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Angle resolved imaging of polymer blend systems: From images to a 3D volume of material morphology

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Abstract

ARXPS has been widely used for thickness calculations, discerning molecular orientation, and estimating both surface enrichment and concentration gradients. For multicomponent heterogeneous samples, not only the average concentration, but also morphology and chemical heterogeneity are important. In this work we demonstrate the results of combining ARXPS and imaging for analysis of polymer blend samples. Challenges in combining the two approaches include locating the same area for image acquisition at multiple take-off angles, the small depth of focus in imaging mode, and the geometrical transformation of images with changing take-off angle. The conversion of the original photoelectron images to a volume representing the top 3–10 nm of the polymer blend requires spatial image transformation to correct for geometry or image warping, automatic image registration, mapping images to concentration with the assistance of AR small area spectroscopy, image morphing and visualization. AR images were used to create volumes from the top 3–10 nm of blends of polyvinylchloride (PVC) and polymethylmethacrylate (PMMA). These volumes allow for the visualization and estimation of the degree of surface segregation and separation of polymer phases.

Keywords: Angle resolved X-ray photoelectron spectroscopy; Angle resolved imaging; 3D morphology; Polymer blend; Volume visualization

1. Introduction

Multicomponent polymeric materials, such as composites, blends and multilayered systems are widely used in a variety of high-technology applications. Many binary polymer pairs are immiscible and produce bulk phase-separated materials on mixing. For such blends, the bulk morphology may extend to the surface or one of the components can be preferentially segregated at the surface [1]. For heterogeneous samples, the concentration variations and local regions of analyte concentration can be more important for an understanding of the behavior of complex systems than average composition. XPS imaging and small area spectroscopy provide this important information, allowing for a correlation of micro- and macro-scale materials properties [2,3]. The region of structure-property determination of the functional material generally extends only a few molecular layers (<10 nm) from the surface into the solid [4]. Imaging and small area spectroscopy represent an integral signal from the top 8–10 nm of the material. Angle resolved XPS (ARXPS) is capable of providing chemical compositions from shallower depths non-destructively by varying the take-off angle (TOA) [5]. The value of combining imaging and angle resolved XPS has not yet been evaluated due to the challenges this problem presents. 3D visualization of imaging data acquired from different depths on the same areas of the samples can, however, enhance understanding of surface and near-surface structure.

In recent years, significant research has been directed towards visualization of scientific data. Recent efforts include the problem of visualizing data from multiple modalities (multimodal) and visualizing data by combining perspectives within the same modality (unimodal) [6–14]. In multimodal visualization, image data from different techniques that use different physical principles are combined to form a new image that contains more interpretable information than

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could be gained using the original data [2,10,11]. Electron tomography is an example of unimodal visualization, where electron microscopy is used to obtain a 3D image from a specimen by tilting the sample through multiple angles [12–14].

AR-imaging XPS also represents a unimodal visualization problem. Here we report on the application of AR-imaging XPS and the scientific visualization of a phase-separated polymer blend. We will discuss the experimental set up for acquiring AR images, image registration, image quantification, volume reconstruction and volume visualization. As a result of the 3D visualization of angle resolved imaging data, the morphology within the top 3–10 nm of the polymer blend and the degree of surface segregation are evaluated in detail.

2. Experimental

2.1. Sample preparation

Polyvinylchloride (PVC) of MW 77.3 kDa and polymethylmethacrylate (PMMA) of MW 100 kDa were obtained from Scientific Polymer Products Inc. As-received materials were used in 2% (wv) solutions of PVC and PMMA in HPLC grade tetrahydrofuran (THF). Solutions containing 50/50 mixture of the two polymers were allowed to sit for 24 h before deposition onto Teflon watch glasses using pipettes. The resulting films were air-dried for 24–48 h. A Cu grid of mesh size 50 (Ted pellar) was glued to the sample. The size of the mesh opening for this grid is 450 μm.

2.2. XPS instrumentation

The XPS spectra and images were acquired on a Kratos AXIS Ultra photoelectron spectrometer using a monochromatic Al Kα source operating at 300 W. The base pressure was 2×10^{-10} Torr, and operating pressure was 2×10^{-9} Torr. Charge compensation was accomplished using low energy electrons. Standard operating conditions for good charge compensation are −2.8 eV bias voltage, −1.0 V filament voltage and filament current of 2.1 A.

To ensure that images acquired at all take-off angles (TOAs) are from exactly the same area on the sample, an opening of the grid was selected and XPS images of the Cu grid were used to set up the positions for all TOAs from this grid opening. Data were acquired at TOAs of 90°, 60°, 45°, 30° and 15°. The grid opening of interest was chosen using low magnification Cu 2p images at 90° TOA. This mode gave images with a field of view (FOV) of 700 μm × 700 μm, so that the whole grid opening of 450 μm × 450 μm is visible within the image. As the sample was tilted to the specified TOAs, the spatial coordinates were adjusted such that the center of the photoelectron image coincided with the center of the grid opening. The positions of the copper grid and the blend sample underneath it differ slightly with respect to the analyzer. The height coordinate *z* needed to be adjusted for optimization of the signal from the polymer blend. This in turn, required adjustment of the lateral positions *x* and *y* for all TOAs. For this last step, the background image for the Cl 2p main peak, acquired at a binding energy of 194 eV, was used.

For all TOAs, low magnification 700 μm × 700 μm elemental and background photoelectron images were acquired for O 1s at 529 and 524 eV, for C 1s at 282 and 278 eV and for Cl 2p at 198 and 194 eV, respectively. A pass energy of 80 eV and 2, 3, 5, 7 and 10 min of acquisition time were used for 90, 60, 45, 30 and 15 TOAs, respectively. The center of the resulting images coincided with the center of the grid, and the grid was fully observable in the FOV.

Small area, high resolution C 1s and survey spectra were acquired from high and low intensity areas in the Cl 2p images. Small area spectra were acquired using 55 μm diameter spot size and acquisition times of 4 min for 90°, 6 min for 60°, 8 min for 45°, 10 min for 30° and 15 min for 15° TOAs. Survey spectra were acquired using an 80 eV pass energy, and C 1s spectra were acquired using 20 eV pass energy.

2.3. Software

Image processing and visualization was performed using Matlab [15]. All image data files were transferred from the Kratos format to a format supported by Matlab, which is an ASCII vamas format.

The Matlab image processing (IP) toolbox was used for spatial transformation of the images. The routine for image registration was written in-house using normalized cross-correlation from the IP toolbox and a mutual information function written by Dennis Lucero [16]. The image morphing routine was written by Dean Krusienski [17]. Graphical user interface (GUI) volumization for visualizing images was written in-house in Matlab.

3. Results and discussion

Blends of polyvinylchloride (PVC) and polymethylmethacrylate (PMMA) form heterogeneous samples with phases of widely varying size that are enriched in PMMA or PVC. A variety of different methods have been applied to the characterization of these blends, initially leading to inconsistencies and conflicting conclusions regarding surface structure [18–22]. The surface heterogeneity of the top side of the PVC/PMMA film, prepared by conventional solvent casting, can be confirmed using photoelectron imaging. Fig. 1 shows Cl 2p, O 1s and C 1s images from 350 μm × 350 μm area. The Cl 2p images, in which bright areas are enriched in PVC, contain the highest contrast levels among the elemental images and contain large features. The O 1s images, in which the bright areas are enriched in PMMA, have lower contrast but still show a good anti-correlation with the Cl 2p images, indicating phase-separation at the surface of the air side of the blend. The C 1s images, to which both polymers contribute approximately equally, are the most featureless and