

X-Ray Photoelectron Spectroscopy of Polystyrene Composite Films

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ABSTRACT

In this paper, X-ray Photoelectron Spectroscopy (XPS) measurements were obtained to determine the chemical structure of these polystyrene (PS) doped and undoped thin films. The purpose is to analyze the graphs and binding energies of each element to determine. The XPS analysis of these pure PS compared doped PS thin film does show a tunable potential for optimum properties. PS has a relative basic host matrix, and it is our hypothesis that first, we can show that XPS can be a useful and resourceful tool in characterizing these thin films for chemical structure and binding information. Secondly, we intend to show that through the addition of dopants, we can affect the binding energies. The results show the impact on O1s binding energies ± 4.43 - 5.57 eV and for C1s ± 1.45 - 9.37 eV. These analyses have been performed in several studies on polymer nanocomposite materials. Here, we introduce the use of the XPS analysis in recent notable polymer nanocomposite studies for various target applications.

Keywords

Polystyrene (PS), XPS, Polymer thin film, Barium Titanate, Strontium Titanate, Lead Zirconium Titanate, Lithium Niobate, Potassium Niobate, Barium Titanate, Lithium Tantalate, Zinc Oxide, Chemical analysis, Binding energies.

Introduction

Polymer surfaces play a significant role in industrial applications such as adhesives, protective coatings, biomaterials, microelectronics, and thin film technology. Polymers are attractive materials for applications due to the considerable flexibility in their chemical structures. In recent years, great efforts have been made in the nanocomposites of conducting polymers and inorganic materials [1,2]. The production of polymer thin films is important for several technological applications and fundamental studies range include stability characterization to surface enrichment [3]. The application of thin films has always been a very important subject for the semiconductor industry and the scientific community. This is especially true for the metal-oxide-semiconductor field effect transistor technology in integrated circuits [4,5]. The surface properties of polymers are in general different from their bulk properties. In practice, the phenomenon of surface segregation enables many applications through the

intentional transfer of additives from the matrix to the surface. Some compounds are very active on the surface and the addition of a very small amount of these additives to a polymer can cover the surface of samples in an almost uniform manner [1].

X-ray photoelectron Spectroscopy (XPS) is also known as electron spectroscopy for chemical analysis (ESCA), a sensitive quantitative spectroscopic technique used as a surface analytical method capable of meeting the strong requirements for the chemical nature of compositional changes through chemical state analyses. When paired with enough data from binding energy databases can provide sufficient information about the chemical composition of a sample. Peaks in the resulting spectra can be attributed to specific compositional and chemical states of the elements in the materials [6-9]. It can also measure the thickness of a surface film and identify the presences of impurities on or near the surface and measuring layer thicknesses. XPS is widely used for the characterization of surfaces of materials for both conductive and nonconductive materials, e.g. nanoscale advanced materials, electrodes of fuel cells, and photo catalysts. [10,4,5]. XPS has been extensively applied to surface chemistry in a wide variety of fields, such as electronics, forensics, and biology. This method focuses on examining surfaces of semiconductors, thin films and

coating (i.e. metal/metal oxide/DNA film), biosensors, and dry powder pharmaceutical materials [10]. For polymers, perhaps the most significant achievements have been the development of new charge compensation systems that can precisely control the surface potential of insulating materials and thereby considerably enhance the energy resolution [1]. However, due to the very thin nature of some of these films, along with the presence of one or more solid/solid interface, influences the nature of the XPS signals and limits the usefulness of some of the standard analysis approaches Chambers et al. [4]. Moreover, severe chemical state damage can occur for both inorganic oxides and organic materials sputtered by certain ion beam irradiations. Recently the cluster ion beam has been utilized for XPS profiling of many organic materials to minimize the damage on the remain surface [6].

PS latex beads are a kind of functional polymer material. These beads have many admirable properties such as nontoxicity, high surface area, strong adsorption ability, and chemical inertness [2]. In this paper, we describe the implementation of XPS analysis using traditional, commercially available equipment, to shed light on the surface composition and binding energies of nanocomposites PS doped and undoped thin films. The intent is to highlight that useful information can be obtained from the spectra and some of the ways in which the properties of heterostructure thin films may be enhanced. Combining with the advantages of PS and the dopants, the structured nanocomposite films should have many excellent properties. For example, Lead Zirconium Titanate PZT is suitable for building the ferroelectric random-access memory, because of its ferroelectricity [5].

Methodology & Design

Methyl Ethyl Ketone (C_4H_8O) was procured from Reagents. Polystyrene ($(C_8H_8)_n$) was obtained from Sigma Aldrich and had an average molecular weight (M_w) of 280 000 $g\ mol^{-1}$. Strontium Titanate, 99% (SrO_3Ti), Barium Titanate, 99.5% ($BaTiO_3$), Lithium Tantalate, 99.5% ($LiTaO_3$), Zinc Oxide, 97% (ZnO), Lithium Niobate, 99.9% ($LiNbO_3$), Potassium Niobate, 99.9% ($KNbO_3$), and Lead Zirconate Titanate, 99% (PZT) were all purchased from Sigma-Aldrich Chemistry as starting materials. Thin films were developed utilizing the solution casting method. It is a low cost and easy fabrication method, and the ability to produce uniform films is essential [3].

A chemical analysis to detect the presence and structure was performed through XPS. X-ray photoemission spectroscopy plays an important role in obtaining information on these films. It provides information about the presence of chemical elements and the bonds in the material. A spectrum is obtained over an energy region that will provide peaks for all detectable elements [8,11]. XPS is based on the well-known photoelectric effect such as a typical $Al\ K\ \alpha$ or $Mg\ K\ \alpha$ sources, while simultaneously measuring the kinetic energy and number of electrons that escaped from the surface and binding energy. The interaction between an X-ray photon and the core-level electron of an atom causes a complete transfer of the photon energy to the electron. The electron then has enough kinetic energy to escape from the surface of the sample.

The electron is referred to as the photoelectron [9,10,1]. A scheme of the photoelectron emission can be seen in Figure 1. As elements have unique binding energies, knowing the electron binding energy allows the identification of elements. XPS can detect all elements except Hydrogen (H) and Helium (He). Furthermore, the electron binding energy is also sensitive to the electronic environment of the atom [1].

The XPS investigations were performed with a Nexsa electron spectrometer with monochromatic $Al\ K\ \alpha$ source radiation with an energy of 1486.68 eV. Binding energy for the aliphatic C1s peak is at 284.8. Because carbon exists to some extent on all samples, C1s is typically used to perform calibration. All spectra were processed using the program Thermo Advantage for data acquisition. Measurements were performed after the sample holder was introduced into the analysis chamber. A schematic of the XPS is shown in Figure 2. The pressure during analysis was $2.8 \times 10^{-7} - 7.7 \times 10^{-7}$ mbar. The X-ray beam size was 400 μm and survey spectra with a pass energy (PE) of 200 eV step size 1 (1361 energy channels) and a dwell time of 10 ms. The number of average periods was 10 with an average of 3 scans.

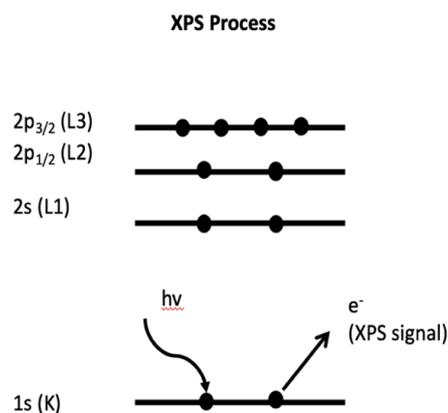


Figure 1. XPS photoemission process

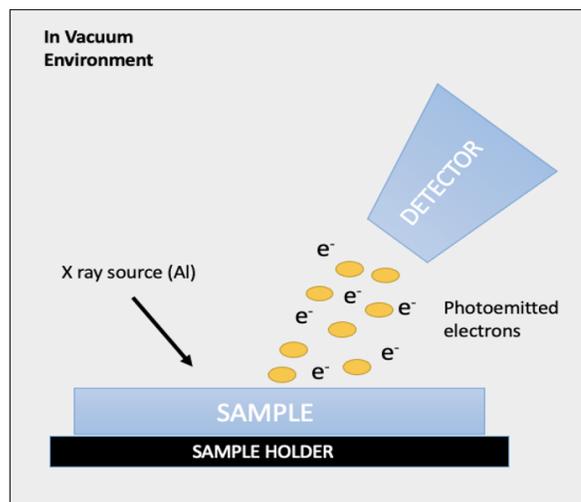


Figure 2. Schematic of XPS

Results

The compositional analysis can be performed by identifying the peaks. After background subtraction, the quantification of peak intensity data was performed. The XPS investigation of the surface of these pure Polystyrene ((C₈H₈)_n) and doped PS thin films show the presence of the elements Oxygen and Carbon. In general, the peak positions of these two elements identified in organic polymer nanocomposites are approximately C1s at 285 eV and O1s at 531 eV [12].

When the binding energy decreases, the electron density of the oxygen increases (Table 1). When an atom is bonded to another atom of an element having a different electronegativity, the electron binding energy may increase or decrease.

Table 1: Comparison of O1s and C1s BE in doped and undoped polystyrene thin films.

Element/ Transition	Binding Energy (eV)							
	Pure PS	PS + BaTiO ₃	PS + PZT	PS + ZnO	PS+ LiNbO ₃	PS+ KNbO ₃	PS+ PbTiO ₃	PS+ BaMgAl
O1s	532.51	531.83	528.08	529.08	538.08	527.08	532.20	529.66
C1s	284.48	284.84	293.85	283.44	289.71	283.03	284.19	290.90

This change in binding energy is called the chemical shift, which can provide information about the structure of a polymer or polymer interaction [1]. When the binding energy decreases, the electron density of the oxygen increases. The O 1s peaks of the samples agree with characteristics of metallic oxides. Table 2 summarizes the position and assignment of characteristic peaks in C1s spectrum. It is noted that the position is often affected by the conditions of samples and measurements; for example, the accumulation of positive charge upon the photoemission of electrons on an electrically insulated surface, i.e., charging effect, the peak positions are often deviated from the representative values and therefore, calibration by positioning C-C (or C-H) peak in C1s region at 285.0 eV is necessary for the peak interpretation [12].

Table 2: C1s typical chemical shift ranges of different functional groups.

Functionality	Binding Energy (eV)
C-H, C-C (hydrocarbon)	285.0
C-N (amine)	285.56-286.41
C-O-H, C-O-C (alcohol, ether)	286.13-286.75
C=O (carbonyl)	287.81-288.06
O-C=O (acid, ester)	289.0
O-(C=O)- (carbonate)	290.3
-CH ₂ CF ₂ - (2F with carbon)	290.6

Figure 3 shows the XPS spectrum of a polystyrene thin film with the chemical peaks as labeled. This survey spectrum scan encompasses binding energy range from 0 to 1400 eV. From this wide spectrum atomic percent (At. %), the percentage of one atom relative to the total number of atoms, can also be determined. The pure PS spectrum shows O1s at 532.51 eV and 4.29 At.%. C1s at 284.48 eV and 95.71 At.%.

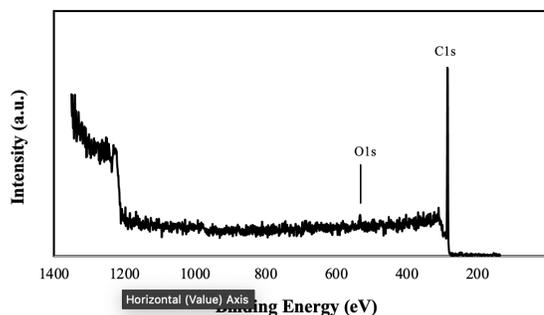


Figure 3: An XPS survey spectrum of a polystyrene thin film synthesized by solution casting.

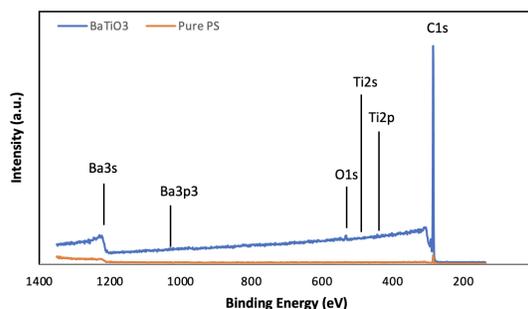


Figure 4: XPS spectrum of pure PS compared to PS + BaTiO₃ thin film with chemical elements labeled.

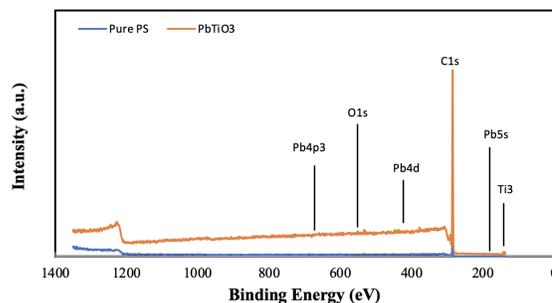


Figure 5: XPS spectrum of pure PS compared to PS + PbTiO₃ thin film with chemical elements labeled.

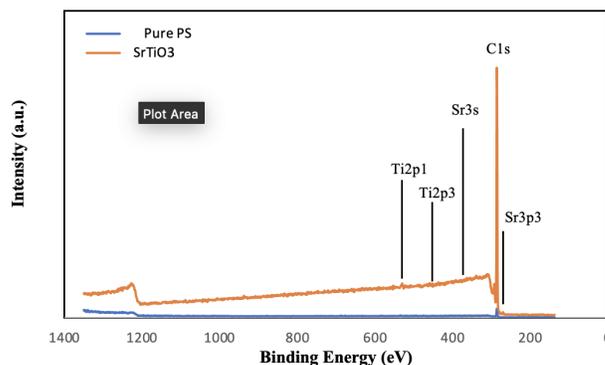


Figure 6: XPS spectrum of pure PS compared to PS + SrTiO₃ thin film with chemical elements labeled.

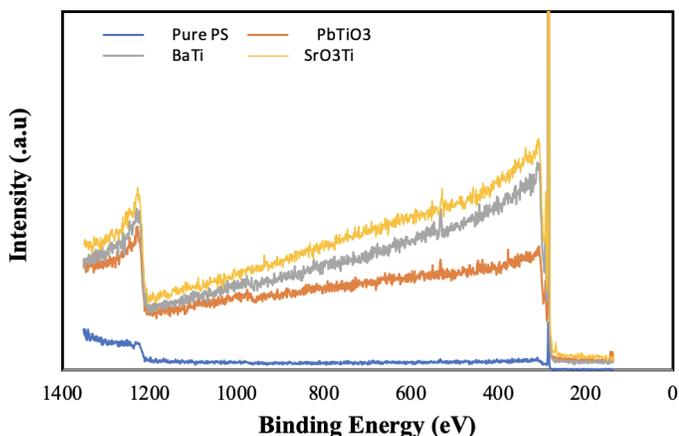


Figure 7: XPS spectrum of all nanocomposite PS thin films doped and undoped for comparison.

The survey scan of PS + BaTiO₃ searched for peaks corresponding with C1s at 284.84 eV, Ba3s at 1290.95 eV, Ba3p3 at 1063.13 eV, O1s at 531.83 eV, Ti2s at 562.89, and Ti2p at 466.08 eV. Seen in Figure 4.

Seen in Figure 5 the peaks can be determined for the PS thin film sample doped with PbTiO₃. The high intensity of the C 1s at 284.19 eV and 96.81 At.%. Pb4p3 at 644.23 eV and 0.06 At.%. Pb4d5 at 414.22 eV and 0.02 At.%. O 1s at 532.20 eV and 1.05 At.%. Pb5s at 149.46 eV and 0.10 At.%. Ti3s at 60.42 eV and 1.49 At.%. Ti3p at 36.09 eV and 0.45 At. %, and Pb5d at 18.89 eV and 0.04 At.%.

The C1s peak can be seen at 284.41 eV and 97.36 At% in the PS + SrTiO₃ sample in Figure 6. Also labeled in Figure 6 were Ti2p1 at 464.36 eV and 0.06 At.%. Ti2p3 at 451.05 and 0.09 At.%. Sr3s at 361.69 eV and 0.64 At.%. Sr3p3 at 268.20 and 0.14 At.%. Sr3d at 133.44 and 0.18 At.%. Ti3s at 55.69 eV and 0.43 At. %, and Sr4p with 18.14 eV and 1.09 At.%.

Figure 7 shows the overlay of the graphs to depict the changes. The graphs have been modified to make the smaller peaks visible. Therefore, these results support the hypothesis that first; XPS can be a useful tool on these thin films to obtain information for applications. Secondly, that these films are tunable through additives.

Graphs not shown include results from the XPS survey scan of the PS thin film doped with PZT. With C1s peak at 293.85 eV for binding energy and 30.35 At.%. Pb4s at 893.84 eV and 2.11 At.%. Ti2s at 561.72 eV and 25.26 At.%. O1s at 528.08 eV and 4.27 At.%. Zr3s at 437.03 eV and 12.39 At.%. Pb4d5 at 412.85 eV and 0.51 At.%. Zr3p1 at 346.46 eV and 8.29 At.%. Zr3p3 at 334.27 eV and 11.56 At.%. Zr3d at 184.25 eV and 3.71 At.%. Pb5d at 20.28 eV and 1.31 At.%.

The PS + ZnO thin film presented a C1s peak at 283.44 eV and 54.37 At.%. O1s with 529.08 eV. Zn2s with 1191.08 eV and 21.38 At.%. Zn2p3 with 1024.08 eV and 0.72 At.%. Zn3s with 139.49 eV and 7.43 At. %, and O2s at 25.98 eV and 16.05 At.%.

As with the PS + PZT developed C1s at 293.85 eV and 30.35 At.%. Pb4s at 893.84 eV and 2.11 At.%. Ti2s with 561.72 eV and 25.26 At.%. O1s with 528.08 eV and 4.27 At.%. Zr3s at 437.03 eV and 12.39 At.%. Pb4d5 at 412.85 eV and 0.51 At.%. Zr3p1 at 346.46 eV and 8.29 At.%. Zr3p3 at 334.27 eV and 11.56 At.%. Zr3d at 184.25 eV and 3.71 At.%. Pb4f7 at 137.09 eV and 0.24 At. %, and Pb5d at 20.28 eV and 1.31 At.%.

Lastly, the XPS scan of PS film doped with LiNbO₃ nanoparticles with C1s at 289.71 eV and 3.60 At.%. O1s at 538.08 eV and 4.68 At.%. Nb3s at 467.08 eV and 3.02 At.%. Nb3p1 at 377.81 eV and 3.73 At.%. Nb3p3 at 351.11 eV at 1.93 At.%. Nb3d3 at 207.85 eV and 0.10 At.%. Nb3d5 at 200.94 eV and 0.20 At.%. Smaller peaks exist for Li1s at 56.14 for 34.46 At.%. Nb4s at 49.24 eV for 44.28 At. %, and Nb4p at 32.61 eV for 3.89 At.%.

Conclusions

In this paper XPS analysis validated the presence of O1s and C1s peaks in each element that was under investigation. By incorporating different dopant nanoparticles into the PS matrix, we were able to show that there was also a change in the binding energies of O1s and C1s related to metal oxides. Supportive of the hypothesis. While the peaks in the XPS survey graphs were not as prominent as we hoped for intensity, the raw data of the scans does produce corresponding information with the appropriate chemical elements with minimum to no contamination present.

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