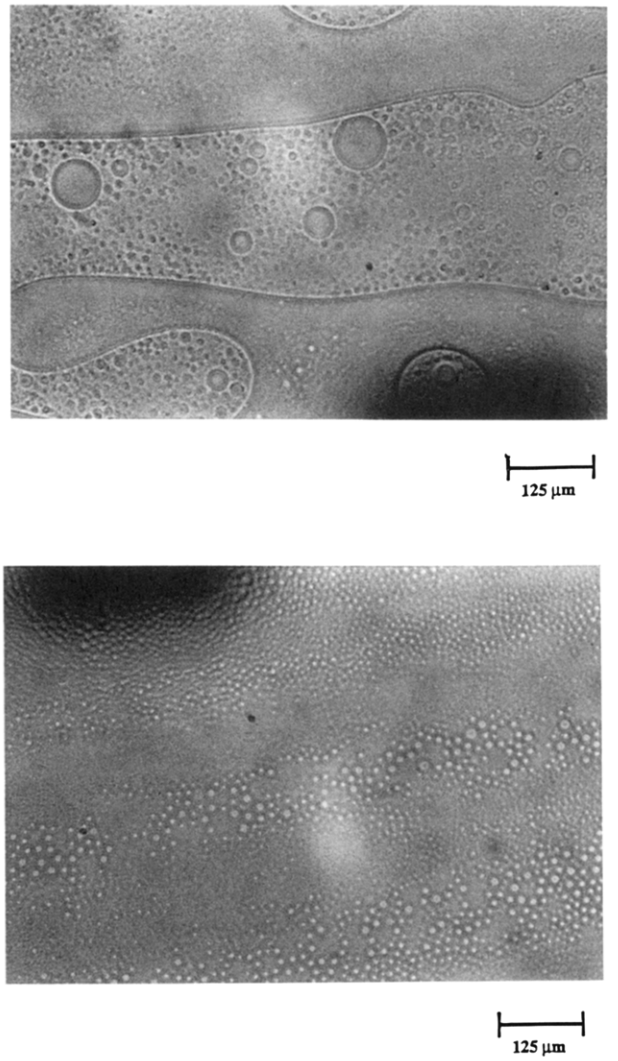


Figure 8. Optical images of (from top to bottom) the blends with 71.7% and 38.8% PMMA concentrations.

phase in a PMMA matrix. In the blend with 38.8% PMMA bulk concentration, the optical images show that the average size of the nodule of the dispersed phase is about 10 μm. For the samples with 7.3% and 2.5% PMMA bulk concentration, no contrast was detected. The size of a possible second phase in the bulk might simply be lower than the resolution of the optical microscope.

The surface morphology was investigated by using the imaging mode of the ToF SIMS spectrometer. Secondary molecular ion images of PMMA were recorded for the peaks at 59 amu in the positive mode and at 85 amu in the negative mode. In all cases, the recorded images (not shown here) appear homogeneous. This means that, if two phases are present at the surface, the domain size of PC-dispersed nodules should be lower than 1 μm, which corresponds to the lateral resolution obtained with the ToF SIMS on polymer materials.[29] If only one phase is present at the surface, it should be a PMMA phase with PC trapped in it. The trapped PC concentration decreases with increasing PMMA bulk concentration.

Conclusion

We have shown that, under our casting conditions, a large PMMA segregation is found at the surface of the PC/PMMA blends. The high molecular ToF SIMS sensitivity combined with the quantitative XPS allowed

us to detect the presence of the two polymers over the whole range of concentrations (ToF SIMS) and to quantify the surface segregation (XPS). The ToF SIMS technique is also shown to be semiquantitative for PMMA surface concentration superior to 80%. A matrix effect is also observed and is probably due to the interaction between the two polymers. Finally, the surface morphology has been shown to be very different from that of the bulk in a large concentration range investigated. It is concluded to be either homogeneous (only one phase) or made of a thin dispersion of PC (nodule size inferior to the micron) in a PMMA matrix.

Acknowledgment. The authors acknowledge Prof. R. Legras and D. Debier for their help in the preparation of the blends and for fruitful discussions. This work was supported by the Biomaterials program of the "Region Wallonne", Belgium. The ToF SIMS equipment has been acquired thanks to the support of the "Region Wallonne", "Fond national de la Recherche Scientifique", and "Loterie Nationale" of Belgium.

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MA946242Z