

Adsorptive properties of albumin, fibrinogen, and γ -globulin on fluorinated diamond-like carbon films coated on PTFE

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Abstract Fluorinated diamond-like carbon (F-DLC) films were deposited on polytetrafluoroethylene (PTFE) using radio frequency (RF) plasma-enhanced chemical vapor deposition (CVD) by changing the ratio of tetrafluoromethane (CF_4) and methane (CH_4). To enhance the adhesion strength of the F-DLC film to the PTFE substrate, the PTFE surface was modified with a N_2 plasma pre-treatment. XPS analysis of the films showed that the C–C bond decreased with increases in the CF_4 ratio, whereas the C–F bond increased with the CF_4 ratio. The F/C ratio of the film also increased with the CF_4 ratio. The pull-out test showed that the adhesion strengths of the films (CF_4 -0–60%) were improved with the plasma pre-treatment. In the film without the plasma pre-treatment, adhesion strength increased with the CF_4 ratio. In contrast, in the case with the plasma pre-treatment, the adhesion strength of the F-DLC film decreased with the increased CF_4 ratio. Regarding the adsorption of albumin, fibrinogen, and γ -globulin, the amount of adsorbed albumin on the film decreased with an increasing CF_4 ratio, and the amount of adsorbed fibrinogen and γ -globulin increased with the CF_4 ratio. The CF_4 -0% DLC film showed the most adsorbed albumin and the least adsorbed fibrinogen and γ -globulin. This indicates

that the CF_4 -0% DLC film has higher anti-thrombogenicity than the F-DLC film.

1 Introduction

Polymeric materials have been used in a variety of industrial fields because of their lightness and flexibility. In particular, polytetrafluoroethylene (PTFE) has been used in biomedical applications such as artificial blood vessels due to its excellent chemical inertness and mechanical properties [1, 2]. Research has shown an improved patency rate with the placement of PTFE-covered stent-grafts [3]. However, thrombosis still occurs on the PTFE surface in clinical trials [4, 5].

Diamond-like carbon (DLC), also known as amorphous hydrogenated carbon (a-C:H), is a class of materials with excellent mechanical, tribological, and biological properties [6–8]. Recently, the DLC films have received considerable attention because of their antithrombogenicity, a property that inhibits platelet adhesion and activation [9]. However, the blood coagulation mechanisms on DLC films in biological environments are not yet well understood. Several studies report that cell adhesion on DLC films is related to surface energy and wettability. In addition, it is reported that antithrombogenicity is improved by fluorine incorporation into the DLC on polycarbonate and silicone [10, 11].

A large number of techniques have been reported for DLC film depositions, with the choice of each technique dependent on the desired DLC film properties. In particular, the radio frequency (r.f.) plasma chemical vapor deposition (CVD) technique is useful for DLC film deposited on polymer substrates because it allows for deposition at low temperatures [12]. However, problems

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with low adhesion strength often occur when the DLC is coated directly onto the polymeric material [13]. Studies show that plasma pre-treatment on the PTFE surface is effective in improving the adhesion strength between the DLC and PTFE [14, 15].

In this study, fluorinated DLC (F-DLC) films were deposited onto the PTFE substrates using a RF plasma CVD method. The plasma pre-treatment was applied to the PTFE surface to improve the adhesion strength of the F-DLC film. The F-DLC films were analyzed by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The surface of the film was observed using a scanning electron microscope (SEM), and the static water contact angle was also determined.

The adhesion strength of the film to the PTFE substrate was measured using a pull-out test. The protein (albumin, fibrinogen, and γ -globulin) adsorption test was also carried out as an indicator of antithrombogenicity.

2 Materials and method

2.1 Sample preparation and analysis

PTFE (10 mm \times 10 mm \times 3 mm; Nafronsheets TOMBO-9000, Nichias Corp.) was used as the substrate. The N₂ plasma pre-treatment on the PTFE substrate and DLC deposition were performed using a PED-301 RF (13.56 MHz) CVD system (Cannon Anelva Corp.), and the N₂ plasma pre-treatment was performed on the PTFE substrate before DLC coating. Nitrogen gas (99.99%) was introduced into the chamber, and the PTFE substrates were modified in N₂ plasma for 5 min at a pressure of 13.3 Pa and a discharge power of 250 W (power density: 7.4 mW/mm²). After pre-treatment, a mixture of CH₄ (99.99%) and CF₄ (99.99%) gases was introduced into the chamber. The coating was carried out at 13.3 Pa and 250 W (power density: 7.4 mW/mm²). The partial flow of CF₄ was varied between 0% and 80%. The coating was applied to fabricate film samples 0.1- μ m thick over time periods from 5.55 min to 5.88 min, according to the chosen coating conditions. The temperature of the substrate remained below 100°C during the deposition process.

The coated films were characterized using an argon laser Raman spectrometer (NRS-2100; Jasco). Raman spectroscopy was performed using the 514.5 nm line from the Ar laser, and the laser power was kept constant at 1 mW at the sample surface. Spectra were recorded from 1100 to 1800 cm⁻¹. The chemical composition of the film surface was observed by XPS (JPS-9010; JEOL). The measurements were carried out using non-monochromatic Mg K α radiation ($h\nu = 1253.6$ eV) at 10 kV and 10 mA. The surface observations of the coated films were carried out

using a scanning electron micrograph (JSM-5600LV; JEOL) under an accelerating voltage of 15 kV.

2.2 Measurement of water contact angle

The wettability of the F-DLC film surface was quantified by measurement of the static water contact angle, which is used to characterize the surface energy of solids [16]. Contact angles were measured from the profile of liquid drops of distilled water (2 μ l) placed on the film surface at room temperature. The reported values of the water contact angle are an average from five samples.

2.3 Pullout test to determine the adhesion of F-DLC films to the PTFE substrates

Aluminum rods (D = 6 mm) were glued onto films coated on a PTFE substrate using an epoxy resin adhesive (SW2214; Sumitomo 3 M). The samples and rods were set in a jig, and the rods were pulled out at a crosshead speed of 1.0 mm/min using a Universal Testing Machine (RTM-1T; A&D Engineering, Inc.) until detachment of the film from the substrate occurred.

2.4 Protein adsorption test of F-DLC films coated on PTFE substrates

The protein adsorption test can be an indicator of the antithrombogenicity of the films. The F-DLC films (CF₄: 0%, 40%, 80%) coated on the PTFE sheet (5 \times 50 \times 0.5 mm³) with plasma pre-treatment were immersed into the protein solution (bovine serum albumin (Wako Pure Chemical Industries), bovine serum fibrinogen (MP Biomedicals, Inc.), or bovine plasma γ -globulin (MP Biomedicals, Inc.)) at a concentration of 1 mg/ml at 37°C. Blanks containing only albumin, fibrinogen, or γ -globulin were also prepared as a control. After a 60 min immersion, 500 μ l of the supernatants were sampled from the blank and the immersion solutions, and the concentrations of albumin, fibrinogen, and γ -globulin were measured with a Micro BCATM protein assay kit (Takara Bio Inc.) according to the manufacturer's protocol using BSA as a standard. Each final result was obtained from an average of three samples.

3 Results and discussion

3.1 Raman spectra of F-DLC films deposited on PTFE substrate

Figure 1 shows the Raman spectra of the films coated on the PTFE substrate. All films exhibited two broad peaks,

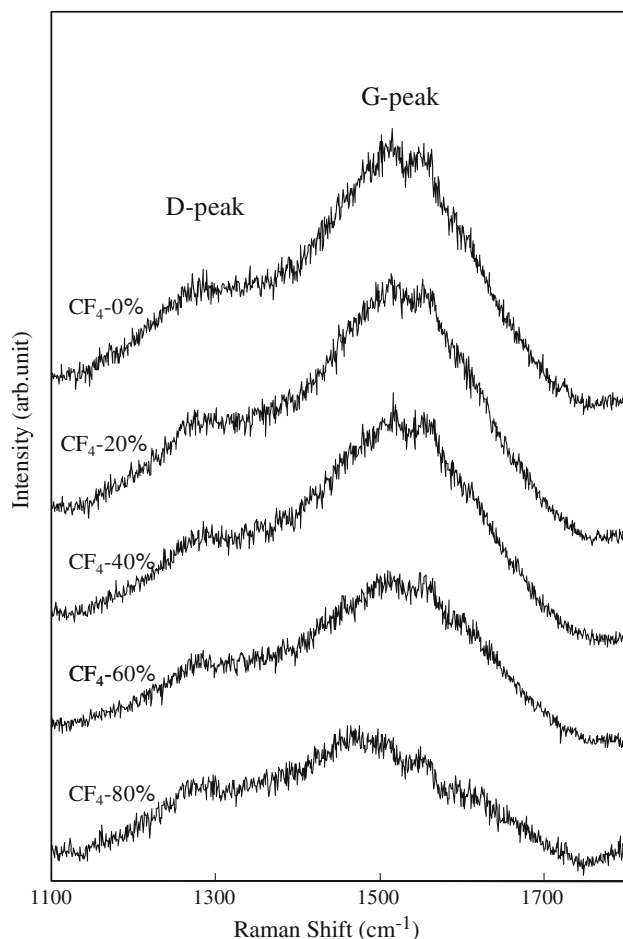


Fig. 1 Raman spectra of films deposited on PTFE substrate with various CF_4 ratios. All films exhibit two broad peaks, which are G and D bands

which are the G and D bands. The G band corresponds to the sp_2 orbital in graphite-like materials, whereas the D band results from the disorder and size of the crystal [17]. Characteristic G and D band peaks were observed at all CF_4 ratios. These results indicate that the DLC was successfully coated onto the PTFE despite fluorine doping.

3.2 XPS spectra of F-DLC films deposited on PTFE substrate

Figure 2 shows C1s and F1s spectra of the films. In the F1s spectra, C–F bonds increased with the CF_4 ratio. The C1s spectrum can be deconvoluted into five Gaussian peaks corresponding to CF_3 , CF_2 , CF, C– CF_x and C–C. The absolute binding energies of CF_3 , CF_2 , CF, C– CF_x and C–C fall within ranges of 292.6–294, 290.3–292, 287.8–289.3, 285.5–287.3 and 283.4–285. The ratio of fluorine to carbon (F/C) can be calculated by the integrated intensity of the various components of the C1s spectrum [11, 18]

$$F/C = (3I_{\text{CF}_3} + 2I_{\text{CF}_2} + I_{\text{CF}}) / I_{\text{C1s}}$$

Table 1 shows the results from the C1s spectra deconvolution. The F/C ratio increased with the CF_4 ratio, and that of the CF_4 -80% film showed the highest ratio (37.3%). These results indicate that a higher CF_4 ratio leads to a higher content of fluorine in the DLC films. This contributes to the lower surface energy of the DLC surface, corresponding to higher hydrophobicity [10, 11].

3.3 SEM observation of the F-DLC surface

Figure 3 shows scanning electron micrographs of the film surface without plasma pre-treatment. Many cracks and irregularities can be seen on all of the film-coated samples. The surface topology is independent of the CF_4 ratio. In contrast, the non-coated PTFE with plasma pre-treatment exhibited the formation of small protuberances at the nanometer scale, and a grainy surface was seen on the film-coated samples (Fig. 4). Some researchers have also reported that O_2 plasma treatment changes the PTFE surface into a fine structure [19, 20]. This observation indicates that the plasma pre-treatment etches the PTFE surface, and after that, the DLC grows on each protrusion on the surface during a CVD process.

Due to CF_4 etching, the higher the CF_4 ratio becomes, the smoother the resulting surface, as seen in Fig. 4. Other studies have reported that the high etching rate of CF_4 (10–50 nm/min at 13 Pa) contributes to a smoother surface [21]. The higher the CF_4 ratio, the more the DLC grown on the surface is etched.

3.4 Water contact angle of the F-DLC surface

Table 2 shows the water contact angle of the film surface with and without plasma pre-treatments. In the film without the plasma pre-treatment, the contact angle was slightly increased with the CF_4 ratio. This is consistent with fluorine content of the DLC film. According to Table 1, the F/C ratios increased with the CF_4 ratio. Other studies have also reported that an increase of fluorine content of the DLC film contributed to its hydrophobicity [9].

In the film with the plasma pre-treatment, the contact angle drastically increased to $122.1^\circ \pm 2.2^\circ$ (CF_4 -0%) and $125.9^\circ \pm 3.1^\circ$ (CF_4 -20%) after DLC coating and gradually decreased with increases in the CF_4 ratio. This trend appears different from that of the film without plasma pre-treatment. In the CF_4 -20–80% film, the contact angle of the film with plasma pre-treatment decreased with increasing CF_4 ratio, while the contact angle of the film without pre-treatment increased with the CF_4 ratio. This opposite behavior observed in comparison of these two materials may be caused by the surface topology. In the SEM

Fig. 2 XPS spectra of F-DLC films deposited on PTFE substrate: **a** C1s spectra; **b** F1s spectra. The C–C bonds decreased with increasing CF₄ ratio, whereas the C–F bonds increased with the CF₄ ratio

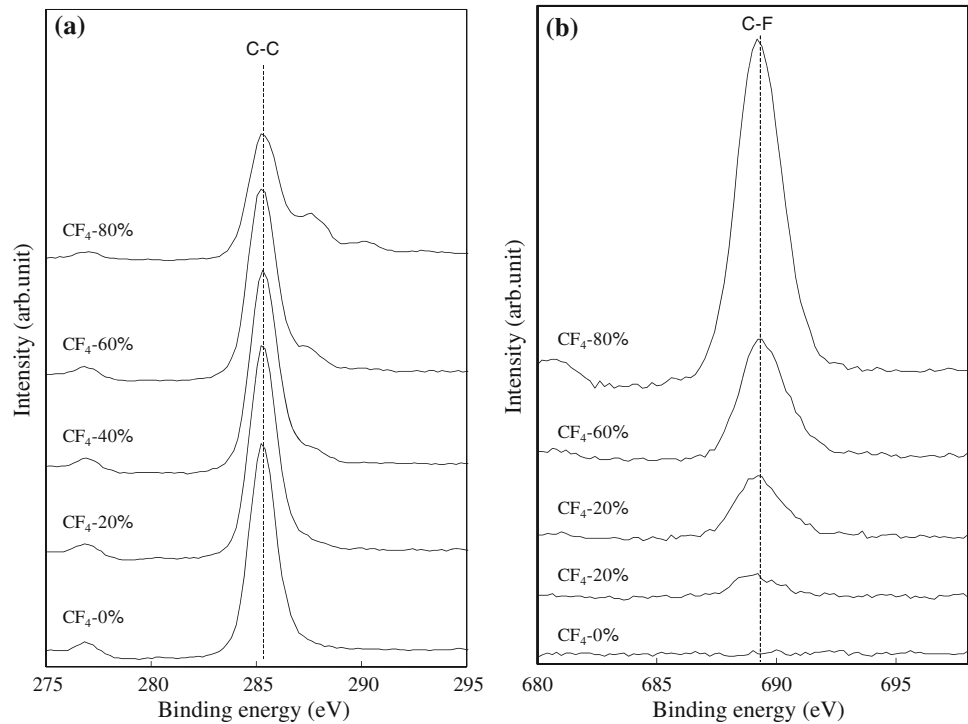


Table 1 Chemical composition of the F-DLC films (%)

	C–C	C–CF _x	C–F	CF ₂	CF ₃	F/C ratio
CF ₄ -80%	60.2	23.6	10.1	6.2	0	37.3
CF ₄ -60%	74.3	14.7	5.8	5.2	0	21.8
CF ₄ -40%	82.3	11.6	3.0	2.9	0	10.9
CF ₄ -20%	90.4	6.3	3.3	0	0	3.6

observations, the surface topology was very different. In the film with plasma pre-treatment, the formation of small protuberances on the surface may have more influence on

the hydrophobicity of the film than the effect of fluorine content of the film.

3.5 Pull-out test to determine the adhesion strength of F-DLC films to the PTFE substrates

Figure 5 shows the pull-out strength of the F-DLC film adhered to the PTFE substrates. In the CF₄-0–60% film, the adhesion strength of the film to the PTFE with plasma pre-treatment was higher than that without the plasma pre-treatment. This suggests that the N₂ plasma pre-treatment

Fig. 3 Scanning electron micrographs of F-DLC film without N₂ plasma pre-treatment. Many cracks and irregularities on the film surface were seen on all film-coated samples

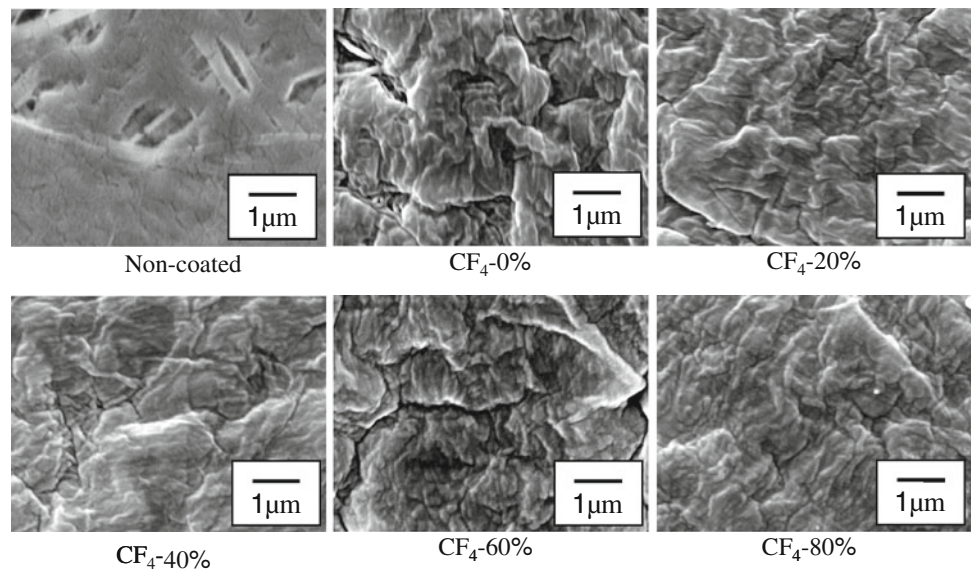


Fig. 4 Scanning electron micrographs of F-DLC film with N₂ plasma pre-treatment. The formation of small protuberances at the nanometer scale was seen on all film-coated samples. Films with higher CF₄ ratios showed smoother surfaces

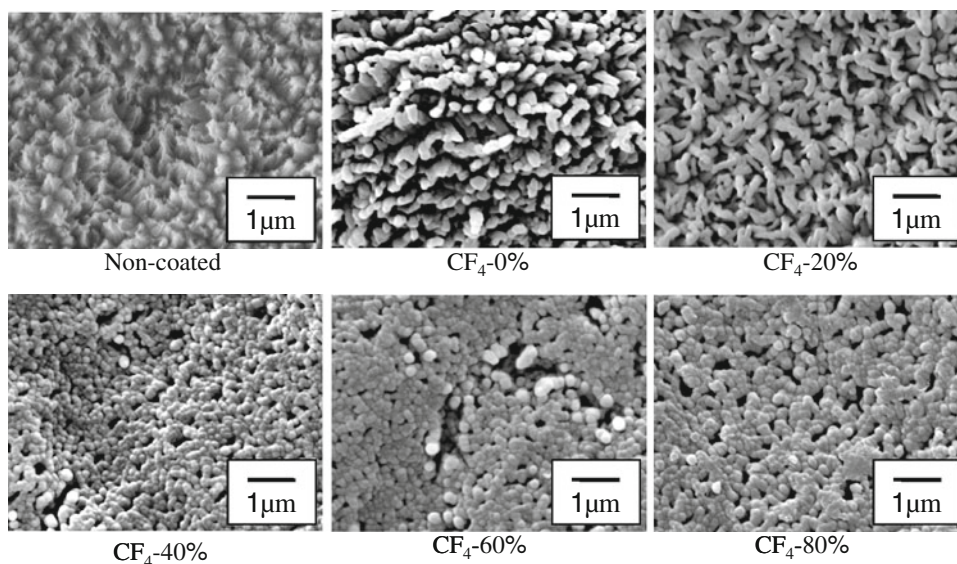


Table 2 Contact angle of test liquids on F-DLC film with and without plasma pre-treatment

	Non-coated	CF ₄ -0%	CF ₄ -20%	CF ₄ -40%	CF ₄ -60%	CF ₄ -80%
Without the plasma pre-treatment	104.9° ± 1.2°	89.8° ± 3.1°	93.2° ± 2.0°	96.5° ± 2.2°	100.5° ± 1.6°	103.8° ± 2.8°
With the plasma pre-treatment	20.5° ± 2.1°	122.1° ± 2.2°	125.9° ± 3.1°	115.5° ± 1.9°	109.9° ± 2.2°	105.7° ± 3.2°

improved the adhesion strength of the F-DLC film. It is reported that the N₂ plasma creates C–N, C=N, and C–N–F groups on the PTFE surface, and the formation of these groups raises the surface energy of the PTFE surface [22]. Therefore, the N₂ plasma pre-treatment is effective in activating the polymer surface [23].

The strength of the film without plasma pre-treatment increased with the CF₄ ratio. This can be explained by the effectiveness of CF₄ etching. Hoshida et al. [24] reported that the CF_x radicals act to etch the polymer surface at the beginning of the DLC deposition, and form nanoscale hills and holes. They also concluded that the DLC fills the holes, contributing to improvement of the adhesion strength of the DLC film. In addition, a higher fluorine content of the F-DLC may also result in more interaction with the fluorine on the PTFE surface.

In contrast, with the plasma pre-treatment, the adhesion strength of the film decreased with increasing CF₄ ratio, the opposite of what was observed with the plasma pre-treatment. This suggests that an excessive content of CF₄ can damaged the PTFE surface and remove the C–N, C=N, and C–N–F groups of the PTFE surface [22, 25].

3.6 Protein adsorption test of F-DLC film on PTFE substrate

Figure 6 shows the amount of albumin, fibrinogen, and γ-globulin adsorbed on the films with plasma pre-treatment.

The control consists of the non-coated PTFE substrate without plasma pre-treatment. The amount of adsorbed albumin on the non-coated PTFE was the lowest in all samples. In the DLC-coated samples, the amount of adsorbed albumin decreased with increasing CF₄ ratio. In general, the albumin has high affinity to hydrophilic surfaces [26, 27]. This result indicates that PTFE has a surface with higher hydrophobicity than that of the DLC and F-DLC film, and the DLC film with the higher CF₄ ratio has the highest hydrophobic surface [10]. However, this result is not consistent with the results from the water contact angle measurements (Table 2). In Table 2, the CF₄-0% film has a higher contact angle than CF₄-40% and CF₄-80% films. This might be because the surface topology, as well as the chemical conditions of the surface, has an influence on the results of the water contact angle measurement. The protuberances on the CF₄-0% film surface, as seen in Fig. 4, might also make the contact angle of the film higher.

The amount of fibrinogen and γ-globulin adsorbed on the films shows similar tendencies. However, the amount of adsorbed γ-globulin was more susceptible to the CF₄ ratio than that of fibrinogen. Kim et al. [26] also reported that the amount of adsorbed γ-globulin on a polymer changed more drastically depending on the degree of wettability of the polymer materials than in the case of fibrinogen. In the DLC-coated samples, the amount of adsorbed fibrinogen and γ-globulin increased with CF₄ ratio. This is the

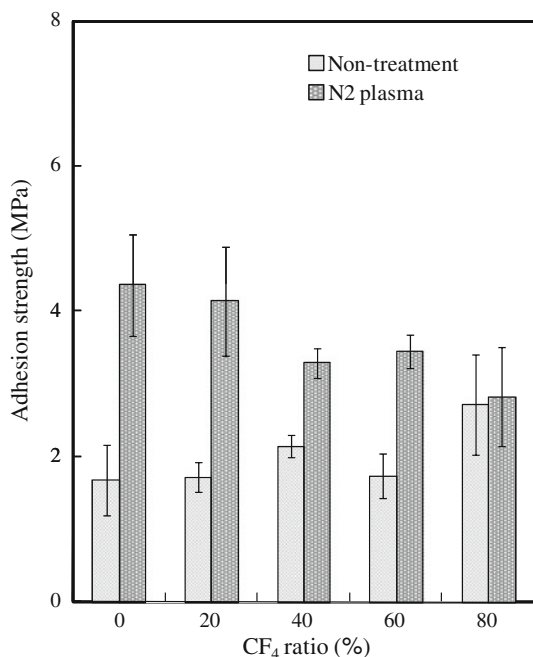


Fig. 5 Pull-out strength of F-DLC film on the PTFE substrate as a function of CF₄ ratio. The strength of the film without N₂ plasma pre-treatment increased with the CF₄ ratio, whereas in the film with the N₂ plasma pre-treatment, the strength decreased with increasing CF₄ ratio

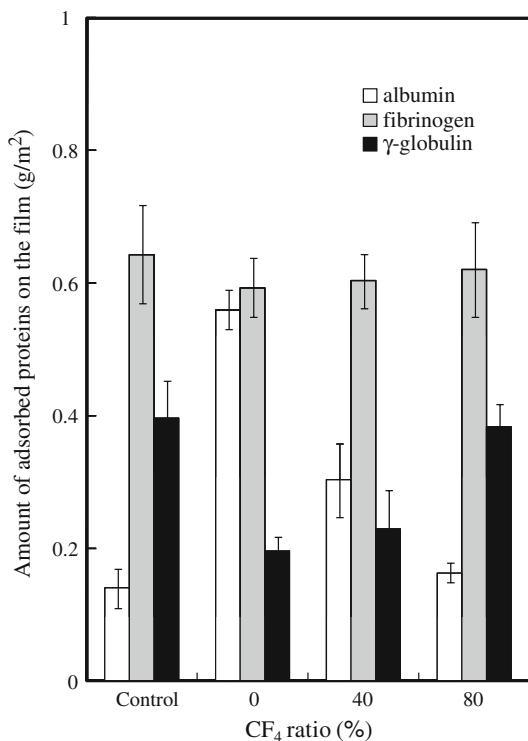


Fig. 6 Amount of proteins (albumin, fibrinogen, and γ -globulin) adsorbed on the F-DLC films. Protein levels were assessed with Micro-BCA. Control: non-coated PTFE. The amount of adsorbed albumin on the film decreased with increasing CF₄ ratio, whereas the amount of adsorbed fibrinogen and γ -globulin on the film increased with the CF₄ ratio

opposite of what was seen with the albumin, and may occur because the fibrinogen and the γ -globulin have a high affinity to hydrophobic surfaces.

Preferential albumin adsorption is known to passivate the surface of an implant, whereas preferential adsorption of fibrinogen and γ -globulin will favor coagulation and platelet activation [28, 29]. Some studies have also reported that an albumin-coated surface remarkably inhibits platelet adhesion and blood coagulation [30, 31]. Between the DLC film and non-coated sample, the DLC film showed more anti-thrombogenicity than non-coated PTFE because the DLC-coated PTFE showed more adsorbed albumin and less fibrinogen and γ -globulin adsorption than the non-coated PTFE.

In the DLC-coated samples, the CF₄-0% film showed the most adsorbed albumin and the least adsorbed fibrinogen and γ -globulin. Hasebe et al. [11] reported the adhesion of human blood platelets and protein adsorption (albumin and fibrinogen) on F-DLC coated on polycarbonate. They concluded the high-adsorbed albumin/fibrinogen ratio on the F-DLC film corresponded to a suppression of platelet adhesion, and the ratio of the F-DLC film was higher than that of the DLC film. The albumin/fibrinogen was reported to be useful for assessing the biocompatibility of a biomaterial [11, 31]. Both fibrinogen and γ -globulin enhance platelet adhesion and activation. In our experiment, the CF₄-0% film showed the highest albumin/fibrinogen and albumin/ γ -globulin ratios in all samples (Fig. 7). This indicates that the CF₄-0% DLC film has a higher anti-thrombogenicity than the F-DLC film, which is inconsistent with previous results. One reason for the difference between their results and ours may be due to the effect of the plasma pre-treatment in our experiment. The PTFE substrate was plasma pre-treated prior to DLC coating for the protein adsorption test sample. The plasma pre-treatment drastically changed the surface morphology of the film on the PTFE, and the roughness was changed depending on the CF₄ ratio, as seen in SEM observations (Fig. 4). This surface morphology might have an influence on the protein adsorption property in our experiment. Another reason to be considered is the difference in the substrate used. They used a polycarbonate as a substrate, while our experiments were done with PTFE.

Protein adsorption on a polymer surface is a complex phenomenon and involves many factors, such as surface chemistry, surface morphology, and surface wettability, among others. From these results, the DLC film (CF₄-0%) with the plasma pre-treatment appears to have a higher potential for application in artificial blood vessels (made of PTFE) to improve patency than the fluorinated DLC film because the plasma pre-treatment can be used to improve the adhesion strength of the film to the PTFE. However, the mechanism of biomaterial-associated thrombosis is still not

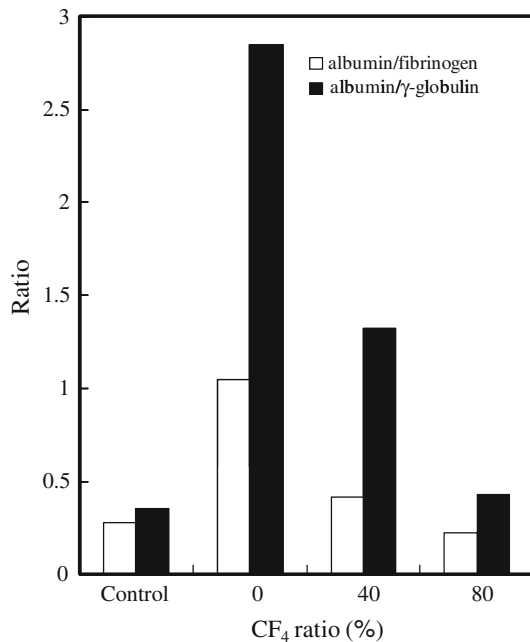


Fig. 7 Albumin/fibrinogen and albumin/ γ -globulin ratios. Control: non-coated PTFE

fully understood. Further studies are needed to investigate all factors related to thrombosis on the F-DLC films.

4 Conclusions

The characteristics of F-DLC films were investigated in the context of chemical composition, adhesion strength, and adsorption of albumin, fibrinogen, and γ -globulin. The following conclusions were derived:

1. In the XPS analysis, the C–C bonds decreased with increasing CF₄ ratio, whereas the C–F bonds increased with the CF₄ ratio. The F/C ratio of the film increased with the CF₄ ratio.
2. The pullout test showed that the adhesion strengths of the films (CF₄-0–60%) were improved with N₂ plasma pre-treatment. In the film without the plasma pre-treatment, adhesion strength increased with the CF₄ ratio. In contrast, in the case with plasma pre-treatment, the adhesion strength of the F-DLC film decreased with an increasing CF₄ ratio.
3. In the protein adsorption test, the amount of adsorbed albumin on the film decreased with increasing CF₄ ratio, and the amount of adsorbed fibrinogen and γ -globulin increased with the CF₄ ratio. The CF₄-0% DLC film showed the most adsorbed albumin and the least adsorbed fibrinogen and γ -globulin.

References

1. Rossi S, Chini F, Straffellini G, Bonora PL, Moschini R, Stampali A. Corrosion protection properties of electroless Nickely PTFE, Phosphate MoS₂ and Bronze PTFE coatings applied to improve the wear resistance of carbon steel. *Surf Coat Technol.* 2003;173:235–42.
2. Parry NG, Feliciano DV, Burke RM, Cava RA, Nicholas JM, Dente CJ, et al. Management and short-term patency of lower extremity venous injuries with various repairs. *Am J Surg.* 2003; 186:631–5.
3. Devine C, Hons BA, McCollum C. Heparin-bonded Dacron or polytetrafluorethylene for femoropopliteal bypass: five-year results of a prospective randomized multicenter clinical trial. *J Vasc Surg.* 2004;40:924–31.
4. Johnson WC, Lee KK. A comparative evaluation of polytetrafluorethylene, umbilical vein, and saphenous vein bypass grafts for femoral-popliteal above-knee revascularization: A prospective randomized Department of Veterans Affairs cooperative study. *J Vasc Surg.* 2000;32:268–77.
5. Barrio J, Ripoll C, Bañares R, Echenagusia A, Catalina MV, Camúñez F, et al. Comparison of transjugular intrahepatic portosystemic shunt dysfunction in PTFE-covered stent-grafts versus bare stents. *Eur J Radiol.* 2005;55:120–4.
6. Suzuki M, Ohana T, Tanaka A. Tribological properties of DLC films with different hydrogen contents in water environment. *Diamond Relat Mater.* 2004;13:2216–20.
7. Vanhulsel A, Velasco F, Jacobs R, Eersels L, Havermans D, Roberts EW, et al. DLC solid lubricant coatings on ball bearings for space applications. *Tribol Int.* 2007;40:1186–94.
8. Field SK, Jarratt M, Teer DG. Tribological properties of graphite-like and diamond-like carbon coatings. *Tribol Int.* 2004;37: 949–56.
9. Hasebe T, Ishimaru T, Kamijo A, Yoshimoto Y, Yoshimura T, Yohena S, et al. Effects of surface roughness on anti-thrombogenicity of diamond-like carbon films. *Diamond Relat Mater.* 2007;16:1343–8.
10. Saito T, Hasebe T, Yohena S, Matsuoka Y, Kamijo A, Takahashi K, et al. Antithrombogenicity of fluorinated diamond-like carbon films. *Diamond Relat Mater.* 2005;14:1116–9.
11. Hasebe T, Yoneta S, Kamijo A, Okazaki Y, Hotta A, Takahashi K, et al. Fluorine doping into diamond-like carbon coatings inhibits protein adsorption and platelet activation. *J Biomed Mater Res.* 2007;83A:1192–9.
12. Takai O, Anita V, Saito N. Properties of DLC thin films produced by RF PE-CVD from pyrrole monomer. *Surf Coat Technol.* 2005;200:1106–9.
13. Guo YB, Hong FCN. Adhesion improvements for diamond-like carbon films on polycarbonate and polymethylmethacrylate substrates by ion plating with inductively coupled plasma. *Diamond Relat Mater.* 2003;12:946–52.
14. Baba K, Hatada R. Deposition of diamond-like carbon films on polymers by plasma source ion implantation. *Thin Solid Films.* 2006;506–507:55–8.
15. Ozeki K, Hirakuri KK. The effect of nitrogen and oxygen plasma on the wear properties and adhesion strength of the diamond-like carbon film coated on PTFE. *Appl Surf Sci.* 2008;254:614–1621.
16. Garg S, Hurren C, Kaynak A. Improvement of adhesion of conductive polypyrrole coating on wool and polyester fabrics using atmospheric plasma treatment. *Synth Met.* 2007;157:41.
17. Ferrari AC. Determination of bonding in diamond-like carbon by Raman spectroscopy. *Diamond Relat Mater.* 2002;11:1053–61.
18. Huang KP, Lin P, Shih HC. Structure and properties of fluorinated amorphous carbon films. *J Appl Phys.* 2004;96:354–60.

19. Noh JH, Baik HK, Noh I, Park JC, Lee IS. Surface modification of polytetrafluoroethylene using atmospheric pressure plasma jet for medical application. *Surf Coat Technol.* 2007;201:5097–101.
20. Liu CZ, Wu JQ, Ren LQ, Tong J, Li JQ, Cui N, et al. Comparative study on the effect of RF and DBD plasma treatment on PTFE surface modification. *Mater Chem Phys.* 2004;85:340–6.
21. Butter RS, Waterman DR, Lettington AH, Ramos RT, Fordham EJ. Production and wetting properties of fluorinated diamond-like carbon coatings. *Thin Solid Films.* 1997;311:107–13.
22. Vallon S, Hofrichter A, Drdvillon B, Klemberg-Sapieha JE, Martinu L, Poncin-Epaillard F. Improvement of the adhesion of silica layers to polypropylene induced by nitrogen plasma treatment. *Thin Solid Films.* 1996;290–291:68–73.
23. Jana DJ, Ai CF, Lee CC. Deposition of nitrogen-containing diamond-like carbon films on acrylic substrates by an ion beam process. *Vacuum.* 2004;74:531–8.
24. Hoshida T, Tsubone D, Takada K, Kodama H, Hasebe T, Kamijo A, et al. Controlling the adhesion between diamond-like carbon (DLC) film and high-density polyethylene (HDPE) substrate. *Surf Coat Technol.* 2007;202:1089–93.
25. Liu CZ, Arnell RD, Gibbons AR, Green SM, Ren LQ. Surface modification of PTFE by plasma treatment. *J Tong Surf Eng.* 2000;16:215–7.
26. Kim SW, Lee RG, Oster H, Coleman D, Andrade JD, Lentz DJ, et al. Platelet adhesion to polymer surfaces. *Trans Am Soc Artif Intern Organs.* 1974;20:449–55.
27. Luensmann D, Jones L. Albumin adsorption to contact lens materials: a review. *Cont Lens Anterior Eye.* 2008;31:179–87.
28. Higuchi A, Sugiyama K, Yoon BO, Sakurai M, Hara M, Sumita M, et al. Serum protein adsorption and platelet adhesion on pluronict-adsorbed polysulfone membranes. *Biomaterials.* 2003;24:3235–45.
29. Kwok SCH, Wanga J, Chu PK. Surface energy, wettability, and blood compatibility phosphorus doped diamond-like carbon films. *Diamond Relat Mater.* 2005;14:78–85.
30. Liu T, Lin W, Huang L, Chen S, Yang M. Hemocompatibility and anaphylatoxin formation of protein-immobilizing polyacrylonitrile hemodialysis membrane. *Biomaterials.* 2005;26:1437–44.
31. Marconi W, Galloppa A, Martinelli A, Piozzi A. New polyurethane compositions able to bond high amounts of both albumin and heparin. *Biomaterials.* 1995;16:449–56.