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The Structure of Thin Films of Polyaniline/Polystyrene Polymer Blends Studied by SIMS

Abstract

In this work, phase separation in thin films of polymer blends was studied. The investigated material was a composite containing conducting polyaniline protonated with camphorsulphonic acid and polystyrene. The films were manufactured by spin-casting in carefully controlled conditions, and investigated by means of secondary ion mass spectroscopy. The influence of preparation conditions on the phase separation process was observed, the most interesting point being the role of humidity in the spin-casting atmosphere.

Key words: *polyaniline, SIMS, phase separation, polymer blends, thin films.*

Introduction

The aim of this work was to study the morphology of thin films of polymer blends, consisting of a conducting polymer (polyaniline protonated with camphorsulphonic acid – PANI-CSA) and an insulating one (polystyrene – PS). The chemical structure of those polymers is shown in Figure 1. From the point of view of phase separation, only bulk materials and thick films ($d \geq 1$ μm) of such systems have so far been studied, e.g. in [1]. Understanding the processes of self–organisation in thin polymer films is an important problem, as it could possibly lead to the manufacture of polymer electronic devices (see for example [2]) with conducting paths embedded in a non-conducting matrix, such as polystyrene.

Polyaniline in its base form (emeraldine base, EB) is a dark blue, insulating powder. Because of its basic character, it may react with organic or inorganic acids forming conducting salts. If the acid molecule is amphiphilic, the hydrophilic part is attached to a PANI chain with an ionic bond, while the hydrophobic part may interact with solvent macromolecules, thus improving solubility (which for undoped PANI is poor because of the stiff double bonds present in its macromolecule). This effect is called counter-ion induced processibility. In the present work camphorsulphonic acid was chosen.

Experimental method

In Secondary Ion Mass Spectroscopy (SIMS) a sample situated in a high-vacuum chamber is irradiated with a beam of ions accelerated to the energy in the range of several keV to several tens of keV. The intensity of positive or negative secondary ions leaving the sample surface as a result of irradiation is then measured in a mass spectrometer (Figure 2), which gives information about the surface composition.

Two modes of operation are possible: *static SIMS* and *dynamic SIMS*. In the former, the current of primary ions is so small that removing one monolayer of atoms from the sample would take several minutes. In contrast, the latter is characterised by a much higher primary ion current. In dynamic SIMS, several tens of monolayers per minute are removed from the sample surface. In this work dynamic SIMS was utilised.

It is possible to obtain four types of data from a SIMS experiment:

- ***isotopic composition of the surface*** – by scanning the mass of secondary ions that are accepted by the mass spectrometer;
- ***SIMS profiles*** – the intensity of chosen secondary ions versus measurement time is analysed. As a result of primary ion irradiation, the outer layers of the investigated material are removed, which allows the analysis of the changes of the sample composition with depth;
- ***SIMS maps*** – the primary beam scans a rectangular area of a sample, which results in a 2-dimensional map of distribution of a certain isotope on the sample surface;
- ***distribution of an isotope within a sample volume*** – several SIMS maps are acquired consecutively (as described in iii), each revealing the composition on a deeper level than the previous one.

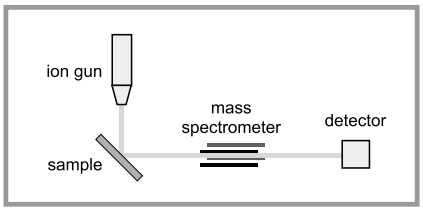

Figure 2. *The idea of the SIMS method.*

Experimental

Polyaniline (PANI, Aldrich) and camphorsulphonic acid (CSA, Aldrich) were dissolved in chloroform ($CHCl_3$) by mixing for a period of six days. Two types of PANI

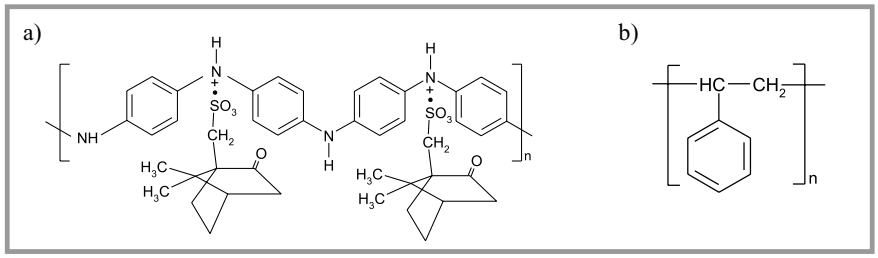

Figure 1. *Chemical structure of a) polyaniline protonated with camphorsulphonic acid b) polystyrene.*

were used: one with M_w=5,000 a.m.u. and the other with M_w=65,000 a.m.u.. The solution was then filtered through a Whatman Puradisc TF 0.2m Teflon filter in order to remove PANI agglomerates. In the next step, polystyrene (PS, PSS Mainz, M_w=125,000) was added. The concentrations of PS was varied from 3 g/cm^3 through 5 g/cm^3 to 10 g/cm^3. Thin films were prepared by spin-casting on a silicon substrate covered with gold. The process was performed in a dry (during preparation the spin coater was washed with argon) and humid atmosphere (the spin-coater was filled with saturated water vapour). The rotation speed was switched between 1000 rpm and 3000 rpm. Finally, each sample was covered with a film of PS, which acted as a 'sacrificial layer', allowing the ion-sputtering conditions during SIMS measurements to stabilise. A sample preparation is schematically shown in Figure 3.

For each sample a SIMS profile was collected. The sample was irradiated with Ga^+ ions of the energy of 5 keV with the ion current of approximately 2 nA. The angle of incidence of the primary beam was 40°, and the size of the sputtered area of the sample 100 mm ´ 100 mm. The depth resolution at these experimental conditions was checked to be 6.7 nm.

In order to convert sputtering time to depth, a sample containing PANI-CSA and PS was prepared. The thickness of the film was first measured with an Atomic Force Microscope (AFM), and then a SIMS profile was collected, which made it possible to calculate the proper conversion coefficient.

Results and data evaluation

For each profile the *m/q*=26 signal, designating $^{26}CN^-$ ions and, consequently, the presence of PANI, was normalised (divided by its integral from the middle point of its first slope to the maximum near the gold surface). Two parameters were determined: film thickness and PANI enrichment near the gold surface. The latter was calculated as the mean value in the range between the point where the signal intersects the horizontal line (intensity = 1, which corresponds to the mean concentration of PANI within the film) and the maximum (Figure 4a).

The influence of polymer concentration on the thickness of films can easily be observed. The plots in Figure 4 correspond to films prepared from solutions with different PS concentration. Films

Table 1. *PANI enrichment near the gold surface for solutions containing low-molecular weight PANI (M_w=5000 a.m.u.).*

PANI-CSA concentration	PS concentration	Rotation speed [rpm]	PANI enrichment	
			Argon	Saturated water vapour
3.7 mg/cm^3	10 mg/cm^3	1000	2,2	1,2
		3000	1,7	1,3
	5 mg/cm^3	1000	2,3	1,2
		3000	2,8	1,1
	3 mg/cm^3	1000	2,6	—
		3000	2,3	—
2.4 mg/cm^3	10 mg/cm^3	1000	5,6	1,3
		3000	3,7	—
	5 mg/cm^3	1000	3,3	1,5
		3000	3,0	1,3
	3 mg/cm^3	1000	2,9	1,2
		3000	3,1	1,5

Table 2. *PANI enrichment near the gold surface for solutions containing high-molecular weight PANI (M_w=65000 a.m.u.).*

PANI-CSA concentration	PS concentration	Rotation speed [rpm]	PANI enrichment	
			Argon	Saturated water vapour
3.1 mg/cm^3	10 mg/cm^3	1000	2,7	1,5
		3000	2,7	1,5
	5 mg/cm^3	1000	2,3	1,5
		3000	1,9	1,5
	3 mg/cm^3	1000	1,5	1,2
		3000	1,9	1,2
1.0 mg/cm^3	10 mg/cm^3	1000	2,7	1,9
		3000	3,7	2,7
	5 mg/cm^3	1000	2,6	2,4
		3000	2,3	2,4 *
	3 mg/cm^3	1000	1,1	1,8 *
		3000	1,9	1,9 *

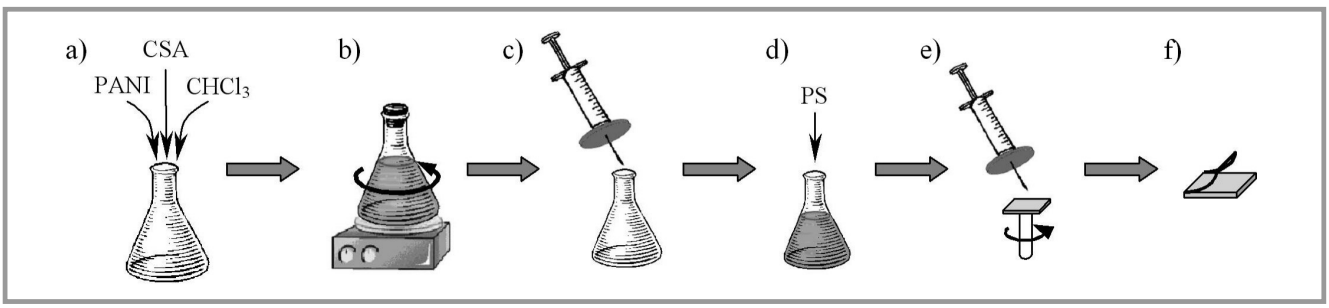

Figure 3. *An outline of sample preparation a) preparing the solution b) solution mixing c) filtering d) adding polystyrene e) second filtering and spin-casting f) covering a sample with a PS film.*

prepared from dilute solutions are thinner than those from solutions with a high polymer concentration. The plots in Figure 5 show the results of film thickness calculations for all samples. On the *x* axes, the total concentration of polymers (i.e. PANI-CSA and PS) is given.

The growth of film thickness with growing polymer concentration may be explained in the following way: the final thickness of a film is ruled by the balance between i) the centrifugal force trying to throw the solution over the edge of a revolving substrate in the spin-coating process, and ii) viscous forces resulting from mutual interactions of polymer macromolecules. The viscosity of a polymer solution is usually a growing function of concentration. Consequently, in the case of dilute solutions, viscosity is too weak a factor to keep a large amount of material on the substrate, which results in a relatively thin film. Similarly, when the rotation speed is high (3000 rpm as opposed to 1000 rpm), the centrifugal force is strong, which again results in a thin film.

As far as PANI enrichment is concerned, it was observed that the atmosphere in which thin films are created strongly influences the phase separation within the sample. The graphs in Figure 6 and Figure 7 show the $^{26}CN^-$ signal. As can be seen from the plots, the films prepared in dry conditions are characterised by a strong peak close to the bottom of the film (near the gold surface). In the case of the samples prepared in humid conditions, the above-mentioned peak is either much smaller or completely non-existent. The results of calculations are gathered in Tables. 1 and 2.

As has already been mentioned, a general tendency can be observed for the films spin-cast in a dry atmosphere to give higher values of enrichment. The exceptions from this rule (marked with an asterisk in Table 2) appear for very thin films (32 nm, 34 nm and 24 nm), for which enrichment is determined with a bigger error. In some cases (designated by a '—' symbol in Table 1) enrichment could not be calculated, since the corresponding SIMS profiles were flat and did not possess a peak. The conclusion may be drawn that, in the case of a dry atmosphere, some sort of chemical interaction between PANI-CSA macromolecules and the gold surface appears (perhaps of its electrostatic nature),

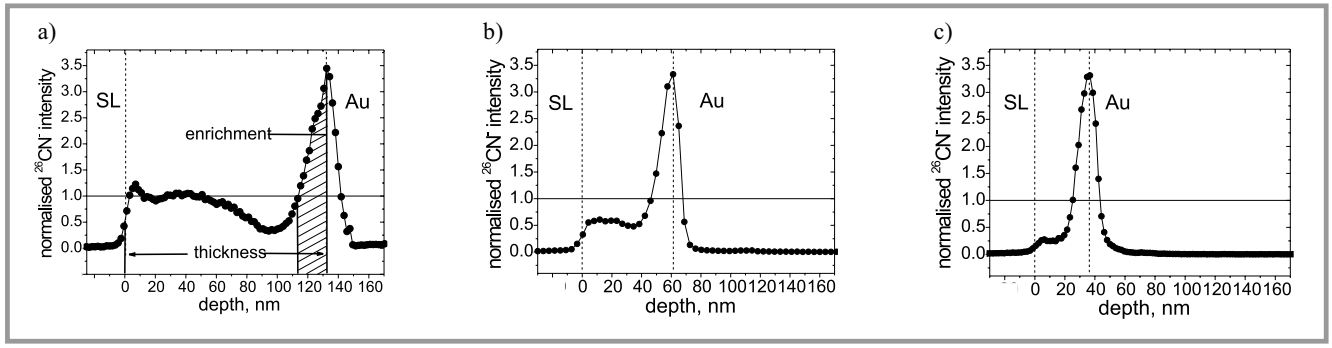

Figure 4. *SIMS profiles. PANI M_w=5000 a.m.u.; spin-cast in Argon; PANI-CSA conc. 3.7 mg/cm^3; rot. speed 1000 r.p.m.; PS conc. a) 10 mg/cm^3 b) 5 mg/cm^3 c) 3 mg/cm^3. SL – polystyrene sacrificial layer. Au – gold substrate.*

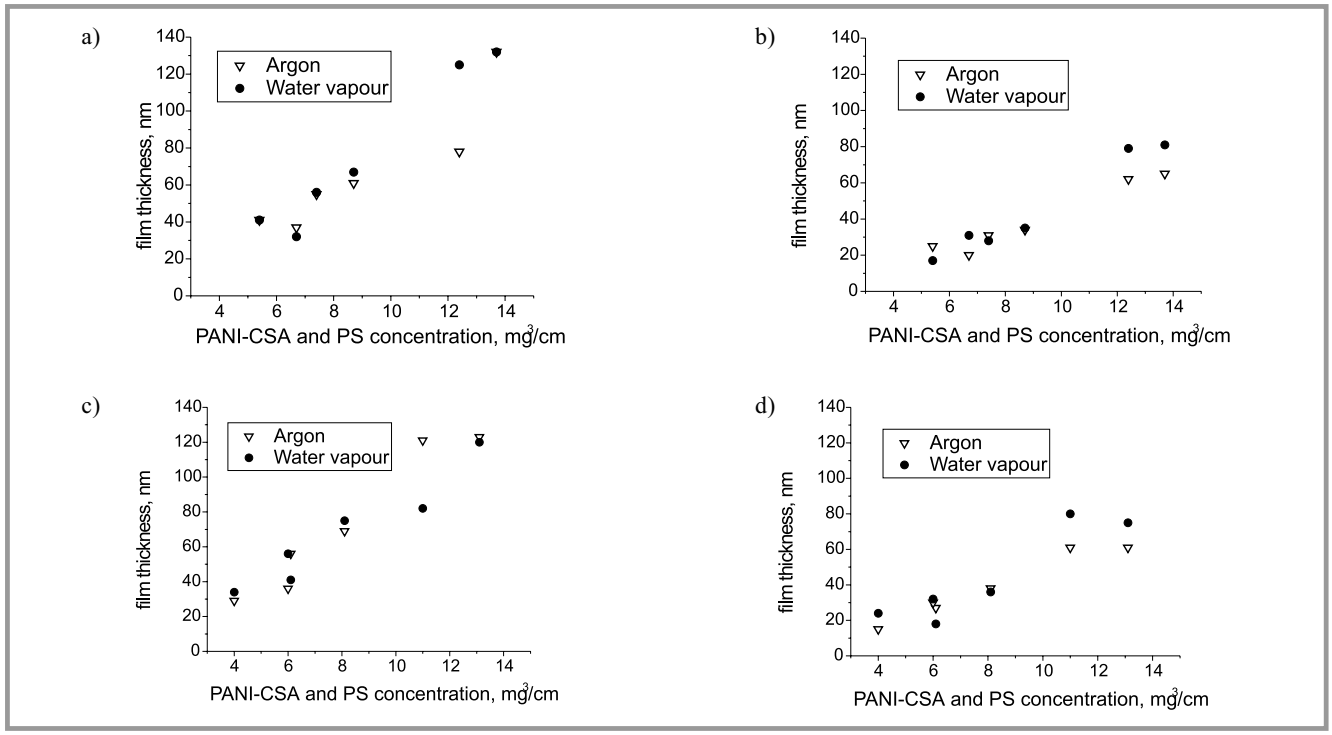

Figure 5. *Film thickness a) PANI M_w=5000 a.m.u., w=1000 rpm b) PANI M_w=5000 a.m.u., w=3000 rpm c) PANI M_w=65000 a.m.u., w=1000 rpm d) PANI M_w=65000 a.m.u., w=3000 rpm.*

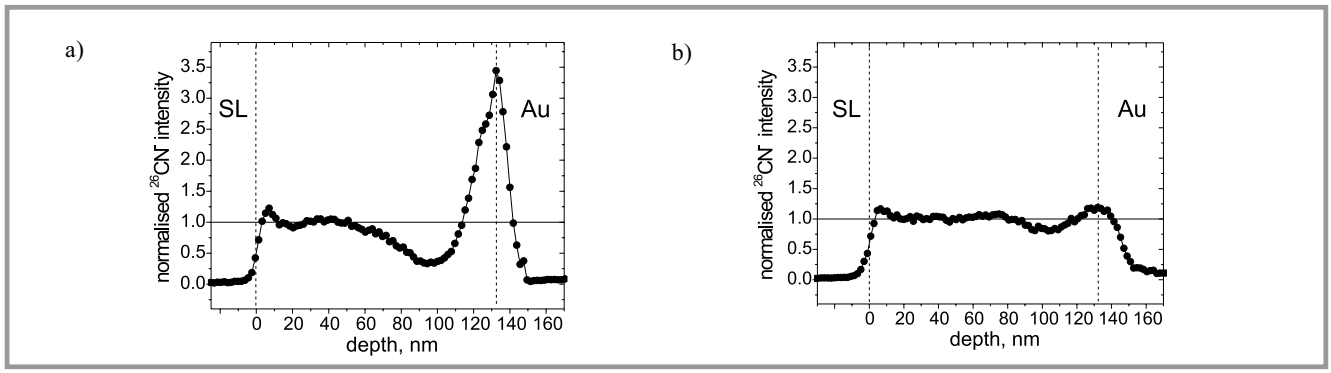

Figure 6. *SIMS profiles of PANI-CSA/PS thin films. PANI M_w=5000 a.m.u., PANI-CSA concentration 3.7 mg/cm³, PS concentration: 10 mg/cm³, rotation speed 1000 rpm, spin-cast in a) argon (dry atmosphere) and b) saturated water vapour (humid atmosphere). SL – polystyrene sacrificial layer. Au – gold substrate.*

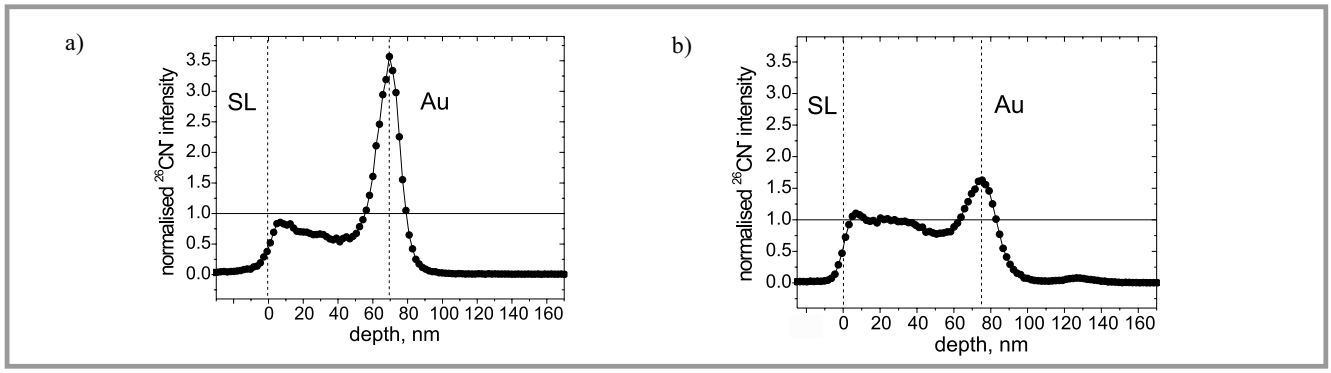

Figure 7. *SIMS profiles of PANI-CSA/PS thin films. PANI M_w=65000 a.m.u., PANI-CSA concentration 3.1 mg/cm³, PS concentration: 5 mg/cm³, rotation speed 1000 rpm spin-cast in a) argon (dry atmosphere) and b) saturated water vapour (humid atmosphere). SL – polystyrene sacrificial layer. Au – gold substrate.*

which is not present in presence of water. A possible explanation for the observed facts is that two mechanisms exist during drying: a PANI agglomeration and a segregation in the direction of gold. In the presence of water, hydrogen bonds between water molecules and polymer chains may be formed (a process described in [5]). Then water molecules connected to different PANI chains may form hydrogen bonds between each other. The segregation towards the Au surface of macromolecules trapped in a polymer network of this kind would be impeded, which would result in a lower enrichment value.

PANI segregation may occur due to electrostatic interaction between PANI macromolecules and gold. Each chain possesses a number of electrically polarised active centres, i.e. the places where CSA is attached to PANI (see Figure 1). Water might surround the centres, thus deactivating them and preventing the polymer from moving towards the gold. The impeding effect of water is less pronounced for long macromolecules (M_w=65,000 a.m.u.), where water cannot fully penetrate the entangled polymer chains.

Another point that may be noted is the fact that enrichment is higher for samples prepared from solutions of low polyaniline content (3.7 mg/cm³ as opposed to 2.3 mg/cm³ and 3.1 mg/cm³ vs. 1.0 mg/cm³). A low PANI concentration means that the mobility of macromolecules is relatively high, so that they manage to travel the way from the bulk of the film to its bottom surface before all the solvent evaporates and the film solidifies.

Conclusions

The strong influence of sample preparation conditions on the phase separation process was observed. In samples prepared in a dry atmosphere, a region rich in polyaniline close to the bottom of the film (near the gold surface) is formed, while in the case of a humid atmosphere this process is not observed. A possible explanation was given in point 5. Moreover, polymer concentration has an effect on the thickness of films.

Acknowledgments

This work was financially supported by the Polish State Committee for Scientific Research, Grant No. 3 T08C 032 27.

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Received 08.12.2004 Reviewed 10.02.2005