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In vitro platelet adhesion and activation of polyethylene terephthalate modified by acetylene plasma immersion ion implantation and deposition

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Abstract

Acetylene (C_2H_2) plasma immersion ion implantation–deposition (PIII–D) was conducted on polyethylene terephthalate (PET) to improve its blood compatibility. The platelet adhesion and activation behavior of PET treated by C_2H_2 PIII–D at different working pressures was investigated. Raman spectroscopy results show that amorphous carbon films were successfully deposited on the PET surfaces. X-ray photoelectron spectroscopy (XPS) analysis indicates that carbon films of various sp^2/sp^3 composition are formed at different working pressures and the sp^3 hybridized C content in the films increases as a function of pressure. Platelet adhesion experiments were conducted to examine the blood compatibility in vitro. Optical microscopy reveals that the amounts of adherent platelets on all modified PET films are less than that on the untreated surface. The adhered platelets on carbon films deposited at 0.5 Pa and 1.0 Pa working pressure are about 32% and 55%, respectively, of that for the untreated PET surface. The platelets are observed to be isolated and round on carbon films deposited at 0.5 Pa, indicating that fewer platelets are activated on the amorphous carbon films. These results thus shows that amorphous carbon films deposited on PET by C_2H_2 PIII–D suppress platelet adhesion and activation, and the extent of the improvement is related to the structure of the carbon films.

Keywords: Plasma immersion ion implantation/deposition (PIII–D); Platelet adhesion; Amorphous carbon film; Polyethylene terephthalate (PET)

1. Introduction

Surface modification techniques such as low temperature plasma treatment [1,2] and ion implantation [3,4] have been attempted to improve the blood compatibility of polymers. The PIII–D technique is an effective approach for the surface modification of materials, incorporating both ion implantation and low temperature plasma processing. PIII–D has been applied to polymers to improve mechanical properties [5] and as a gas barrier [6,7]. However, relatively little work has been reported on the surface modification of polymers by PIII–D to enhance properties of blood compatibility.

In the work described here, amorphous hydrogenated carbon (a-C:H) films were fabricated on PET using C_2H_2 PIII–D at different working pressures and the characteristics of the carbon films were investigated. The blood compatibility in vitro was evaluated by platelet-rich plasma (PRP) contact experiments.

2. Experimental

A 10 μm thick PET film was laid on a stainless steel substrate attached to an insulated stainless steel electrode in

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Table 1
Instrumental parameters for the synthesis of a-C:H films

Sample	Working pressure (Pa)	Bias voltage (kV)	Pulse frequency (Hz)	Pulse width (μs)	RF power (W)	Time (min)	Thickness (nm)
PET–C1#	0.5	−5	100	20	300	40	102
PET–C2#	1.0	−5	100	20	300	40	195
PET–C3#	2.0	−5	100	20	300	40	245

the center of the vacuum chamber. C_2H_2 was bled into the chamber and the plasma was sustained by radio frequency (RF). A high negative pulsed voltage was repetitively applied to the sample holder. The detailed deposition parameters are listed in Table 1. Chemical composition and structural information were determined using Raman spectroscopy and XPS. The samples were immersed in human fresh PRP and incubated at 37 °C for 120 min. After rinsing, fixing and critical point drying, the specimens were examined using optical microscopy and scanning electron microscopy (SEM).

3. Results and discussion

The Raman spectra (Fig. 1) of the deposited films are consistent with the spectra of diamond-like carbon films [8]. They can be fitted by two Gaussians peaked at about 1530 and 1350 cm^{-1}, corresponding to the G and D bands of graphite. With decreasing working pressure, the G-peak position at 1530 cm^{-1} shifts slightly toward low frequency and the D-peak at 1350 cm^{-1} becomes more dominant. The positions of the G and D bands can be correlated with the sp^2/sp^3 bonding ratio. An increase of the I_D/I_G ratio, a widening of the D-peak and a narrowing of the G-peak are caused by increase of the graphite-like component in the amorphous carbon films [9]. The Raman results indicate that the a-C:H films structure becomes more graphitic with decreasing working pressure.

Fig. 2 shows the C_{1s} XPS spectra with the curve fittings. Three peaks at 284.5, 285.2 and 286.4 eV are used here, employing Lorentzian–Gaussian functions. The peaks

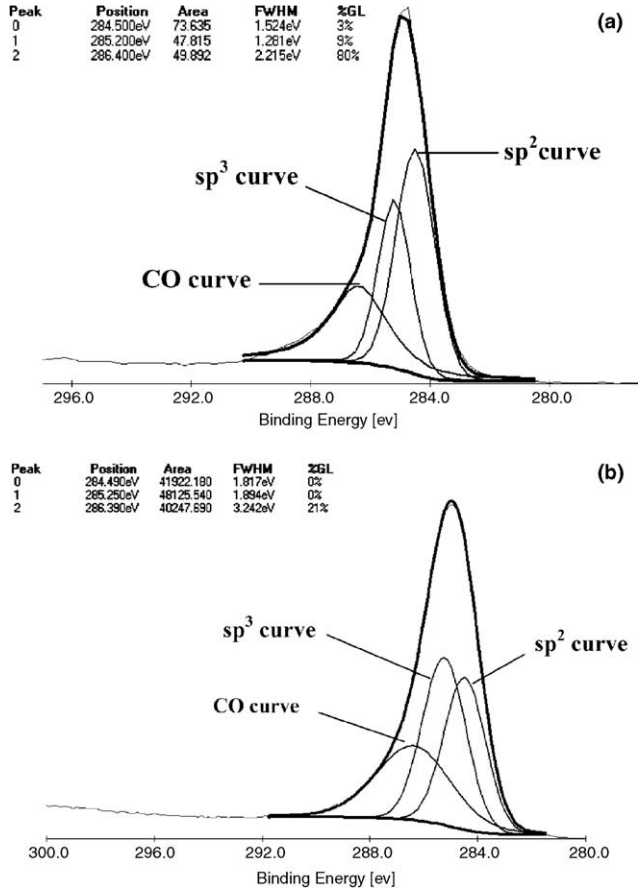

Fig. 2. Comparison of C_{1s} XPS spectra of a-C:H films fabricated at working pressures of (a) 0.5 Pa and (b) 2.1 Pa.

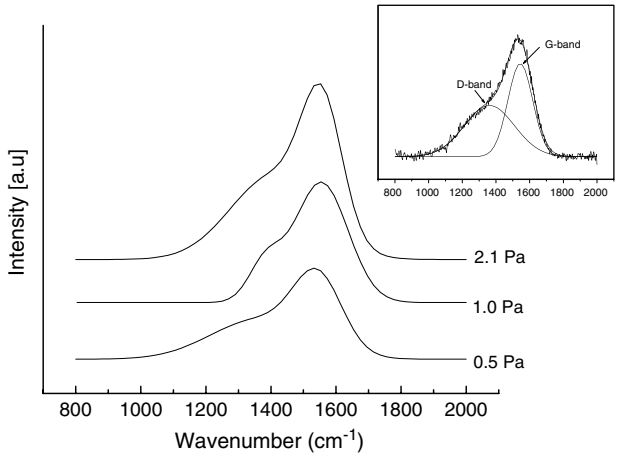

Fig. 1. Raman spectra of a-C:H films fabricated at different working pressures.

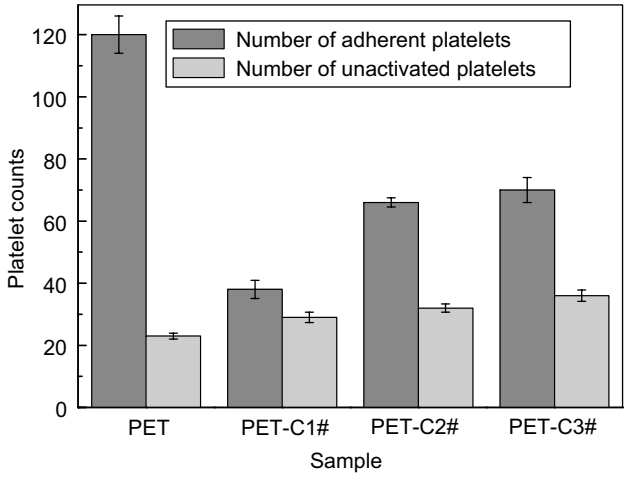

Fig. 3. Number of platelets adhered on the surface of the PET and modified-PET films.

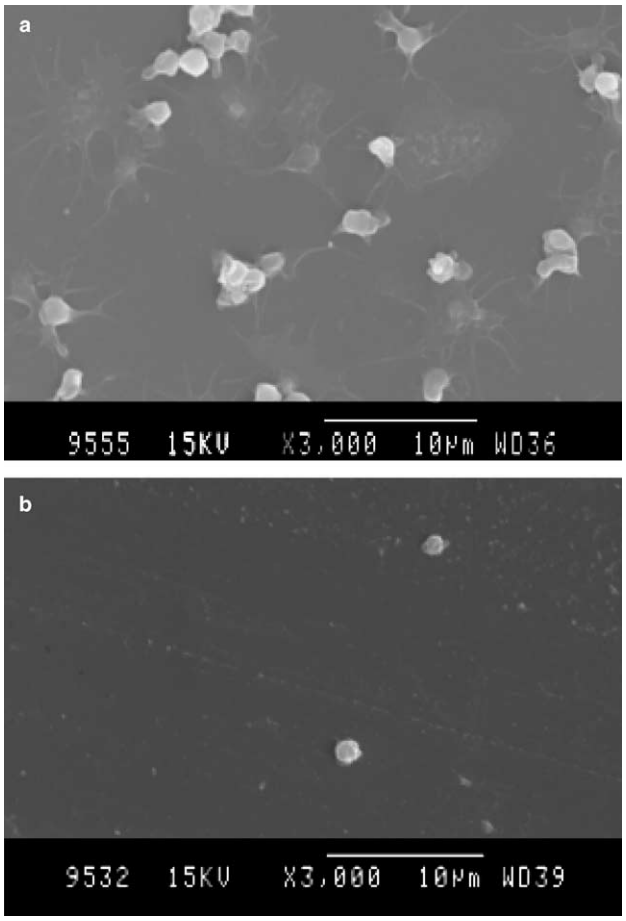

Fig. 4. Morphology of adherent platelets on (a) PET and (b) PET–C1#.

include contributions from sp^2 carbon (C=C), sp^3 carbon (C–C) and C–O. The sp^3 hybridized C content in the films increases as a function of working pressure. The sp^3 content has a value of approximately 39.4% at a working pressure of 0.5 Pa and rises to a maximum (52.1%) at 2.1 Pa. Thus, the amorphous carbon films deposited at 0.5 Pa is more graphitic.

Platelet adhesion and activation are indicators of antithrombogenicity of surface-modified PET films. Fig. 3 displays the statistic numbers of adherent platelets on the surface of the PET control and PET–C series after 120 min incubation. The number of adherent platelets on all PET–C series is lower than for the untreated surface. The adhered platelets on the carbon film deposited at 0.5 Pa and 1.0 Pa working pressure are about 32% and 55%, respectively, of that for the untreated PET surface. This suggests that adhesion of platelets is suppressed by the amorphous carbon films deposited on PET.

As shown in Fig. 4, platelets are observed to be isolated and round on carbon films deposited at 0.5 Pa, indicating that less platelets are activated on amorphous carbon films. In comparison, most of the adherent platelets on the PET control are in aggregation and spreading pseudopodium. These results thus show that amorphous carbon films deposited on PET by C_2H_2 PIII–D suppress platelet adhesion and activation, and the extent of the improvement is related to the structure of carbon films.

4. Conclusion

Hydrogenated amorphous carbon films were fabricated on PET by acetylene plasma immersion ion implantation–deposition at different working pressures. Raman and XPS results reveal that film graphitization is promoted at lower working pressure. In conclusion, amorphous carbon films deposited on PET by PIII–D suppress platelet adhesion and activation. The extent of the improvement is related to the carbon film structure.

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