*New Diamond and Frontier Carbon Technology*
Vol. 17, No. 6 2007
MYU Tokyo

NDFCT 546

# Recent Advances in Diamond-Like Carbon Films in the Medical and Food Packing Fields

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(Received 14 November 2007; accepted 8 February 2008)

***Key words:*** diamond-like carbon, biocompatibility, medical devices, gas barrier, PET bottle, atmospheric pressure

Diamond-like carbon (DLC) films have been widely used for many applications due to their outstanding properties such as high hardness, chemical inertness, and high electrical resistivity. The mechanical properties of DLC fall between those of graphite and diamond; the material possesses low-friction coefficient, low wear rate, high hardness, excellent tribological properties, and good corrosion resistance. DLC is an excellent candidate for use as biocompatible coatings on biomedical implants, which is due to not only its excellent properties but also its chemical composition containing only carbon and hydrogen, which are biologically compatible with human cells. In our laboratory, we have developed fluorinated DLC film (F-DLC) by combining the advantages of fluorine doping with conventional DLC characteristics and evaluated its biocompatibility as a surface coating for human blood-contacting devices in the medical field. We present an overview of DLC and F-DLC coatings for medical devices and our data regarding the biocompatibility of F-DLC coatings. In addition, we have developed a possible application of DLC films with high-gas-barrier properties for food and beverage containers, especially for PET bottles. We have recently developed a unique and cost-effective atmospheric-pressure glow plasma-enhanced chemical vapor deposition (CVD) technique as a substitute for the low-pressure CVD technique. This technique has the potential to become the next-generation technique for the film-coating industry.

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## 1. Introduction

Diamond-like carbon (DLC) has been actively studied in the field of material engineering. DLC consists of dense amorphous carbon or hydrocarbon with high hardness, chemical inertness, and high electrical resistivity. The mechanical properties of this film fall between those of graphite and diamond; it possesses a low-friction coefficient, low wear rate, high hardness, excellent tribological properties, and good corrosion resistance.[1,2] These mechanical, electrical, optical and chemical properties have promoted the use of DLC coating in mechanical and electrical fields. DLC has been found useful in food/beverage and biomedical fields due to its excellent gas barrier properties. DLC coating is also considered for widespread use as a surface coating for medical applications, such as coronary stents,[3–5] heart valves[6] and orthopedic implants.[7]

In this paper, we present our recent study on the application of DLC to the biomedical and food/beverage fields. Furthermore, we introduce newly synthesized high-gas-barrier DLC films under atmospheric pressure prepared by atmospheric-pressure glow (APG) plasma chemical vapor deposition (CVD), which is expected to become the next-generation technique for the film-coating industry. Finally, we summarize our recent data on the fracture behavior of polymer-DLC composites and the adhesion properties of DLC-deposited polyethylene.

## 2. DLC Coating for Medical Applications

A large number of medical devices such as hip joints, vascular grafts, artificial heart valves, interventional devices (stents, guidewires and catheters), dental roots and intraocular lens have been gaining prominence with the development of medical engineering and are implanted into human bodies every year. However, almost all biomaterials are far from being completely biostable and inert. The healing response to implanted biomedical materials involves varying degrees and stages of inflammation and healing processes, which in some cases leads to device failure.[8] Thrombogenic complications also remain as one of the main problems for blood-contacting devices and can trigger life-threatening device failure. The initial local response to foreign surfaces in the body is primarily catalyzed by surface-absorbed proteins that trigger numerous processes, such as cellular activation, inflammatory and complement activation, and attraction of circulating platelets. To reduce the risk of platelet aggregation/thromboembolism and complications following the life-long course of anticoagulants, the improvement of the biocompatibility and haemocompatibility of biomaterials is highly demanded.

Surface coating is one method of improving both the mechanical and physical properties of implants in direct contact with blood and tissue. There has thus been substantial interest in developing ways to modify the surfaces of metal and polymer implants to increase biocompatibility. Many groups are working on a variety of blood-compatible coatings, including a photoheparin formulation. Heparin is a potent anticoagulant purified for decades from ruminants or porcine tissues; however, with

the emergence of bovine spongiform encephalopathy (BSE), or mad cow disease, only porcine-derived heparin is allowed in the United States and Europe. Regulators in Europe, United States and Japan are also concerned about the possible side effects of the use of large amounts of heparin for patients, which can make it difficult to bring heparin-coated products to the market. Therefore, there is an urgent need to develop nonbiologic alternatives to heparin coating for medical devices. In fact, some companies made a decision to suspend the production of heparin-coated catheters and devices, which is really inconvenient and disadvantageous both for medical doctors and patients.

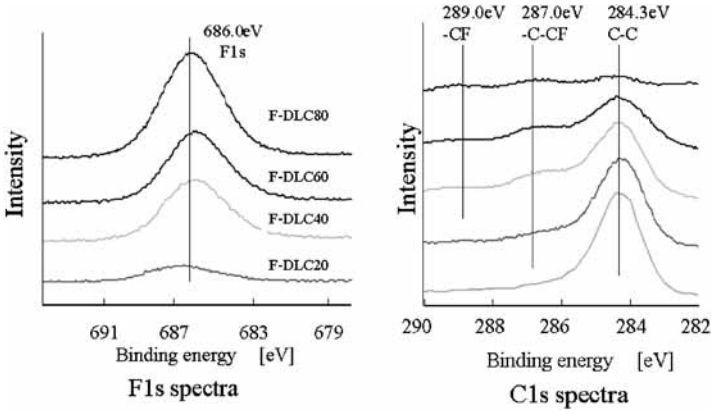
Several recent attempts were made to improve the tribological properties of DLC coatings by adding elements, such as silicon (Si), fluorine (F), nitrogen (N), oxygen (O), tungsten (W), vanadium (V), cobalt (Co), molybdenum (Mo), titanium (Ti) and boron (B), or combinations of these, into the film.[3,9–11] We developed fluorine-doped DLC film (F-DLC) by combining the advantages of fluorine doping with conventional DLC characteristics and evaluated its haemocompatibility and biocompatibility as a surface coating for blood-contacting devices. We present an overview of DLC and F-DLC coatings for medical devices and our recent data in terms of the biocompatibility of F-DLC coatings.

## 3. Characterization of DLC and F-DLC Coatings

Surface fluorination of materials has generally been found to create surfaces with improved blood compatibility, hydrophobicity, and chemical stability.[12] It has been reported that the incorporation of fluorine into DLC film greatly reduces its surface energy[13,14] and film hardness but largely preserves other DLC properties.[15] For the comparison of DLC with F-DLC, we prepared DLC and F-DLC films by radio frequency (RF) plasma-enhanced CVD (RF-CVD) and compared them using X-ray photoelectron spectroscopy (XPS), contact angle measurement and scanning electron microscopy (SEM).

The local spectra of C1s and F1s for DLC, F-DLC20, F-DLC40, F-DLC60 and F-DLC80 by XPS are shown in Fig. 1. Each F-DLC film was denoted according to the partial pressure of $C_2F_6$ as follows: for example, F-DLC20 means that F-DLC films were deposited under a partial pressure of $C_2F_6$ at 20% of the total pressure. Each spectrum could be divided into three main peaks, which were centered at ~284.4, ~287.0 and ~289.0 eV, respectively. As shown in Fig. 1, the peak intensity for the F1s (686.0 eV) gradually increased (Fig. 1(a)) with $C_2F_6$ partial pressure during deposition and the peak intensity for the C-C bond (284.4 eV) gradually decreased (Fig. 1(b)). This indicates that the pressure of $C_2F_6$ affects the ratio of fluorine at the topmost surface of the films. Furthermore, in the spectra of F-DLC films, peaks suggesting bonds between carbon and fluorine were present. The spectra of F-DLC20, F-DLC40, F-DLC60 and F-DLC80 confirmed the presence of C-CF bonds (287.0 eV) as well as C-C bonds.

The wettability of SUS316L, DLC and F-DLC60 were evaluated by measuring the static contact angles between a droplet of double-distilled, deionized water and the samples surfaces.[16] SUS316L showed the lowest contact angle of 62.2±3.9°. The DLC coating showed a larger contact angle (92.8±4.6°), while the F-DLC coating exhibited the




(a) (b)

Fig. 1. XPS spectra of DLC, F-DLC20, F-DLC40, F-DLC60 and F-DLC80. (a) F1s XPS. (b) C1s XPS.

largest contact angle (105.2±2.5°). DLC and F-DLC have more hydrophobic surfaces than SUS, with F-DLC having the most hydrophobic surface. The more hydrophobic the surface, the higher the interfacial free energy between the solid and liquid phases. The interfacial free energy determines the wetting characteristics, and hence the wall shear stress generated when the liquid comes into contact with the surface. The polarization of C-F and C-CF bonds on the topmost surface of F-DLC, as demonstrated by XPS, can lower the surface energy and result in increased contact angles.

## 4. Haemocompatibility of DLC and F-DLC Coatings

The first major event when a medical device comes in contact with blood is the adsorption of plasma proteins, such as fibrinogen, fibronectin, vitronectin, and the von Willebrand factor, as well as tissue and complement factors. The presence of these adsorbed blood proteins has a profound effect on the biocompatibility of a specific material and its interaction with blood components. The amount and composition of the proteins adsorbed on the surface are also important for evaluating the blood compatibility of the materials. As a rule, gamma globulin and fibrinogen promote platelet and leukocyte adhesion and possibly activation, whereas albumin tends to neutralize these effects. The ratio of adsorbed albumin to fibrinogen is reported to determine the haemocompatibility of the biomaterial.[10]

The protein adsorption process results in platelet adhesion and the activation of the coagulation pathways, leading to thrombus formation.[17–19] As regards the coagulation cascade, artificial surfaces are considered to activate thrombin by activating the intrinsic coagulation pathway. Thrombin is a proteolytic enzyme that promotes the activity of several clotting factors and acts in the final common pathway of the blood clotting process inducing the cleavage of fibrinogen to fibrin.

Platelet adhesion followed by aggregation and spreading is the process by which platelets form thrombus. Platelets respond to minimal stimulation and become activated when they come in contact with any thrombogenic surface such as injured endothelium, subendothelium and artificial surfaces. Platelet activation is initiated by the interaction of an extracellular stimulus with the platelet surface. This interaction involves the coupling of the agonist to specific receptors on the platelet plasma membrane. During activation, platelets attach to the sample surface and they change in shape by developing pseudopodia as their activation level increases.[20] These activated platelets aggregate and lead to the thrombus formation on the substrates (Fig. 2).

A number of promising results have indicated the good biocompatibility of DLC films in *in vitro* and *in vivo* preclinical studies. For example, less platelet adhesion and activation associated with a high albumin/fibrinogen adsorption ratio on the DLC surfaces and the excellent biocompatibility of DLC films was confirmed in various types of cell culture.[3,7,21–26] It has been reported that DLC coatings do not induce any histological changes and that they show excellent biocompatibility in an *in vivo* implantation model.[27] These studies have demonstrated that DLC coatings show no toxicity toward certain living cells and no inflammatory response or loss of cell integrity. A number of clinical applications for DLC coatings are now being considered by commercial manufacturers of various surgical implants. DLC coating is therefore being considered for widespread use as a surface coating for coronary stents,[3–5] heart valves[6] and orthopedic implants[7] in the clinical situations.

One of the major limitations of DLC coating technology is the occurrence of microcracks on the surfaces.[28] In coatings with high internal stress, interface cracks can lead to the complete delamination of the coating. The flaking of DLC coatings was observed not on certain polymer substrates, but on the metal substrates due to poor adhesion and cracking. The crack spacing was observed to increase with thickness, tending to saturate beyond ~500 nm.[29] The DLC coatings must therefore be optimized in order to minimize the risk of film breakdown.

Doping some elements into DLC films or the use of an a-Si:H/a- Si:C:H interlayer

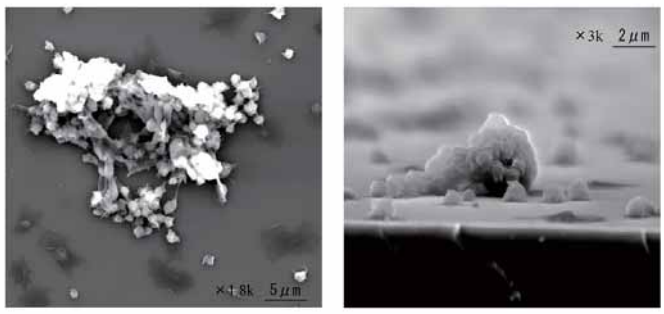



Fig. 2. SEM images of thrombus formation on the substrate (SUS 316L). Local platelet activation promotes the recruitment of platelets and the formation of thrombus.

may help minimize the risk of adhesion failure or film cracking. There have been several recent attempts to improve the tribological properties of DLC coatings by adding elements, such as Si, F, N, O, W, V, Co, Mo, Ti and B, or combinations of these, into the film.[9,10] Different film properties, such as tribological properties, electrical conductivity, surface energy and biological reactions of cells in contact with the surface, can therefore be continuously adapted to desired values. For example, surface fluorination of materials has generally been found to create surfaces with improved blood compatibility, hydrophobicity, and chemical stability.[12] It has been reported that the incorporation of fluorine into DLC film greatly reduces its surface energy[13,14] and film hardness but largely preserves other DLC properties.[15]

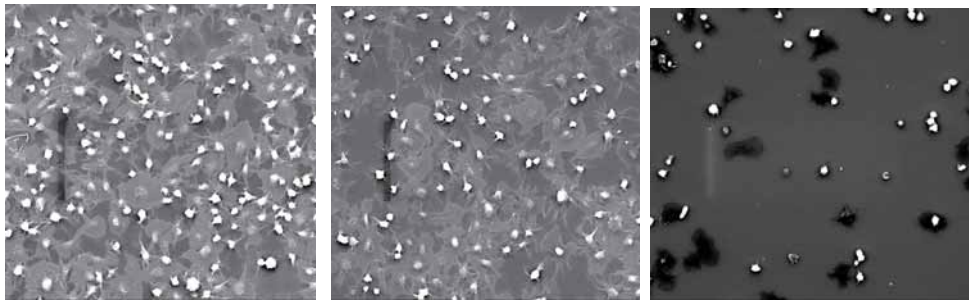
We have recently reported that the *in vitro* whole blood model confirmed that platelet loss was lower in the DLC and F-DLC groups than in the noncoated group (SUS316L), which suggests the adhesion of a smaller number of platelets to DLC- and F-DLC-coated materials.[30] We have also reported that markers of mechanically induced platelet activation (beta-thromboglobulin = beta-TG) and activated coagulation (thrombin-antithrombin three complex = TAT) were markedly reduced in the F-DLC-coated group.[16] Furthermore, we have verified that platelet adhesion and activation were actually suppressed in F-DLC coating groups (Fig. 3).[30]

These results suggest that thrombogenicity was significantly reduced in the F-DLC coating group. However, adsorption of proteins by foreign surfaces from blood is a very complex process and cannot be adequately predicted from the behavior of pure protein solutions. Further studies are needed to verify the biocompatibility of F-DLC films.

## 5. Possible Application of DLC and F-DLC for Medical Devices

### 5.1 *Application for vascular stents*

The implantation of intracoronary stents continues to be a growth area of interventional cardiology. In spite of considerable progress in antithrombotic therapy and implantation techniques, interventional endovascular therapy and the use of stents



(a) (b) (c)

Fig. 3. Morphology of adherent platelets on Si (a), DLC (b) and F-DLC (c) surfaces observed by SEM. (a) Si substrate: Dense platelet layers. (b) DLC: Low density of platelets in comparison with that in the case of Si. (c) F-DLC60: Few platelets.

in coronary arteries are still complicated by a substantial rate of thrombotic occlusions and restenosis. Restenosis is related to patient-, lesion-, and procedure-specific factors. Procedure-specific factors are affected by the interventional technique and stent characteristics. The design and material affect vascular injury and cellular response. Next to the optimization of stent properties and profiles, stent materials and coating have been recently investigated to improve haemocompatibility and tissue compatibility. This is even more important because it has become clear that the treatment of restenosis, especially in-stent restenosis, still has poor results, and the best way to diminish these refractory restenotic lesions is their prevention.

The thrombogenicity of the stents is associated with platelets, predominantly with activated platelets. Patients undergoing coronary angioplasty and stenting procedures are known to be at higher risk for the reocclusion and restenosis of the vessel when platelets express increased numbers of activation-dependent antigens. Shear forces and blood-biomaterial interaction induce the activation of platelets.

Along with medical approaches and technical alterations to the interventional procedures such as intravascular ultrasound-guided stenting and high-pressure implantation techniques, a major focus of efforts to further reduce stent-associated thrombosis and in-stent restenosis has been the improvement of biocompatibility. One of the problems of vascular stenting is the thrombogenicity of stent metal itself. *In situ* thrombus formation sets the stage for the temporal cascade of molecular and cellular reactions that cause extracellular matrix deposition by modified smooth muscle cells and remodeling, which leads restenosis due to intimal hyperplasia. All currently available stents are made of metal. The most recent available stents are manufactured using SUS316L stainless steel and nickel-titanium alloy (Nitinol). Gutensohn *et al.*[4] reported that a significant release of metal ions, such as nickel and chromium, was detected from the surface of a noncoated stent, which might enhance the platelet activation and leukocyte activation in the surrounding tissue. They also showed that the metal ion release from the SUS316L stents, which may negatively affect the haemocompatibility of a surface, could be suppressed by the DLC coating.

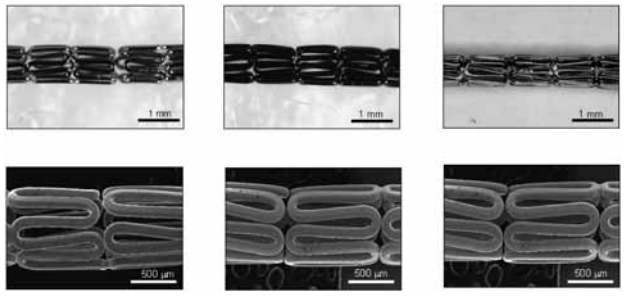
There is no question that a "drug-eluting stent" has a dramatic impact on endovascular therapy for heart diseases. Avoiding systemic toxicity, stent-based local drug release at the site of vascular injury via a polymeric-coated stent is an attractive therapeutic method of achieving an effective local concentration of drug for a designed period. The safety and efficacy of such an approach critically depends on the delicate combination of drugs, polymers, and the kinetics of release. A drug-eluting stent is a device releasing into the bloodstream single or multiple bioactive agents that can deposit in or affect tissues adjacent to the stent. Drugs can be simply linked to the stent surface, embedded and released from within polymer materials, or surrounded by and released through a carrier. The carrier can coat (strut-adherent) or span (strut-spanning) the stent struts. A recently published pooled analysis of 11 trials[31] suggested that drug-eluting stents show benefits over bare-metal stents by reducing the need for later revascularization and reducing the risk of cardiac events. Although the safety profiles of coronary drug-eluting stents do not seem to differ from those of bare metal stents in the short-to-medium term, concern has arisen about the potential for late stent thromboses related to a delayed endothelialization

of the stent struts.[32] McFadden *et al.* suggested that the potential risk of stent occlusion should be considered when the discontinuation of antiplatelet therapy is contemplated in patients with drug-eluting stents. Their findings have potentially serious clinical implications. Future stents should be made less thrombogenic and biocompatible by modifying the metallic surface, or coating it with antithrombotic and/or antiproliferative agents or a membrane eluting antithrombotic or/and antiproliferative drugs.

A few *in vitro* and *in vivo* studies using DLC-coated stents are presented. In an *in vitro* experiment, Gutensohn *et al.*[4] analyzed the intensity of the platelet activation antigens CD62p and CD63. They showed that the DLC coating of a SUS316L coronary stent resulted in a decrease in the concentrations of the CD62p and CD63 antigens indicating low platelet activation on DLC and a low tendency of thrombus formation.

In an *in vivo* experiment, Schroeder *et al.*[3] reported on DLC-coated stainless steel stents, which were implanted into pigs for 6 weeks. Their histopathological observation on the stents showed a decreased thrombus formation for the DLC-coated stents compared with the uncoated stents. Due to the good haemocompatibility of DLC, a few companies have DLC-coated implants already commercially available or in the state of development. The company Sorin Biomedica produces heart valves and stents that are coated with approximately 0.5-µm-thick Carbofilm™. This coating is produced by PVD from a carbon target. A clinical study on coated stents, implanted in 122 patients, resulted in a low restenosis rate of 11% after 6 months. The company PHYTIS sells DLC-coated stents on which they report a reduced rate of restenosis due to the DLC coating and a necessary target revascularization in only 3.27% of the lesions treated.

We coated the DLC or F-DLC film on commercially available coronary stents (GFX Ⅱ, S670, Medtronic Inc., MN, USA) in order to assess the possibility for practical use by way of example. The surfaces of coated stents were examined by scanning electron microscopy (SEM) (JSM-840, JEOL Ltd., Tokyo, Japan). As shown in Fig. 4, both the surfaces of DLC (Fig. 4(b)) and F-DLC (Fig. 4(c)) films were very smooth without any




(a) (b) (c)

Fig. 4. Availability of DLC and F-DLC films on commercially available coronary stents. (a) Uncoated stainless-steel stent (GFXII, S670, Medtronic Inc., MN, USA). (b) DLC-coated stent. (c) F-DLC-coated stent. Macroscopic findings (upper case) and SEM findings (lower case) of these stents were observed. The surfaces of coated stents were smooth without any cracking of the films.

cracking and peeling off. Hasebe *et al.* confirmed the acceptable tissue compatibility of F-DLC in the *in vivo* rat subcutaneous implantation model;[16] however, there has been no data about the haemocompatibility of F-DLC-coated stents in the *in vivo* model so far. On the basis of these results, we are planning a long-term animal study to investigate the biological performance of the F-DLC-coated stents. In addition, further studies are needed in order to examine the availability of F-DLC coating for three-dimensional medical stents without the risk of film breakdown in various clinical settings.

### 5.2 *Application for intravascular guidewires*

Intravascular guidewires are widely utilized to guide and place catheters for diagnostic angiography and balloon catheters for percutaneous transluminal angioplasty (PTA) in the vascular lumens of the human body. For example, to perform diagnostic angiography followed by therapeutic intervention in the human vascular system, a guidewire is first inserted into the vessel and guided through the tortuous path desired for the catheter, after which the catheter is threaded over the guidewire. As the catheter is inserted and advanced over the guidewire, it ultimately negotiates the same tortuous path. However, the inability to pass the guidewire through tight stenoses or torturous vessels is the most common cause of failed interventional endovascular therapy. Thus, the lubrication performance of guidewires is critical for successful procedures.

After the catheter is placed in its final operative position, the diagnostic guidewire can be removed and the catheter is used to perform angiography with contrast material; however, guidewires for PTA and stent placement usually remain in the target vessels throughout the entire procedure. Because the duration of many of these interventional procedures is relatively long, the possibility of thrombotic embolus formation on the guidewire surface increases the risk of downstream occlusion in the coronary, cerebral, and femoropopliteal regions. Therefore, the distal part of an intravascular guidewire should be not only flexible, nonkinking, radiopaque and lubricious, but also antithrombogenic.

We have recently reported the lubrication performance of DLC- or F-DLC-coated guidewires (SUS316L) deposited by RF-CVD.[33] The lubrication performance of DLC- or F-DLC-coated guidewires was evaluated under *in vitro* conditions using a novel friction simulator. Our results showed that DLC and F-DLC coatings improved the lubricity of coated guidewires by approximately 30% when compared with uncoated guidewires (SUS316L) under *in vitro* conditions with strong friction drag.[33]

In other lubricity tests, Maguire *et al.*[29] and McLaughlin *et al.*[34] found that the friction coefficient for conventional DLC coatings is better than that for PTFE coatings for guidewires. Finished catheters and guidewires are typically spray-coated with a thin layer of PTFE, silicone overlays and other hydrophilic coatings, which reduce the friction coefficient. Furthermore, Magurie *et al.*[29] recently reported that doping with silicon and the use of an a-Si:H interlayer in guidewire coating help minimize the risks of adhesion failure and film cracking.

Lubricious coatings have been used in a wide variety of medical devices, including those for use in cardiology, urology and neurology, and for many diagnostic applications. Angioplasty balloons, Foley catheters, urethral stents, microcatheters and guidewires

all benefit from the incorporation of lubricious coatings. Hemodialysis equipment is also coated to reduce patient trauma. Further study is needed in order to investigate the durability and adhesion strength of DLC- or F-DLC-coated guidewires using an a-Si:H/a-Si:C:H interlayer.

## 6. Background of Food and Beverage Application

Consumption of polyethylene terephthalate (PET) bottles has noticeably increased because of their excellent characteristics: they are highly transparent, light in weight, unbreakable, convenient, cost-effective, resealable and recyclable. PET bottles are gradually taking the place of metal cans and glass bottles. Carbonated soft drinks, tea, water, soy sauce and edible oil are currently mostly packed in PET bottles. Compared with other plastics, PET is a remarkably well-balanced material for beverage containers in terms of commonly required properties of strength, clarity, gas retention, flavor retention, flexible moldability and low cost.

The gas barrier property of PET is better than that of high-density polyethylene as well as that of polypropylene. However, PET bottles are still not good enough to hold taste-controlled beverages such as beer, juice and wine because the permeation of oxygen, carbon dioxide gases, water vapor and flavors is still not negligible. The permeation causes the continuous ingress and release of gases through the bottle surface, resulting in a serious deterioration of the beverages in terms of flavor.

The existing ways to improve the gas barrier properties of PET bottles are generally classified into four major approaches: multilayers, coatings, scavenging agents and composite fortifications.[35] The multilayer technology is an easy way to produce a gas barrier bottle, but the improvement of the gas barrier properties through this technology is not that significant; it instead has serious problems in recycling. From the viewpoint of productivity, cost and recyclability, coating is the most reliable, suitable and promising method of improving the gas barrier property of PET bottles. Coating technology for gas barrier enhancement is relatively new. The advent of coating technologies has brought about an industrially favorable situation where an extremely high performance can be achieved with a relatively thin material. Blocking the passage of gas molecules through the PET wall using ultrathin gas barrier films minimizes the negative impact on the recycling process due to minimal contamination by different materials. We will introduce applications of the DLC films in food/beverage containers, especially focusing on PET bottles in the next chapter.

## 7. Gas Barrier Properties of DLC Films on PET Bottles

It is necessary to estimate the allowable gas permeation rates of PET bottles. For example, in the case of beer, typical 500 ml uncoated PET bottles permeate oxygen gas at 0.03 cc/bottle/24 h, which equals 0.09 ppm/24 h. Assuming that the allowable concentration limit of the oxygen gas in the beer is 1 ppm, the uncoated PET bottles can preserve the quality of beer for only 12 days. Comparing these results with those for metal cans and glass bottles, which can preserve the quality of beer for about 9 months,

the shelf life of untreated PET bottles is extremely low. Therefore, it is required to improve the gas barrier properties of PET bottles at least 10 times more in order to store beer in PET bottles.

Table 1 shows the oxygen transmission rate (OTR) and carbon dioxide transmission rate (CO2TR) of DLC-coated bottles at different temperatures. The gas barrier properties of DLC-coated PET bottles were significantly improved as expressed in terms of the barrier improvement factor (BIF). Both OTR and $CO_2$TR increased when heated, indicating the degradation of the gas barrier properties as temperature increasing. Although DLC films are known to be thermally stable materials, it was found from our experiments that the thermal diffusion of molecules still has a great impact on the gas permeation property of the coated bottle.[36] Table 1 also shows the values of activation energy, $E_p$, during the gas transmission, determined from Arrhenius plots. It indicates that the DLC coating layers improved the thermal stability, i.e., the gas barrier property, of the whole bottle.[37] As the DLC-coated layer has high thermal stability, the Ep values of the DLC-coated bottles ranged from 50 to 70% of that of the uncoated bottle. DLC-coated bottles show a marked improvement in gas barrier properties, highly comparable to those of the glass bottles.

## 8. Synthesis of High-Gas-Barrier DLC Films at Atmospheric Pressure

The major difficulty lies in productivity and in cost. DLC films are synthesized by a CVD method that can be enhanced by low-pressure plasma. Generally, glow plasma, suitable for the synthesis of highly uniform films, was stable only at low pressure. However, the low-pressure plasma technique causes a problem that triggers an increase in process time for the vacuum processing, which may eventually lead to a significant decrease in productivity. To improve the system further, the generation of glow plasma under atmospheric pressure has been desired, enabling the construction of a compact and high-speed contacting system.

Table 1
OTR and CO2TR of DLC-coated PET bottles in different temperatures.

| | Uncoated PET | | DLC-coated PET | | BIF[a] | |
|---|---|---|---|---|---|---|
| | $O_2$ | $CO_2$ | $O_2$ | $CO_2$ | $O_2$ | $CO_2$ |
| Temperature (°C) | | | | | | |
| 20 | | 0.0032 | | 0.00034 | | 9.4 |
| 23 | 0.07 | | 0.035 | | 20 | |
| 30 | 0.1132 | 0.0048 | 0.0043 | 0.00044 | 26.3 | 11 |
| 40 | 0.2167 | 0.0071 | 0.0061 | 0.00059 | 35.5 | 12.1 |
| $E_p$[b] (cal/mol) | 12231 | 7286 | 6044 | 5186 | | |

Unit : OTR $cm^3$/bottle/24 h/atm; $CO_2$TR g/package/24 h/0.21 atm
[a]Barrier improvement factor (BIF) refers to the reciprocal ratio of the transmission rate of a-C:H-coated bottles to that of uncoated bottles.
[b]Apparent activation energy for permeation process.

Okazaki *et al.* suggested the following three conditions required to stabilize glow plasma at atmospheric pressure:[38–40] (i) to use a power source frequency of over 1 kHz, (ii) to insert a dielectric plate between the two metal electrodes, and (iii) to use helium as dilution gas. Reducing the dilution gas was necessary due to its considerable cost in using a substantial amount of helium (He) gas. By changing the shape of the upper electrode as well as the material of the dielectric plate, it was found that glow plasma could be stabilized in air, argon (Ar), oxygen and nitrogen.[41,42] An atmospheric-pressure glow (APG) plasma technique thus became more practical and the studies of surface modification,[43] fluorination[44,45] and thin-film deposition have progressed considerably.

Figure 5 shows a schematic diagram of APG plasma CVD equipment, where the plasma is generated and sustained by parallel-plate electrodes with a plate size of 60× 70 $mm^2$. Both electrodes are covered with dielectric plates. PET substrates were placed between the electrodes. A pulsed power supply operated at a frequency of 9 kHz was used for the plasma source. $C_2H_2$ was supplied as process gas, generally used for the synthesis of DLC films at low pressure.

It was found that in order to produce $C_2H_2$ plasma at higher pressure, higher voltage was necessary. A high voltage of ~10–20 kV is needed when generating $C_2H_2$ plasma at atmospheric pressure. Sparkover voltage varies not only with pressure but also with the type of gas. He plasma can be generated at ~2–3 kV, much lower than the voltage needed to generate nitrogen plasma that is normally operated at ~10–12 kV. The sparkover voltage of other noble gases such as Ar or neon (Ne) is also low, but the voltage range needed is not as wide as that of He. He can be stabilized even at 15 kV. Plasma of several gases that are only stable at high voltage can be generated and stabilized at lower voltage if the gases are mixed with He. In this way, the plasma of most gases can be formed at atmospheric pressure by the APG plasma technique.

The OTRs of the film deposited for 15 s at flow rates of 1 and 3 l/min were under the measuring limit of the OX-TRAN® permeability testing equipment, which denotes

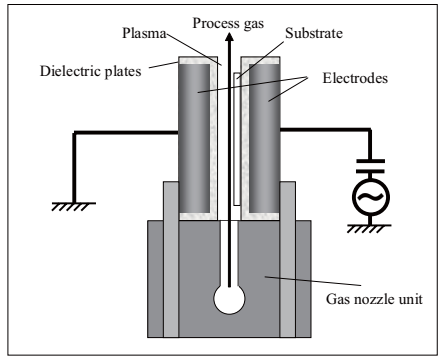



Fig. 5. Schematic diagram of APG plasma CVD equipment. Plasma is sustained between parallel-plate electrodes covered with a dielectric plate.

an almost perfect gas barrier property. It was found that DLC films synthesized at atmospheric pressure show an extremely high gas barrier property, sufficiently high for the APG plasma technique to be practically used for food packaging. Although almost complete blockage of gas has been realized by coating DLC films on the PET substrates synthesized at atmospheric pressure, the deposition time of 15 s is still too long considering mass production. In order to reduce the deposition time, improvement in the hardware (mainly in the plasma source) is desired.

From these results, we confirmed that DLC films could be synthesized even at atmospheric pressure, while the gas barrier properties of the films were comparable to those of the films synthesized at low pressure. Our study suggests that the APG plasma technique can be used as a substitute for the low-pressure plasma technique.

## 9. Fracture Behavior and Adhesion Property of DLC-Polymer Composites

DLC coatings have specifically been used as thin films deposited on hard materials such as metals as well as very flexible materials such as polymers. Since there are occasionally substantial differences in the chemical and physical characteristics between DLC and such soft and hard substrates, when they are practically utilized as composites, it is necessary to carefully investigate the mechanical properties and fracture behavior of the composites. The fracture behavior of a thin DLC surface of those composites is usually quite complicated, presenting unusual fracture behavior due to the complex interaction between DLC and the substrates.

The fracture behavior of thin hard films other than DLC, coated on metals was widely investigated. Agarawal *et al.* observed the shear strength and crack surface of copper coated with thin ceramic film.[46] They found transverse cracks when mechanically stretched. Ye *et al.* introduced three types of cracking processes on thin films due to residual strain in brittle substrates and a weak interface between the films and substrates.[47] Chen *et al.* observed periodic cracking on thin titanium nitride (TiN) film coated on stainless steel.[48]

Fracture and mechanical studies of DLC-coated substrates have not been extensively performed, until recently when Ogwu *et al.* examined periodic cracking in thin DLC film coated on stainless steel when exposed to biological fluids.[49] The fracture surface and the characterization of the mechanical properties of DLC film were also discussed by Choi *et al.*, Cho *et al.* and Aoki *et al.*[50–52]

The deformation of the substrates becomes more significant as well as problematic, since the fracture behavior becomes much more complicated, when softer polymeric materials are used as substrates instead of traditionally utilized hard metals. There have only been a few papers that dealt with DLC-polymer composites. Ollivier *et al.* assessed the adhesion between DLC films and PET films through simple tensile testing and surface microscopy.[53] Aoki and Ohtake improved the wear resistance of DLC films by using segment-structured DLC films on aluminum substrates.[52] They developed this method after they studied the morphology of the DLC sample that presented a segmented surface (i.e., lattice-like fracture) automatically generated when DLC was coated on polymers.

Tsubone *et al.* investigated the fracture surface of DLC-polymer composites by focusing on the moduli of materials, namely, both polymers and DLC, and investigated how the resulting polymer-DLC composites act in terms of fracture behavior when they were mechanically deformed.[54] The moduli of materials were changed by choosing different materials possessing different Young's moduli. It was found that the fracture behavior of such polymer-DLC composites was characterized by lattice-like cracks and microbuckling aligned regularly over the extended surface of the thin DLC films. The periodicity and mechanism of fracture surfaces were found to be significantly related to the moduli of DLC as well as polymers. The lattice pattern of the fractured DLC films on polymer substrates with higher moduli showed smaller length and width in their fractured "lattice" periodicity. It was also found that the polymers with harder DLC had a higher crack number than the polymers coated with softer fluorinated DLC (F-DLC). Moreover, the number of the cracks of the composites with poor adhesion is lower than that of the composites with good adhesion. The results were confirmed using two different polymers with similar Young's moduli but with different levels of adhesion to DLC films.

Tsubone *et al.* also discussed the gas barrier properties of DLC-coated polymers, especially when the polymers are deformed.[55] PET, polyethylene (PE) and polypropylene (PP) for semicrystalline polymers, and polymethyl methacyrlate (PMMA) for an amorphous polymer were selected for the investigation. The polymers were coated with thin DLC films, followed by experiments on the gas barrier properties of the resulting DLC-polymer composites. Some of the DLC-polymer composites markedly improved in terms of their gas barrier properties while they presented horizontal crack lines and vertical microbuckling lines on the DLC surface under deformation as mentioned above. They found that the gas barrier property of the polymer substrates with lower residual strains was less damaged, when the substrates were mechanically deformed, than that of the polymer substrates with higher residual strains. The degradation of the gas barrier property after mechanical deformation is, therefore, significantly dependent on the residual strain of the polymers and the number of cracks on DLC films.

Hoshida *et al*. investigated the adhesion properties of PE coated with thin DLC films.[56] The adhesion force of DLC-deposited PE was found to be 20 times as high as that of nontreated PE. Further improvement in adhesion was observed in F-DLC. By applying fluorine ($C_2F_6$) etching to DLC, the peel strength eventually increased up to a value 60 times higher than that of pure PE without any pretreatment. From the surface observation and experimental results of the surface free energy of modified PE, they surmised that the mechanism behind this phenomenon is principally due to the formation of nanoscale anchors that were formed during the DLC deposition process. Further etching of the PE substrate by fluorine radicals eventually increased the number of the anchors, leading to a significant improvement in the adhesion between PE and F-DLC.

All these experimental results imply that the chemical and physical properties of both DLC and polymers directly affect the properties of highly functionalized DLC-coated polymers. For the future practical use of such DLC-polymer composites, targeting, for example, daily-use products, industrial tools and medical devices, the comprehensive

assessment and profound understanding of the fundamental properties of both DLC and polymers as well as their interaction properties are therefore obviously crucial.

## 9. Summary

We demonstrated that the biocompatibility and haemocompatibility of DLC and F-DLC are excellent. DLC and F-DLC appear to be promising candidate coating materials for blood-contacting devices, such as cardiovascular interventional devices, artificial organs and pacemakers. Further animal and preclinical studies are needed to investigate the biological performance of the F-DLC-coated materials.

In addition, the practical applications of high-gas-barrier DLC films for PET bottles, synthesized by RF-CVD at low pressure, were discussed. The gas barrier properties of the coated bottles were technically improved, leading to the enhancement of the food preservation performance of the bottles. Furthermore, the synthesis of high-gas-barrier carbon films has been developed at atmospheric pressure using APG plasma CVD. From the oxygen transmission testing results, we found that the APG plasma technique can be effectively and practically used for food packaging.

From the experiments of fracture and adhesion behavior, the chemical and physical properties of both DLC and polymers directly affected the properties of functionalized DLC-coated polymers. For the future practical use of DLC-polymer composites, understanding of the fundamental properties of both DLC and polymers, as well as their interaction properties, is crucial.

## References

1) L. A. Thomson, F. C. Law, N. Rushton and J. Franks: Biomaterials **12** (1991) 37.
2) G. Dearnaley: Clin. Mater. **12** (1993) 237.
3) A. Schroeder, G. Francz, A. Bruinink, R. Hauert, J. Mayer and E. Wintermantel: Biomaterials **21** (2000) 449.
4) K. Gutensohn, C. Beythien, J. Bau, T. Fenner, P. Grewe, R. Koester, K. Padmanaban and P. Kuehnl: Thromb. Res. **99** (2000) 577.
5) F. Airoldi, A. Colombo, D. Tavano, G. Stankovic, S. Klugmann, V. Paolillo, E. Bonizzoni, C. Briguori, M. Carlino, M. Montorfano, F. Liistro, A. Castelli, A. Ferrari, F. Sgura and C. Di Mario: Am. J. Cardiol. **93** (2004) 474.
6) H. S. Tran, M. M. Puc, C. W. Hewitt, D. B. Soll, S.W. Marra,V. A. Simonetti, J. H. Cilley and A. J. DelRossi: J. Invest. Surg. **12** (1999) 133.
7) M. Allen, B. Myer and N. Rushton: J. Biomed. Mater. Res. **58** (2001) 319.
8) J. M. Anderson: Prob. Gen. Surg. **11** (1994) 147.
9) A. Dorner-Reisel, C. Schurer, G. Irmer, F. Simon, C. Nischan and E. Muller: Anal. Bioanal. Chem. **374** (2002) 753.
10) R. Hauert: Diamond. Relat. Mater. **12** (2003) 583.
11) S. C. H. Kwok, J. Wang and P. K. Chu: Diamond. Relat. Mater. **14** (2005) 78.
12) J. Y. Ho, T. Matsuura and J. P. Santerre: J. Biomater. Sci. Polym. Ed. **11** (2000)1085.
13) M. Grischke, A. Hieke, F. Morgenweck and H. Dimigen: Diamond. Relat. Mater. **7** (1998) 454.
14) M. Grischke, K. Trojan, H. Dimigen and K. Bewilogua: Surf. Coat. Technol. **74–75** (1995) 739.

15) R. Memming: Thin Solid Films **143** (1986) 279.
16) T. Hasebe, A. Shimada, T. Suzuki, Y. Matsuoka, T. Saito, S.Yohena, A. Kamijo, N. Shiraga, M. Higuchi, K. Kimura, H. Yoshimura and S. Kuribayashi: J. Biomed. Mater. Res. A. **76** (2006) 86.
17) J. M. Courtney, N. M. Lamba, S. Sundaram and C. D. Forbes: Biomaterials **15** (1994) 737.
18) J. I. Sheppard, W. G. McClung and I. A. Feuerstein: J. Biomed. Mater. Res. **28** (1994) 1175.
19) N. B. Holland and R. E. Marchant: J. Biomed. Mater. Res. **51** (2000) 307.
20) N. Nurdin, P. Francois, Y. Mugnier, J. Krumeich, M. Moret, B. O. Aronsson and P. Descouts: Eur. Cell. Mater. **5** (2003) 17.
21) L. Lu, M. W. Jones and R. L. Wu: Biomed. Mater. Eng. **3** (1993) 223.
22) R. Lappalainen, H. Heinonen, A. Anttila and S. Santavirta: Diamond. Relat. Mater. **7** (1998) 482.
23) C. Du, X. W. Su, F. Z. Cui and X. D. Zhu: Biomaterials **19** (1998) 651.
24) S. Affatato, M. Frigo and A. Toni: J. Biomed. Mater. Res. **53** (2000) 221.
25) M. Allen, F. Law and N. Rushton: Clin. Mater. **17** (1994) 1.
26) S. Linder, W. Pinkowski and M. Aepfelbacher: Biomaterials **23** (2002) 767.
27) M. Mohanty, T. V. Anilkumar, P. V. Mohanan, C. V. Muraleedharan, G. S. Bhuvaneshwar, F. Derangere, Y. Sampeur and R. Suryanarayanan: Biomol. Eng. **19** (2002) 125.
28) Z. H. Xu and D. Rowcliffe: Surf. Coat. Technol. **161** (2002) 44.
29) P. D. Maguire, J. A. McLaughlin, T. I. T. Okpalugo, P. Lemoine, P. Papakonstantinou, E. T. McAdams, M. Needham, A. A. Ogwu, M. Ball and G. A. Abbas: Diamond. Relat. Mater. **14** (2005) 1277.
30) T. Saito, T. Hasebe, S. Yohena, Y. Matsuoka, A. Kamijo, K. Takahashi and T. Suzuki: Diamond. Retat. Mater. **14** (2005) 1116.
31) M. N. Babapulle, L. Joseph, P. Belisle, J. M. Brophy and M. J. Eisenberg: Lancet **364** (2004) 583.
32) E. P. McFadden, E. Stabile, E. Regar, E. Cheneau, A. T. Ong, T. Kinnaird, W. O. Suddath, N. J. Weissman, R. Torguson, K. M. Torguson, K. M. Kent, A. D. Pichard, L. F. Satler, R. Waksman and P. W. Serruys: Lancet **364** (2004) 1519.
33) T. Hasebe, Y. Matsuoka, H. Kodama, T. Saito, S. Yohena, A. Kamijo, N. Shiraga, M. Higuchi, S. Kuribayashi, K. Takahahi and T. Suzuki: Diamond. Relat. Mater. **13** (2005) 129.
34) J. A. McLaughlin, B. Meenan, P. Maguire and N. Jamieson: Diamond. Relat. Mater. **5** (1996) 486.
35) G. Bockner: *Proc. Barrier PET Packaging Brussels* (2004) p. 2.
36) A. Shirakura, M. Nakaya, N. Yoshimura and T. Yamasaki: *Proc. 13th IAPRI Conf. Stockholm* (2004) p. 29.
37) D. W. Van Krevelen: *Properties of Polymers* (3rd. edn. Elsevier, Amsterdam, 1990) p. 457.
38) S. Kanazawa, M. Kogoma, T. Moriwaki and S. Okazaki: J. Phys. D: Appl. Phys. **21** (1988) 838.
39) T. Yokoyama, M. Kogoma, S. Kanazawa, T. Moriwaki and S. Okazaki: J. Phys. D: Appl. Phys. **23** (1990) 374.
40) T. Yokoyama, M. Kogoma, T. Moriwaki and S. Okazaki: J. Phys. D: Appl. Phys. **23** (1990) 1125.
41) M. Kogoma, S. Okazaki, N. Kanda, H. Uchiyama and H. Jinno: Proc. Jpn. Symp. Chem. **4** (1991) 345.
42) S. Okazaki, M. Kogoma, M. Uehara and Y. Kimura: J. Phys. D: Appl. Phys. **26** (1993) 889.
43) S. Kanazawa, M. Kogoma, S. Okazaki and T. Moriwaki: Nucl. Instrum. Methods Phys. Res., Sect. B **37–38** (1989) 842.
44) K. Tanaka, T. Inomata and M. Kogoma: Thin Solid Films **386** (2001) 217.

45) M. Kogoma, R. Takahashi and S. Okazaki: Symp. Plasma Sci. Mater. **7TH** (1994) 125.
46) D. C. Agrawal and R. Raj: Acta Metallurgica **37** (1989) 1265.
47) T. Ye, Z. Suo and A. G. Evans: Int. J. Solids. Struct. **29** (1992) 2639.
48) B. F. Chen, J. Hwang, G. P. Yu and J. H. Huang: Thin Solid Films **352** (1999) 173.
49) A. A. Ogwu, T. Coyle, T. I. T. Okpalugo, P. Kearney, P. D. Maguire and J. A. D. McLaughlin: Acta Materialia **51** (2003) 3455.
50) H. W. Choi, K. R. Lee, R. Z. Wang and K. H. Oh: Diamond. Relat. Mater. **15** (2006) 38.
51) S. J. Cho, J. W. Chung and K. R. Lee: Diamond. Relat. Mater. **14** (2005) 1270.
52) Y. Aoki and N. Ohtake: Tribology Int. **37** (2004) 941.
53) B. Ollivier, S. J. Dowey, S. J. Young and A. Matthews: J. Adhes. Sci. Technol. **9** (1995) 769.
54) D. Tsubone, T. Hasebe, A. Kamijo and A. Hotta: Surf. Coat. Technol. **201** (2007) 6423.
55) D. Tsubone, H. Kodama, T. Hasebe and A. Hotta: Surf. Coat. Technol. **201** (2007) 6431.
56) T. Hoshida, D. Tsubone, K. Takada, H. Kodama, T. Hasebe, A. Kamijo, T. Suzuki and A. Hotta: Surf. Coat. Technol. **202** (2007) 1089.