

SURFACE CHARACTERIZATION OF POLYMERS BY XPS AND SIMS TECHNIQUES

ANALIZA POVRŠINE POLIMEROV Z METODAMA XPS IN SIMS

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Polymers are very often subjects of different surface treatments. To understand and control the basic processes during surfaces modifications, analyses with advanced analytical techniques are required. We present two of such state of the art techniques, X-ray photoelectron spectroscopy – XPS and secondary ion mass spectroscopy – SIMS, often applied for characterization of polymers surfaces. In this work we give an overview of these techniques and their advantages and limitations related to polymer characterization. The combined use of these techniques is demonstrated in the application example, in which the cotton fibers were characterized before and after deposition of fluorine-based thin coating.

Keywords: X-ray photoelectron spectroscopy, XPS, TOF-SIMS, polymers, cotton

Polimerni materiali so pogosto predmet površinskih obdelav. Za razumevanje in kontrolo osnovnih procesov, ki potekajo med površinskimi modifikacijami, je potrebna uporaba naprednih analitskih tehnik. Predstavljamo dve takšni moderni tehniki: rentgensko fotoelektronsko spektroskopijo – XPS in masno spektroskopijo sekundarnih ionov – SIMS, ki se pogosto uporabljata pri karakterizaciji površin polimernih materialov. V delu predstavljamo osnove teh tehnik ter njihove prednosti in omejitve, povezane s preiskavo polimerov. Kombinirana uporaba obeh analitskih tehnik je predstavljena na primeru preiskave bombažnih vlaken pred nanosom tanke plasti na osnovi fluorovih spojin in po njem.

Ključne besede: rentgenska fotoelektronska spektroskopija, XPS, TOF-SIMS, polimeri, bombaž

1 INTRODUCTION

Polymers are widely used materials in everyday life. Their inertness, low specific weight, low production cost, variability of mechanical properties and other unique properties, make them even more attractive for future applications. Among modifications of polymers the polymer surface treatments play an important role since many surface related properties are crucial for technological applications of these materials. These applications are relevant for improvement of wettability, adhesion, surface barrier properties, biocompatibility, thin film deposition ... The reason for surface modifications is often the intrinsic property of many polymers, i.e. low surface energy, which should be changed in order to improve polymers compatibility with other materials and processes. Another reason for modification can be to introduce new functional properties at the polymer surface. The technological processes for polymer surface modifications are physical (corona, plasma, UV, laser treatments ...) and chemical (wet treatment, surface grafting ...) modifications ¹. The effect of such surface modification may be followed by different more or less sophisticated analytical tools. Surface analytical techniques with high surface sensitivity have been used to understand basic phenomena during surface modifications. Among them are X-ray photoelectron spectroscopy – XPS and secondary ion mass spectroscopy – SIMS, which were very often applied for advanced surface characterization of organic

and inorganic solid surfaces ²⁻⁵. Both of them have very high surface sensitivity combined with high elemental and molecular sensitivity. There are many other methods to analyze polymer surfaces like optical, electron and scanning probe microscopy, vibrational spectroscopies (FTIR, Raman spectroscopy), methods for surface energy measurements like contact angle measurements and others ¹.

The aim of this work is to present the main features of XPS and SIMS techniques as two state of the art analytical techniques for surface polymer characterization. Both of them have very high surface, elemental and molecular sensitivity. The main features and limitations of these two techniques are described in relation to polymer surface characterization. An application of combined use of the XPS and SIMS technique is given for cotton fabric.

2 X-RAY PHOTOELECTRON SPECTROSCOPY – XPS

XPS analyses give information on the chemical composition and chemical bonds of solid surface ^{2-4,6}. During the XPS analysis, a sample is illuminated with the monochromatic X-ray light in an XPS spectrometer and the energy of emitted photoelectrons from the sample surface is analyzed. In the photoelectron spectrum, which represents the distribution of emitted photoelectrons as a function of their binding energy,

Table 1: Comparison of main features of two surface analytical techniques XPS and SIMS**Tabela 1:** Primerjava glavnih značilnosti dveh površinsko občutljivih tehnik: XPS in SIMS

Feature	XPS	SIMS
Main information	Elemental composition and type of chemical bonds of surface atoms	Type of atoms, molecules and pendant groups at surface
Surface sensitivity	From 3–6 nm for polymers	1–2 uppermost monolayers (1 nm)
Sensitivity for elements	All, except H and He	All
Need for ultra-high vacuum ambient	Yes	Yes
Spatial resolution	1–100 μm	Less than 1 μm
In-depth information for thin films	Yes	Yes
fautoImaging	Limited	Yes with high resolution and sensitivity
3D analysis	No	Yes with high resolution and sensitivity
Quantification	Yes	Limited
Typical acquisition time for high resolution spectrum	1–3 min	5–15 min
Required expertise for data interpretation	High	High

peaks can be observed which are typical of elements present on the sample surface. The analysis area can be from some microns to mm in diameter and the signal during the XPS analysis originates from the surface layer up to 6 nm in thickness. During the analysis, two types of XPS spectra are usually recorded. Firstly, a spectrum through a wide energy range is acquired, in which the peaks of present elements are identified. Their concentration is calculated by dividing the peak intensities with the relative sensitivity factors provided by the XPS spectrometer manufacturer⁶. The attained results are normalized to 100 %. The relative error at the calculation of surface composition is approximately 20 % of reported value, while the elemental sensitivity is about 0.5 %. The XPS method does not enable the analysis of hydrogen and helium. In addition to wide energy range spectra, high-energy resolution spectra of characteristic peaks of the elements like C 1s, O 1s and others (N 1s, S 2p, Cl 2p, F 1s, Si 2p ...) are recorded through a narrow energy range. From the shape and binding energy of the peaks within these XPS spectra, the chemical bonding of surface elements can be identified with the help of data from the literature. For example in the case of organic materials one can identified from the carbon C 1s spectrum (energy range 282–297 eV) the bonding of carbon atoms like C-C/C-H, C-O, C=O, C-N, O-C-O, O=C-O, C-F and others. In addition to this other spectral features like shake-up peak in C 1s spectrum at 292 eV helps to identify aromatic pendant groups. During the analysis, the polymer samples are usually charging electrically, thus, a low-energy electron gun-neutralizer should be used. Prior to the spectra processing, spectra should be shifted, so that within the spectrum of carbon C 1s, the peak typical of the chemical bonds C-C/C-H is at the binding energy of 285.0 eV. The analysis took place in an ultra-high vacuum, which was during the analysis approximately 10^{-7} Pa or less. For precise XPS analysis of chemical bonding of surface atoms a special X-ray source should be used. In such a source X-rays are

emitted from the Al-anode with energy of 1486.6 eV and they are additionally monochromatized by special monochromator in order to reduce their energy spread to about 0.25 eV. The total recommended energy resolution during polymer analysis is 0.6 eV.

In order to get depth distribution of elements beneath the surface, ion bombardment with argon ions with energy of few keV was traditionally applied what results in a control removal of surface material. By subsequent XPS analyses one can in this way obtain XPS depth profiles presenting the concentration of elements as a function of sputtering time what can be converted into depth. In this way also polymers and thin organic films can be analyzed. Unfortunately due to local damage of chemical bonds in soft material like polymers and preferential sputtering effects very limited information on subsurface chemical bonds can be obtained by depth profiling. In last years large progress was achieved towards reducing surface damage introducing ion bombardment by cluster ion beams like C_{60}^+ .

Table 1 gives some characteristic features of the XPS technique. XPS technique was often applied for characterization of surface modifications of polymeric materials by other and also by our research group^{7–24}.

3 SECONDARY ION MASS SPECTROSCOPY – SIMS

SIMS is an analytical technique for compositional analysis of the solid surfaces and thin films^{2,5}. Due to its ability to identify the molecular structure i.e. type of molecules at the surface, SIMS technique was extensively applied in last decades just for polymer analyses^{12,15,24}. During the SIMS analysis the surface is bombarded with focused high energy (1–30 keV) ion beam what results in the ejection or sputtering of the species from the solid surface. Most of the emitted particles are neutral but small fraction of them is charged ions which are called secondary ions. They are measured

with a mass analyzer to determine the elemental composition and molecular structure of the surface. SIMS is a very surface sensitive technique because the emitted particles originate from the 1–2 top-most monolayers (1 nm). During the SIMS analysis the surface atoms are removed from the surface therefore the SIMS is locally destructive. In order to obtain chemical information of the original surface, the primary ion dose must be low enough ($<10^{13}$ cm $^{-2}$) to prevent a surface damage. This regime is so-called "static SIMS" mode and it is widely used for the characterization of polymer surfaces. If the primary ion dose is large enough it can be used to erode the surface layer in a controlled manner. In this way information on the in-depth distribution of elements can be obtained similar as it was described above for XPS depth profiling. This, so called "dynamic SIMS" mode is widely applied for depth-profiling of thin films, layer structures and dopant concentration. Layers of up to few microns thick can be depth-profiled using SIMS technique.

The sensitivity of the SIMS technique depends on the yield of secondary ion sputtering which is a function of the specimen's material (matrix effect), and the type, energy and incidence angle of the primary beam of ions. This is a reason for limited possibility for precise quantification of SIMS results in terms of surface composition. On the other hand the sensitivity of the SIMS technique is very high and is in the range of 10^{-6} . This technique allows the routine measurement of many trace elements at very low concentration, even in the ppb-range. The proper choice of primary ions is important for optimum sensitivity²⁵. For different materials different types of ion guns should be used to provide an optimum detection sensitivity for secondary ions. In general inorganic materials do not exhibit very complex structure with high mass units. Therefore for inorganic materials the SIMS spectra acquired in the low mass region (up to 100 u) can provide enough information for successful analysis. Opposite is valid for organic materials containing often ingredients with very high molecular mass. In this case it is important to get as much information as possible from the SIMS spectra in the high mass region (above 200 u) where small mass differences between similar molecular structures can be distinguished. For this purpose ion beams with high yield of surface sputtering of higher mass secondary ions is required. In last decade liquid metal ion sources (LMIG) for enhanced excitations in organic SIMS analyses were developed. They are based mainly on gold and bismuth clusters of atoms, like Au_3^+ , Bi_3^+ , Bi_5^+ . Similar characteristics are valid also for the ion beam of the C_{60}^+ clusters. Such ions sources provide enhanced increase for sputtering of high mass secondary ions and are very suitable for the analysis of organic and bio-organic systems. In the case of inorganic materials oxygen ions are usually used for analysis of electropositive elements or those with low ionization potentials, whereas electro-

positive ions like cesium atoms are better for sputtering negative ions from electronegative elements.

From the construction point of view there are three basic types of ion guns. In one, ions of gaseous elements are usually generated by electron ionization, for instance noble gases (Ar^+ , Xe^+), oxygen (O^-), or even ionized molecules such as SF_5^+ or C_{60}^+ . This type of ion gun is easy to operate and generates high current ion beams. A second source type, the surface ionization source, is one that generates Cs^+ primary ions. A third source type, the liquid metal ion source (LMIG), operates with metals or metallic alloys, which are liquid at room temperature. While a gallium source is able to operate with elemental gallium, recently developed sources for gold, indium and bismuth use cluster ions. The LMIG source provides a high focused ion beams (<60 nm) for high-resolution work with moderate intensity and is additionally able to generate short pulsed ion beams. It is therefore commonly used in static TOF-SIMS instruments. Highly focused ion beam allows chemical or molecular imaging of the surface, an analytical approach in which focused ion beam is rastered over the surface and mass spectra are collected at every pixel point. Retrospectively, for any peak in the mass spectrum, an image can be generated.

The mass analyzer may be a quadrupole mass analyzer, magnetic sector mass analyzers or time-of-flight (TOF) analyzer. They differ with respect to transmission, mass resolution, mass detection (parallel or sequential) and sensitivity. Among them the TOF-SIMS analyzers provide the highest sensitivity and mass resolution, a much greater mass range and they are preferred for static SIMS analyses of polymers. In SIMS measurements the spectra of positive and negative ions are measured. The TOF-SIMS spectra obtained from polymer surfaces can be divided into three regions. In the first low mass range (up to 300 u) ions consisting of end groups, fractions of repeat units, or side chains are detected (e.g. $C_xH_y^{+/-}$). In general the detection of these low mass fragments is sufficient for an identification of inorganic materials. In the second range (300–2000 u), typically ions consisting of multiple repeat units with and without the loss of functional groups are detected, what is important for polymer analyses. In the third high mass range (up to 10 000 u) intact oligomer ions can be observed. These quasimolecular ions are typically formed by an attachment ($M + H$) or loss of hydrogen ($M - H$) and are important for recognition of surface species. Recently developed polyatomic or cluster ions primary sources such as gold (Au_n^+), bismuth (Bi_n^+) and C_{60}^+ (buckminster fullerenes) overcome the problem of insufficient yields of these higher mass species observed under atomic primary bombardment²⁶. The use of cluster ions has also another advantage. It decreases also the residual chemical damage on the surface comparing to monoatomic ions due to larger size, shallower implantation depth and higher sputtering yields. For these

reasons cluster ions are also very suitable for molecular depth profiling of most organic and biological samples, where in-depth molecular distribution is measured.

At this point we can compare also the acquisition time between SIMS and XPS techniques. In the TOF-SIMS instruments due to the time-of-life type of measurements whole mass spectrum is acquired in parallel at very high sensitivity. This is a reason that the typical acquisition of SIMS spectrum at one point takes about 1–3 min. It depends also on the required mass region and mass resolution. This time is shorter than typical time needed for acquisition of high-energy resolution spectra of different elements in the XPS analysis. In the XPS analyses such acquisition time is typical from 5 min to 15 min.

In comparison to other surface analytical techniques the SIMS offers several advantages, namely the ability to identify all elements, including H and He and the ability to identify elements present in very low concentration levels, such as dopants in semiconductors. Some of the SIMS main features are summarized in **Table 1**.

4 APPLICATION OF XPS AND SIMS TECHNIQUES FOR COTTON FIBERS CHARACTERIZATION

In the following an example is given, which shows the combined application of XPS and SIMS techniques for surface characterization of cotton fabrics treated with fluoroalkylsilane (FAS). The cotton is an example of the natural polymer and it was often characterised by XPS and SIMS techniques^{11,12,15,16,18,20,23}. The thin fluoroalkylsilane treatment was applied in order to modify the wettability of the cotton surface towards the hydrophobic surface. Surface analyses were performed on the untreated and treated cotton fabrics. The XPS and SIMS techniques were used to follow the surface composition, chemical bonds of surface atoms, molecular structures and spatial distribution of coated material.

The XPS analysis was performed in the XPS spectrometer produced by Physical Electronics Inc., model TFA XPS. The Al monochromatized source of X-ray light with the power of 200 W was used. The energy resolution was approximately 0.7 eV and the analysis area was about 0.4 mm in diameter. **Figure 1** shows an XPS survey spectra obtained on the cotton

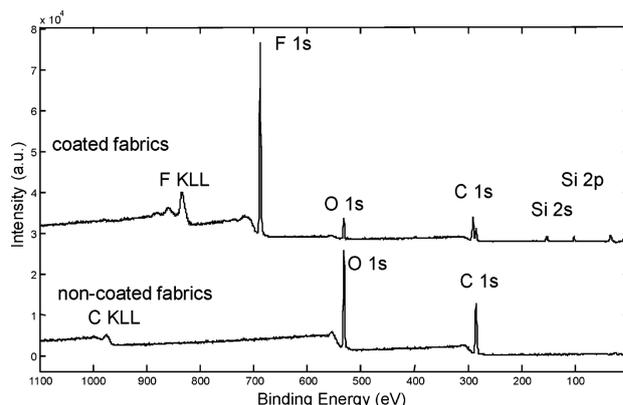


Figure 1: XPS survey spectra obtained on the surface of the non-treated cotton fabrics (lower) and on fabrics treated with fluoroalkylsilane (upper).

Slika 1: Pregledni XPS-spektri, dobljeni na površini neobdelane bombažne tkanine (spodaj), in na tkanini, obdelani s fluoroalkilsilanom (zgoraj)

fabrics and the fabrics after treatment. In the spectrum of untreated sample the peaks of C 1s and O 1s are present indicating the pure cotton surface. The surface composition deduced from this spectrum is given in **Table 2**. There is the mole fraction 61.6 % of C and 38.4 % of oxygen on the surface. This composition corresponds well to expected cotton nominal composition. As mentioned above XPS method can in addition to surface composition yield also information on bonding of surface atoms. **Figure 2a** shows high-energy resolution carbon C 1s spectrum obtained on the untreated sample. The spectrum is composed from more peaks, which were identified by de-convolution procedure. After C 1s spectrum de-convolution into different components, C1, C2, C3, we assigned them to different chemical bonds of carbon atoms. In this case a peak C1 at binding energy of 285.0 eV is assigned to C-C and C-H bonds, a peak C2 at 286.4 eV is assigned to C-O, a peak C3 at 287.8 eV is assigned to C=O and O-C-O bonds. The origin of peaks C2 and C3 is related to backbone of the cellulose molecules from the cotton matrix. The C1 component related to C-C/C-H bonds probably originates from some non-cellulosic components as waxes or pectine or from additives or surface contamination. Namely the C-C/C-H bonds are not present in cotton backbone structure. The relative concentration of C1, C2, C3 components is given in **Table 2**.

Table 2: Surface composition and relative concentration of different bonds of carbon atoms obtained by the XPS analysis of the cotton fabrics before and after treatment with fluoroalkylsilane

Tabela 2: Sestava površine in relativne koncentracije kemijskih vezi ogljikovih atomov, dobljene z XPS-analizo bombažne tkanine pred obdelavo s fluoroalkilsilanom in po njej

Sample	$x(C)/\%$	$x(O)/\%$	$x(F)/\%$	$x(Si)/\%$	C1 (%), C-C/C-H	C2 (%), C-O	C3 (%), C=O, O-C-O	C4 (%), O=C-O	C5 (%), CF ₂	C6 (%), CF ₃
Non-treated cotton fabrics	61.6	38.4	0	0	38.0	43.4	18.6	0	0	0
Treated fabrics	37.7	9.6	48.6	4.2	15.9	18.6	3.1	5.0	48.4	9.0

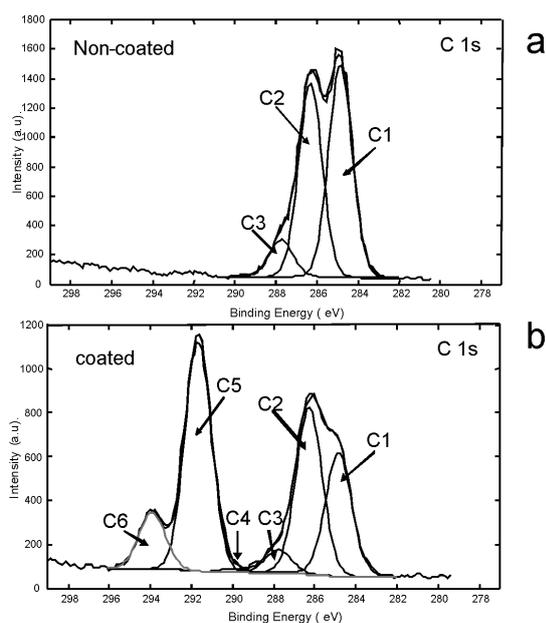


Figure 2: XPS high-energy resolution spectra C 1s obtained on the non-treated cotton fabrics (a) and fabrics treated with fluoroalkylsilane (b). The spectra are deconvoluted in the C1–C6 peaks presenting different C-atom bonds.

Slika 2: Energijsko visoko ločljivi spektri XPS C 1s, dobljeni na površini neobdelane bombažne tkanine (a), in na tkanini, obdelani s fluoroalkilsilanom (b). Spektri so bili razstavljeni na vrhove C1–C6, ki pomenijo različne vezi ogljikovih atomov.

After the treatment of the cotton fabrics with fluoroalkylsilane, the upper XPS survey spectrum present in **Figure 1** was obtained. In addition to C 1s and O 1s the peaks of F 1s, Si 2p and Si 2s appeared indicating successful deposition of functional coating. The new surface composition is also given in **Table 2**. The major element on the surface is fluorine (48.6 %) originating from the deposited coating. The deposition of

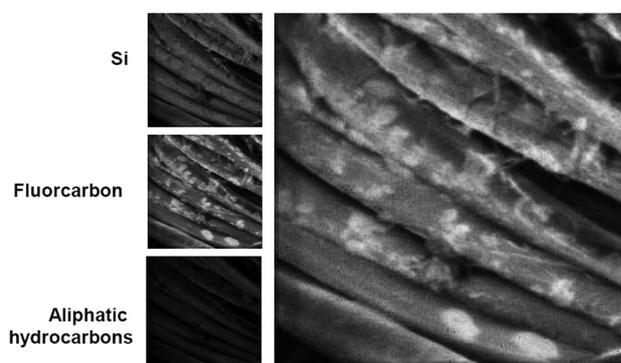


Figure 4: TOF-SIMS images obtained on the cotton fibers treated with fluoroalkylsilane. Images were taken using raster size of $(80 \times 80) \mu\text{m}$. Images on left side were obtained summarizing the signals of Si_xO_y clusters (left top), fluorocarbon (left middle) and aliphatic hydrocarbons (left down). An image on the right side is a composite image obtained from three images on the left.

Slika 4: TOF-SIMS-slike, dobljene na bombažnih vlaknih, obdelanih z fluoroalkilsilanom. Slike so bile posnete po področju $(80 \times 80) \mu\text{m}$. Slike na levi strani so bile dobljene iz signalov, značilnih za Si_xO_y spojine (levo zgoraj), fluoroogljkovih spojin (sredina levo) in alifatskih ogljikovodikovih spojin (levo spodaj). Slika na desni strani je dobljena kot vsota slik na levi strani.

functional coating can be recognized also in different chemical bonding of the surface atoms with respect to untreated cotton. Carbon C 1s spectrum from the coated cotton surface is shown in **Figure 2b**. New peaks are present in this spectrum representing new types of C-atoms bonding. The two peaks are at binding energies of 291.7 eV (C5) and 293.9 eV (C6). These energies are characteristic for CF_2 and CF_3 bonding which shows the fluorinated-carbon compound on the surface. Also the ratio between the C1 and C2 peaks changed after coating deposition (**Table 2**). Applying the XPS method we concluded on the surface composition and chemical

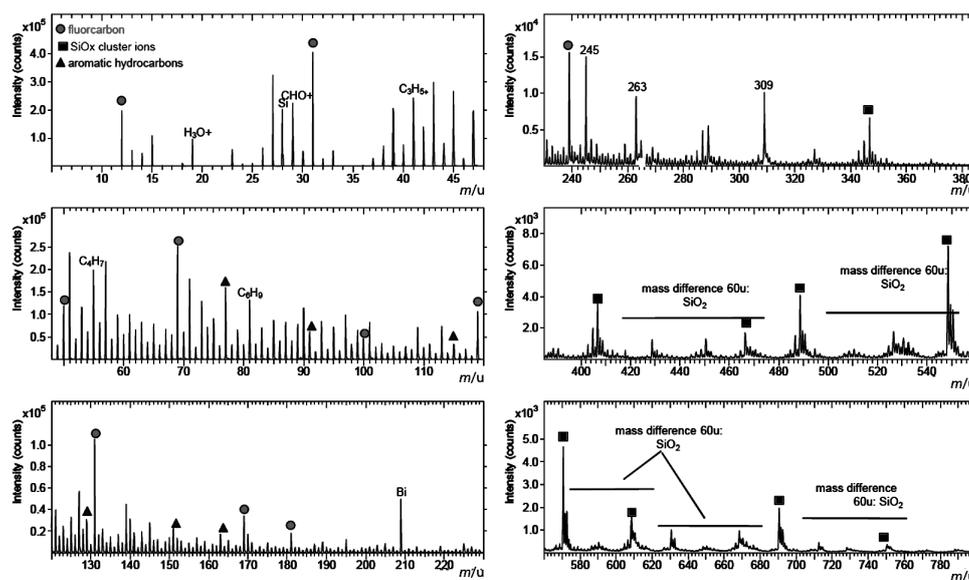


Figure 3: TOF-SIMS spectra of positive polarity obtained on the cotton fibers treated with fluoroalkylsilane

Slika 3: TOF-SIMS-spektri pozitivnih ionov, dobljeni na bombažnih vlaknih, obdelanih s fluoroalkilsilanom

bonding of elements on non-treated cotton fabrics and on the fabrics after coating deposition.

Due to the lack of spatial resolution of the XPS method there is an open question how the deposited coating is distributed over the surface. Is the coating homogeneously distributed or there are some non-treated regions. To analyse the homogeneity of the applied coating we carried out the SIMS analysis on the treated sample. The SIMS instrument with TOF mass analyzer was used. The primary ion beam of Bi-ions of energy 25 keV was produced by LMIG source. In the first step the spectroscopic analysis was performed at one point. A typical SIMS mass spectrum in the range between 5 u and 790 u obtained with positive ions from the treated fabrics is presented in **Figure 3**. The spectrum consists of great number of peaks at different masses. The peaks assignment is more complicated comparing to XPS method. Anyhow there are known groups of peaks at characteristic masses belonging to expected chemical molecules and their fragments. In the case of coated cotton the SIMS spectrum shows the main peaks at masses m/u (12, 31, 69, 131, 240), which originate from the fluorocarbon compound due to fluoroalkylsilane treatment, the peaks at (77, 116, 129) u originating from aromatic hydrocarbons and peaks at (347, 407, 488, 548) u originating from the SiO_x clusters. Beside mentioned peaks which were used to identify the molecular structure of the surface, other peaks exist in the SIMS spectrum, as for example at 18 u (H_3O^+), 28 (Si), 29 (CHO^+), 41 (C_3H_3^+), 55 (C_4H_7) ... After SIMS point analysis the SIMS images were recorded analyzing the region of (256×256) pixels and acquiring the whole mass spectra at each pixel. The characteristic peaks of fluorocarbon compound, aromatic hydrocarbons and a peak from the SiO_x clusters were used to construct the images, which help to follow the distribution of deposited coating. These SIMS images are presented in **Figure 4** as three separated images (on the left side) and as a composite image. These results show that different species are distributed in different manner. From the composite image it can be recognized that there are regions where the SiO_x -clusters and fluorocarbon compounds from the fluoroalkylsilane film are more concentrated. In this way we conclude that some inhomogeneities from the coating deposition process which can be further improved by modifying process parameters.

5 CONCLUSIONS

In this work the main features of XPS and SIMS analytical techniques were presented and discussed. Both of them are relevant for surface characterization of polymer materials. These two techniques have very high surface sensitivity. The main features of the XPS method are the ability to obtain quantitative information on chemical composition and on types of chemical bonds in particular of carbon atoms, which are the most abundant

in organic materials. On the other hand the main features of the SIMS techniques are the ability to obtain the chemical information of the type of atoms, clusters and molecules at the surface with very high lateral resolution. The combination of both methods gives the very complete information on polymer surface chemistry. The combined use of the XPS and SIMS techniques was demonstrated on the analyses of cotton fibers coated with fluorine-containing film. XPS data confirm the formation of film through the presence of fluorine and C-F bonds on the cotton surface. The spatially resolved SIMS images revealed partially nonuniform distribution of coated surface species related to the reactivity of deposited material.

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