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SURFACE ANALYSIS AND MODIFICATION OF FLUOROCARBON-END CAPPED POLYESTER ULTRATHIN FILMS

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We report the characterization and modification of materials based on biodegradable polyesters and fluorocarbon chemistry. Ultrathin films with thickness less than the maximum ESCA detecting depth were prepared by spin-coating method to avoid any effects of preferential surface orientation. Quantitative angle-dependent ESCA was used to investigate number-average molecular weight (Mn) of end-functionalized polymers, fluorocarbon end-capped poly(lactide)s (F-PLA). The exposure time of F-PLA ultrathin films to Methanol/H_2 plasma controlled densities of hydroxyl groups on the surface, and then these groups provide sites for the covalent attachment of a specific component such as proteins or peptides.

Keywords: fluorocarbon; molecular weight; plasma; ultrathin film

INTRODUCTION

The surface-layer properties of polymers have recently received great attention in practical applications, such as biomaterials, adhesives, paints and coatings, and so on, since these are strongly related to the associated functional properties. A desired polymer surface sometimes often cannot

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be obtained from the material itself but through chemical or physical modification. It has been well known that the component of a lower surface free energy in multicomponent polymeric systems are preferentially concentrated at the air surface region in order to minimize the air/material interfacial free energy [1–6]. Although blending is an attractive method to change surface properties because of the common use of commercially available polymers, one limitation to blending is the need to have polymer miscibility in many cases. Much emphasis has been placed on controlling the surface structure of copolymers. Modification for low energy surfaces, which provides a opportunity to control properties, adhesion, wetting, dewetting, and mobility, can be achieved by copolymerizing only a small amount of a block component having low surface energy, such as silicon or fluorine-containing polymers [2–4]. Although the property and structure of fluorinated polymers with incorporation of fluorocarbons into the polymer backbone and on the side chain have been extensively investigated, there have been few reports of modification by end group functionalization of short fluorocarbons [4].

In the present study, we report characteristics the poly(lactide) (PLA) ultrathin films with fluorocarbon end groups (F-PLA) because ultrathin films with thickness less than the maximum electron spectroscopy for chemical analysis (ESCA) detecting depth were prepared by spin-coating method to avoid any effects of preferential surface orientation. The number of molecular weight of F-PLA ultrathin films was measured by angle-dependent ESCA and it is compared to that measured by nuclear magnetic resonance spectroscopy. The surface functionalization of FPLA ultrathin films was performed by radio frequency glow discharge (RFGD). This surface modification can produce controlled densities of hydroxyl groups on the material surface and then these groups provide sites for the covalent attachment of a specific component such as protein or peptide. Thus, cell adhesion can be controlled by adapting plasma modifications to these new fluorocarbon surfaces.

EXPERIMENTAL

Materials

l- and *dl*-lactide (LA) were obtained from Aldrich and were recrystallized from anhydrous ethyl acetate. 2-(perfluorodecyl) ethanol (F10C2-OH, Daikin) was dried in a vacuum oven before use. All other chemicals were of reagent grade and were used without further purification. Single fluorocarbon-terminated polyesters were directly synthesized by the ring open polymerization of lactones using with a small amount of hydroxyl terminated fluorocarbon.

Plasma Treatments

The RFGD apparatus used for surface modification has been described previously [7] and uses an in-line vacuum leak valve in concert with a vapor chamber and flow meter for gas mixing. The RFGD chamber containing films was pumped down to 100 mtorr and then purged with methanol/H_2 (vapor) for 10 min at 500 mtorr. The pressure in the chamber was then reduced to 100 mtorr and the RFGD plasma was activated. To achieve thermodymanically stable states, all measurements were carried out after 1 month of plasma treatment.

Surface Characterization

The chemical compositions of the 2D films were obtained using a Perkin-Elmer Physical Electronic Model 5300 ESCA. ESCA measurements were performed with MgKa All C1s spectra were referenced to the neutral carbon of PLA at 285 eV, in order to correct charging effects. In the curve fitting, a Shirley type nonlinear background substraction was used [8] and the C1s peaks were fitted using a least-squares routine assuming a Gaussian/Lorentzian (90/10) sum function. The ultrathin and thick (ca. 5 μm) films were prepared by a spin coating (Photo Resist Spinner, Headway Research Inc.) and solvent-casting methods, respectively, using chloroform as a solvent on a clean silicon wafer.

RESULTS AND DISCUSSION

Since the design of the materials is based on principles of surface segregation of a component with the lower surface energy, the polymers with fluorocarbon end groups can dramatically alter surface properties due to the surface segregation of lower surface energy fluorocarbons [2,4]. To determine the surface composition of fluorocarbon end groups of F-polyester on the surface composition, angle-dependent ESCA was used. Figure 1 shows the high-resolution ESCA spectra of C1s regions of F10C2-*l*-PLA14 thick film at various photoelectron takeoff angles. The C1s region measured at takeoff angle of 90° showed contributions from C−O functional groups at 287.1 eV and O=C−O at 289.1 eV from the PLA, and $C-F_2$ at 291.5 eV and $C-F_3$ at 293 eV from the fluorocarbon. From the intensity of the $C-F_2$ fraction (from fluorocarbon) compared to that from O=C−O or C−O (from polyester), the intensity of this peak increases with increasing photoelectron takeoff angle. This suggests that the concentration of fluorocarbon end group is much higher at the topmost surface than at the deeper regions.

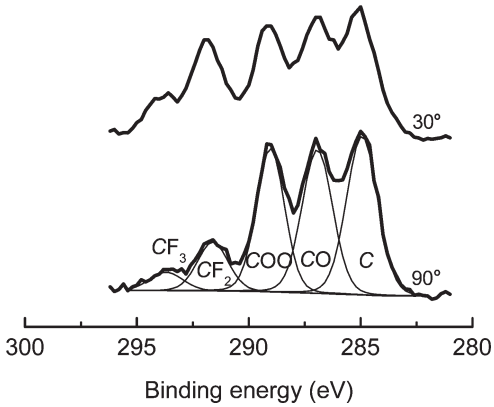

FIGURE 1 C1s spectra of F10C2-*l*-PLA11 thick film taken at different takeoff angles.

Ultrathin films with thickness (less than the maximum ESCA detecting depth) are very useful tool to avoid any effects of preferential surface orientation [9]. The F10C2-*l*-PLA14 ultrathin film on a clean silicon wafer was prepared by a spin coating using chloroform as a solvent. ESCA survey spectra of F10C2-*l*-PLA ultrathin film on silicon wafer taken at 90° takeoff angle showed two new small peaks in lower binding energy region.(not shown here) These peaks correspond to Si2p and Si2s of the silicon wafer as a substrate. From the ESCA sampling depth as a function of the takeoff angle, the thickness of the film (2D film) is below 11.2 nm, corresponding to sampling depth of Si2p at 90° takeoff angles [3]. Therefore, the spectrum taken at the 90° takeoff angle reflects the contribution of both whole sample and some of the substrate. High resolution C1s spectra of F10C2-*l*-PLA ultrathin film measured at takeoff angle of 90° are shown in Figure 2. In order to calculate Mn, the CF_2/CO ratio was used to avoid the contribution of silicon substrate in the C1s region. Then, the Mn ($= 563 + 72.1^* n$) of F10C2-PLA was calculated by the following equation,

$$I_{\underline{C}F2}/I_{\underline{C}-O} = 9/(1+n)$$

where Ii is the integrated intensity of a core-electron photoemission spectrum and n is the ratio of lactide unit to fluorocarbon unit. 563 and 72.1 are the molecular weights for F10C2-O- and lactide monomer unit, respectively. Table 1 summarizes the average number molecular weights of F-PLA measured by different instruments, NMR, ESCA, and SEC. The Mn determined by ESCA measurement is equivalent to that from NMR. However, the Mn measured by SEC, using a direct PS calibration method, is much higher than those of NMR and ESCA.

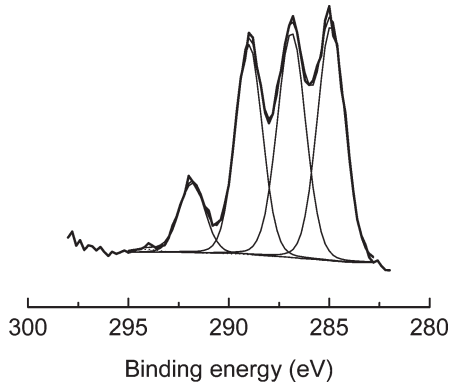

FIGURE 2 C1s spectra of F10C2-*l*-PLA11 ultrathin film taken at takeoff angle of 90°.

Plasma discharge processes provide a unique and powerful technique for altering the surface properties of materials without changing their bulk properties. Figure 3 shows atomic ration profiles of F10C2-*l*-PLA thick films as a function of plasma exposure time. The F1s/O1s ratio progressively decreased as the treatment time is increased and the relative variation in F1s/O1s ratio is much small as a photoelectron takeoff angle is increased. This result might indicate that fluorocarbon groups at the topmost are changed to an oxygen-containing bond by the plasma treatment. In order to confirm newly formed functional groups by the plasma treatment, FT-IR spectra of F10C2-*l*-PLA ultrathin films before and after exposure to methanol/H_2 plasma were recorded, as shown in Figure 4. After the plasma treatment, new and strong peaks were observed at 3750, 1750, and 1200 cm^{-1}, corresponding to hydroxyl, ester, ether, respectively. These peaks may be result from surface hydroxyl groups or

TABLE 1 Mn of Fluorocarbon End-capped Polyesters Measured by Different Instruments

	Mn		
Sample code	ESCA	^{1}H-NMR	SEC[a]
F10C2-*l*-PLA4	3,710 ± 300	3,810	5,100
F10C2-*l*-PLA11	10,520 ± 1,500	11,730	11,500

[a] Calculated from universal calibration using the following a and K values: PS, $a = 0.794$ and $K = 0.49 \times 10^{-4}$ (dl/g); *l*-PLA, $a = 0.73$ and $K = 5.45 \times 10^{-4}$ (dl/g); *dl*-PLA, $a = 0.77$ and $K = 2.21 \times 10^{-4}$ (dl/g).

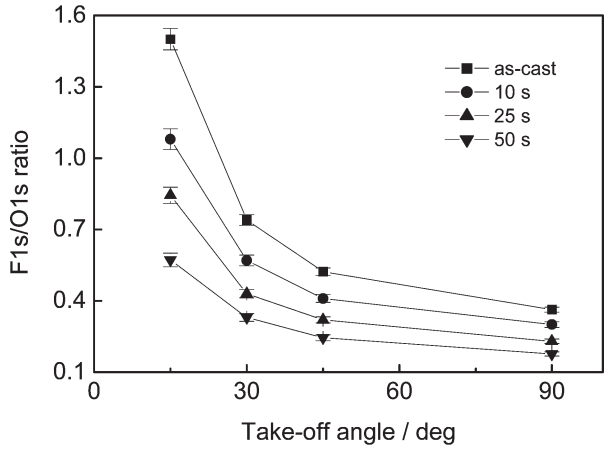

FIGURE 3 Atomic ratio of F1s/O1s *vs*. sampling depths profiles of F10C2-*l*-PLA11 thick films as a function of treatment time of methanol/H_2 plasma.

from the carboxylic acid functionality. The exposure of F-PLA ultrathin films to Methanol/H_2 plasma produced controlled densities of functional groups on the surface, and then these groups provide sites for the covalent attachment of a specific component such as proteins or peptides. Therefore, cell adhesion may be controlled by adapting plasma and chemical modifications from a previous work [7].

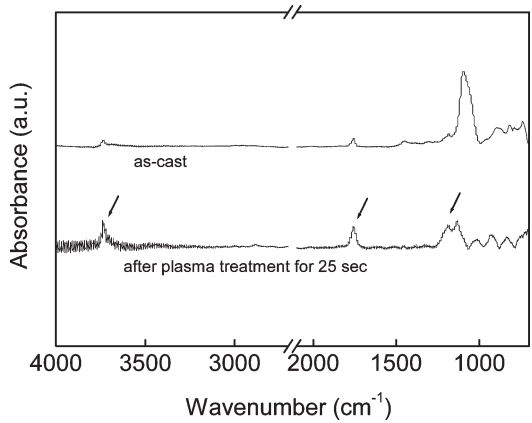

FIGURE 4 FTIR spectra of F10C2-*l*-PLA11 ultrathin film before and after methanol/H_2 plasma treatment for 25 sec.

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