

Wettability, interface structure, and chemistry in functionalized poly(chloro-*para*-xylylene) films



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ABSTRACT

Genetically hydrophobic polymer interfaces are functionalized by oxygen plasma and systematically analyzed using contact angle measurements, atomic force microscopy, and high resolution X-ray photoelectron spectroscopy. High resolution C 1s core level spectra indicate that approximately three of five hydrogen-abstracted carbon sites at the surface become terminated in equal weight by aldehyde and carboxylic acid. Without altering the global structure of the interface, the plasma treatments at $E_{RF} > 100$ J generate a network of small protuberances which grows with E_{RF} , and a wavelength selection with a characteristic length scale increasing with E_{RF} . While the polymer surface is continuously eroded in the rate of ~ 4 nm/100 J, a delicate balance between the growth of the network of the local structure and the progression of the wavelength selection allows the polymer interface to maintain a relatively high level of the low molecular weight materials, which is responsible for the enhanced surface concentration of carbonyl group during the abrasive functionalization process above $E_{RF} \sim 100$ J. The sharp increase in the wettability of the polymer interface upon the plasma treatment is closely related to the surface concentration of the total polar functional group containing oxygen rather than that of a specific functional group.

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1. Introduction

Poly(chloro-*para*-xylylene), commercially known as parylene-C, is a family of chemical vapor-deposited polymer that was developed several decades ago [1]. Parylene has favorable thin film-forming characteristics and excellent electrical properties that have attracted considerable attention in the fabrication of field effect transistors as polymer gate dielectrics and a flexible gas barrier [2–5]. Parylene was recently adapted for biomedical applications [6–9] by taking advantage of its biocompatibility, high chemical resistance, ability to produce a pin-hole-free conformal coating, and resistance to swelling in aqueous environments. However, vapor-deposited parylene films genetically form oxygen-free hydrophobic (or poor wettable) interface and thus poor adhesion with other surfaces has been a major hurdle in achieving reliable and durable performance of electronic and biomedical devices. Surface engineering through incorporation of functional group for improved biocompatibility, adhesion, and metallization is

of fundamental and technological interest. There have been extensive studies regarding the effect of functionalization of polymer interfaces by ultra violet (UV) activations [10–13], active plasma treatments [9,14], activated water vapor [15], acid treatments [16], and ion bombardment [17]. The changes in the wetting properties of the polymer interface have been probed with various combinations of contact angle, AFM and XPS measurements [9,15–17]. However, in many cases, a complete picture based on clear understanding of the cross correlations among wettability, interface structure, and surface chemistry has not been achieved. Equilibrium wetting on a solid surface is conventionally quantified by the contact angle at which a liquid vapor interface meets the solid-liquid interface. Under a liquid drop, the polymer interface primarily interacts with the liquid through dispersion forces so that the contact angle as a measure of the interface wettability is determined by the outermost chemical structure of the polymer surface. In addition, the interface roughness significantly affects the contact angles such that, in the homogeneous wetting regime, the roughness increases (decreases) the measured contact angle for a hydrophobic (hydrophilic) interface [18,19]. Therefore, the contact angle for a measure of wettability, atomic force microscopy (AFM) for a measure of structural properties, and X-ray photoelectron spectroscopy (XPS) for quantification of the chemical compositions of the interface are complementary and essential for the

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fundamental understanding of the effect of surface functionalization, especially when an abrasive treatment, such as active plasma, may cause significant changes in the structural properties of the interface. Moreover, quantitative chemical analysis based on the XPS core level spectra, which provide important insight regarding the functionalization mechanism, has not been achieved for the parylene system. X-ray induced sample damage and/or insufficient quality of the native sample often complicate the analysis of the XPS spectra obtained from polymeric films. Halogen-containing polymers, such as parylene-C, degrade fairly quickly [20,21]. Most of the previous XPS results on parylene films appear to suffer significant degradation by X-ray photons and contamination on the native film, which are commonly manifested in a core level scan by broadening of the spectrum linewidth, erratic lineshape that does not match the expected chemical compositions, and the presence of oxygen contamination even in native films.

In this study, parylene-C (chloro-*para*-xylylene) films were deposited on a SiO₂ layer naturally grown on Si substrates using a chemical vapor deposition method, and the surface was functionalized with oxygen (O₂) plasma under various treatment conditions. After correction of several issues regarding the X-ray induced degradation, high-resolution XPS spectra were obtained, reflecting the intrinsic chemical properties of the polymer interface. The wettability, changes in the interface structure and progressions of the oxygen-related functional group induced by the plasma treatments were quantified to provide a better understanding of the surface functionalization mechanism and for use as a practical guideline to determine the optimal condition for plasma modification of a polymer interface depending on the application.

2. Experimental method

Parylene-C films were deposited in a custom-built chemical vapor deposition reactor consisting of a sublimation furnace, a pyrolysis furnace, and a deposition chamber backed by a diffusion pump. Dimer molecules (di-chloro-di-*p*-xylylene) obtained from Daisan Kasei Co. (Japan) were sublimed in a quartz tube at 120 °C and then cracked into monomers in a pyrolysis furnace at 660 °C. The monomers were subsequently condensed and polymerized on precut SiO₂/Si substrates of 1 cm × 1 cm size in the deposition chamber, at room temperature. During deposition, the pressure was typically in the range of 1 mTorr, resulting in a growth rate of 20 nm/min. Several batches of polymer films, with approximately 40 samples of 1700 nm thick films in one batch, were grown with an identical condition and used to examine various effects of the surface modifications. Plasma treatments were performed on several samples at a time in an inductively coupled RF reactor. Once the reactor chamber reached the base pressure of 10 mTorr, the chamber was flooded with oxygen. The chamber pressure was regulated at 150 mTorr with a flow of oxygen before a power of 6.8 W was applied to the RF plasma coil in order to initiate surface modification for various durations. Changes in the film thickness before and after plasma treatment were accurately determined with spectroscopic ellipsometry. The static sessile drop method was employed to measure the contact angle that was formed by a drop of 7 μL deionized water on the polymer surface at room temperature. The effect of plasma treatment on the surface morphology was characterized by AFM (XE100, Park system) using a non-contact mode. Topographic AFM images were taken from several different locations on each parylene-C film with various scan sizes ranging from 2 μm × 2 μm to 5 μm × 5 μm. High resolution XPS analysis was performed on the AXIS-Nova (Kratos). The monochromated Al K_α X-ray source was operated at a reduced power of 30 W for core level spectra. Scan steps of 0.05 eV with a dwell time of 0.15 s and a pass energy of 20 eV were employed. The sampling depth given by the

measurement setup was approximately 9 nm, which was sufficient to cover the average height fluctuations of 6 nm. To avoid radiation damage by X-ray photons during acquisition of the XPS spectrum, the number of scans at a single position, a cross-section of approximately 10 μm in diameter, was limited to four. For each of the C 1s, Cl 2p, and O 1s core level spectra, data obtained from three or four different spots depending on the signal to noise ratio were averaged. No noticeable change in the lineshape due to degradation was observed during any of the four scans at each position.

3. Results and discussion

The effects of the O₂ plasma treatments on the contact angles of various energies applied to a RF plasma coil (E_{RF}) are displayed in Fig. 1, which is constructed with data obtained from five separate runs on a new set of polymer films within three hours of the plasma treatment. The hydrophobic nature ($\theta = 87 \pm 0.7^\circ$) of the native surface drastically changed to hydrophilic ($\theta = 31 \pm 1.2^\circ$) when treated with O₂ plasma at E_{RF} as low as 10 J, and the contact angle became nearly independent of further treatments. The actual contact angle measured has been known to vary with the treatment conditions employed and the time lapsed in air after the treatment [22,23]. Nevertheless, the contact angle data are reproducible within a few degrees ($\sim \pm 2^\circ$) at each E_{RF} value. In general, the large increase in the interface wettability was associated with changes in the structural and/or chemical properties of the polymer interface. Fig. 2 shows representative AFM images from the same film (a) before and after plasma treatments with (b) $E_{RF} = 136$ J, and (c) $E_{RF} = 680$ J. The overall structure seemed to remain nearly the same, but small swollen spots appeared all over the interfaces treated with $E_{RF} > 100$ J. Detailed structural analysis of the interface is exhibited in Figs. 3 and 4. The insets in Fig. 3 shows that the topological characteristics of the native polymer films grown in a batch are fairly uniform. Changes in the roughness (i.e., $\sigma_{rms}(\text{after}) - \sigma_{rms}(\text{before})$) due to plasma treatments are shown in the upper panel.

The roughness is defined by $\sigma_{rms} = \sqrt{\langle [h(\vec{x}) - \langle h \rangle]^2 \rangle}$ where $h(\vec{x})$ is the interface height at position \vec{x} and $\langle \dots \rangle$ denotes a statistical average over the scan area. The lower panel displays the plasma-induced changes in the correlation length that is determined from a two-dimensional correlation function, $C(r) = \langle [h(\vec{x} + \vec{r})h(\vec{x})] \rangle$, using a relation $C(\xi) = C(0)/e$. The two global scaling parameters, roughness ($\sigma_{rms} = 6.1 \pm 0.1$ nm) and correlation length ($\xi = 131.6 \pm 1.6$ nm), are essentially the vertical and the lateral size of an average interface structure, respectively. The data indicate

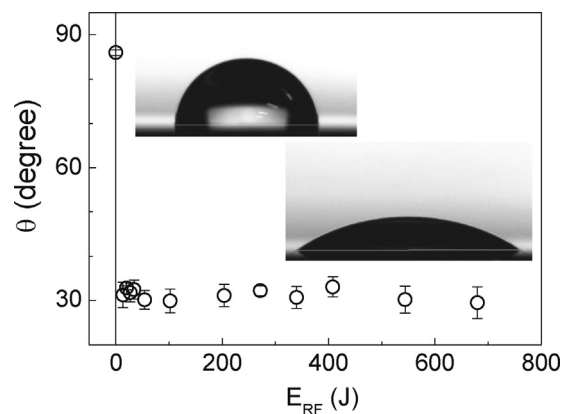


Fig. 1. Contact angle vs. energy applied to the RF plasma coil (E_{RF}). The inset displays a representative image of a water droplet on the parylene-C interface, native and functionalized with $E_{RF} = 680$ J.

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