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Diamond-like carbon films for PET bottles and medical applications

Akira Shirakura [a,*], Masaki Nakaya [a], Yoshinori Koga [b], Hideyuki Kodama [c],
Terumitsu Hasebe [c], Tetsuya Suzuki [c]

[a] *Research Laboratories for Packaging, Kirin Brewery Co., Ltd. 1-17-1 Namamugi, Tsurumi-ku, Yokohama, Kanagawa 230-8682, Japan*
[b] *National Institute of Advanced Industrial Science and Technology Umezono, Tsukuba, Ibaraki 305-8561, Japan*
[c] *Center for Materials Science, Keio University School of Science and Technology 3-14-1 Hiyoshi, Kohoku-ku, Yokohama, Kanagawa 223-8522, Japan*

Abstract

The unique properties of diamond like carbon (DLC) film, including its chemical inertness and impermeability, make it possible for new applications in food, beverage and medical market segments. Although these fields involve relatively higher risk for customers, the expected great advantages of DLC films have driven extensive efforts. In this paper, we present our recent results of development in high gas barrier polyethylene terephtalate (PET) bottles for beverage use. We also demonstrate that DLC or fluorinated DLC is a promising candidate coating material for orthopedics implants and blood contacting devices, such as artificial joints, cardiovascular interventional devices, artificial organs and pacemakers.

A unique technique of plasma CVD method has been applied to deposit DLC films on the inside surface of PET bottles. The DLC-coated PET bottle exhibits extremely high gas barrier properties against oxygen, carbon dioxide and flavors compared to conventional bottles. For the practical use of PET bottles as a commodity, high speed and low cost coating are essential and lately our newly developed high speed coating machine has been successfully operated for the large production of hot tea drink bottles.

Keywords: Diamond-like carbon; Gas barrier; PET bottles; Medical applications

1. Introduction

Over the last decade, diamond-like carbon (DLC) has been actively studied in the field of material engineering. DLC consists of dense amorphous carbon or hydrocarbon with high electrical resistivity, high refractive index and chemical inertness. The mechanical properties of this film fall between those of graphite and diamond; possessing a low-friction coefficient, low wear rate, high hardness, excellent tribological properties and excellent corrosion resistance [1,2]. These famous mechanical, electrical, optical and chemical properties have propelled the use of DLC coatings in mechanical and electrical fields. Recently, DLC has been found useful in the food/beverage and biomedical fields due to its excellent properties as a gas barrier and its biocompatibility as well as the many other useful properties of DLC.

The objective of this paper is to review the application of DLC to the food/beverage and biomedical fields. The beverage application is seen in gas barrier coatings for polyethylene terephtalate (PET) bottles, the most important container for beverage products, while the principal biomedical application is found in biocompatible/blood-compatible coatings for medical devices.

2. Background of food and beverage application

The use of plastic containers in the food and beverage market has dramatically increased because they are lightweight, unbreakable, convenient, resealable and they may be clear. PET bottles have gradually replaced glass bottles and metal cans as the most common packaging for liquid foods, such as carbonated soft drinks, tea, water, soy sauce and edible oil. In 1976, PET bottles were first introduced in Japan for soy sauce. Since the first commercial debut in 1978 for the soft drink market in the U.S.A., the total amount of PET bottle usage has rapidly expanded to approximately 250 billion units in the year of 2004, corresponding to 10 million metric tons of PET resin, and a further growth by an average of over 10% annually is expected to reach beyond 300 billion units in 2006 [3].

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* Corresponding author. Tel.: +81 45 521 0072; fax: +81 45 505 3925.
E-mail address: akiras@kirin.co.jp (A. Shirakura).

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Compared to 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. However, PET bottles have a significant limitation in use for sensitive products, such as beer, juice and wine, due to the permeation of gases such as oxygen, carbon dioxide, water vapor and flavors. Both gas ingress and release through the wall of the bottle may have a great impact on the quality of products. For example, oxygen in the air may enter the plastic bottle and accelerate product deterioration such as odor formation and loss of vitamins. Another example is found in the release of carbon dioxide from a plastic bottle filled with a carbonated soft drink. The retention of carbon dioxide level is quite important for carbonated soft drinks to keep fizziness, especially when private size containers are used, because the large surface area relative to the liquid volume allows carbonated beverages to go flat quickly. An excellent way to inhibit the gas movement through plastic packages and protect the product quality is found in the use of materials characterized by small gas permeability. These materials are referred as high gas barrier materials. The existing gas barrier enhancement technologies for PET bottles are generally classified into four major approaches — multilayer, coatings, scavenging agents and composite fortification [4]. Multilayer technology is the present major commercialized approach due to its easy availability for bottle makers; however, it has a relatively small gas barrier improvement, and it presents some difficulties for the PET recycling stream and cost [5].

Coating technology for gas barrier enhancement is relatively new. The advent of coating technologies made possible a product where extreme performance could be achieved with quite thin wall material. Blocking the passage of gas molecules through PET wall (Fig. 1) using ultrathin gas barrier films minimizes the negative impact on the recycling process due to very low level contamination by different materials. Many coating materials have been subjected to practical trials. As a result, diamond-like carbon (DLC) and silicon oxide are the currently favored materials in this industry. DLC is principally formed through plasma enhanced chemical vapor deposition (PECVD) methods, while silicon dioxide is fabricated through sputter deposition, electron beam evaporation (PVD) or PECVD methods [6]. Silicon oxide coating has a longer history than DLC coating for the gas barrier improvement of transparent plastic films, and has been studied using PVD and PECVD techniques since the early 1980s [7,8]. However, the intrinsic brittleness of silicon oxide films requires rather complicated conversion processes in order to withstand mechanical stress and stretching on a PET bottle surface. Recent progress for forming a cushion layer between PET and silicon oxide layer enabled the production of commercial level silica coated PET bottles [9,10]. Recently, high gas barrier PET bottles coated by DLC (more precisely defined as amorphous hydrocarbon (a-C:H)) have been commercially available in the market. Thus, worldwide competition between two superior barrier coating technologies is in progress.

3. Gas barrier properties and the principle of barrier coating

The permeation of gas molecules through a polymeric membrane is a result of combined process of sorption, diffusion and desorption. The permeant passes through thermally fluctuated micro voids existing among tangled polymer chains. The permeability coefficient refers to the number of molecules passing through the film, per unit of time, area, thickness and pressure difference.

$$P = QL/tAp$$

Where P = permeability coefficient ($\mathrm{cm^3 \cdot cm/cm^2 \cdot sec \cdot MPa}$), Q = amount of gas permeated ($\mathrm{cm^3}$ at standard condition), L = averaged thickness of film (cm), t = time (sec), A = permeation area ($\mathrm{cm^2}$), and p = pressure difference (MPa).

The gas barrier property of polymer films is usually expressed in permeability coefficient, while the gas transmission property of PET bottles such as for oxygen and carbon

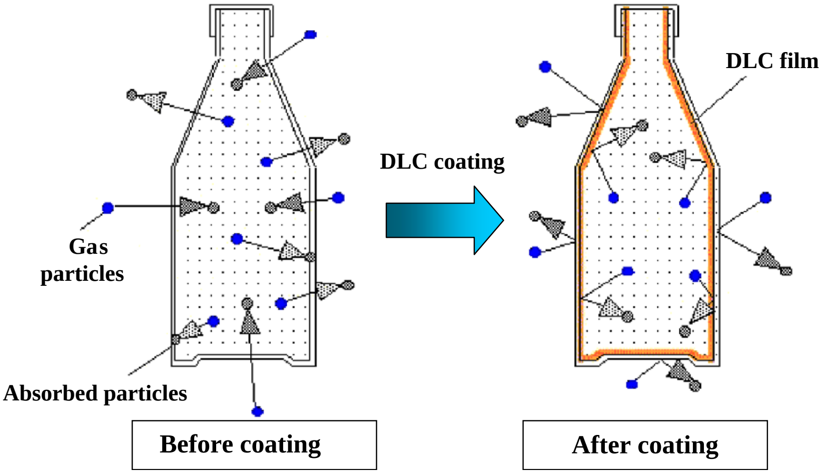

Fig. 1. The gas barrier mechanism of DLC coating on PET bottles. DLC films block the passage of gas molecules. Gas molecules can pass through uncoated plastic, but it is quite difficult to pass through DLC films.

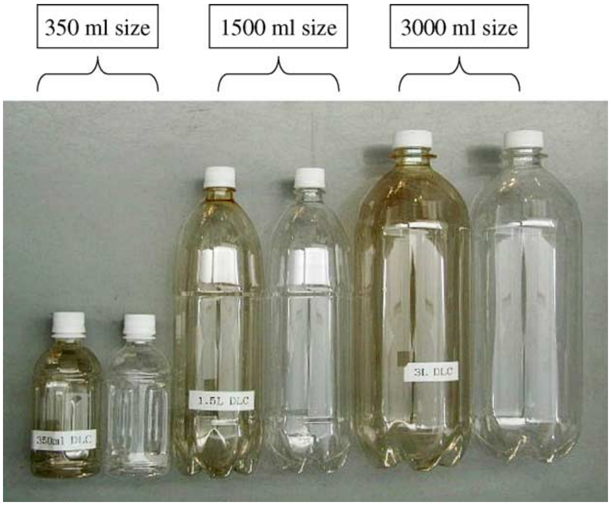

Fig. 2. Examples of DLC-coated PET bottles. For each size, left bottles are DLC-coated and right bottles are uncoated.

Table 1
Physical and chemical properties of Kirin's DLC coating

Surface morphology: quite even and smooth
Thickness: 10–40 nm
Density: 1.2–1.6 g/cm^3
Brittleness: soft enough to follow the bends of PET wall
Color: slightly tinted with brown to gold
Atomic composition: C 55–75 at.% and H 25–45 at.%
Physical structure: amorphous carbon and hydrogen 3D-network
Chemical structure: basically mixture of carbon sp^2 and sp^3 bonds
Binding mechanism to PET substrate: chemical bonds

dioxide is often simply indicated as the gas transmission rate of the whole bottle, for example, in the unit of cm^3/day. bottle. The oxygen transmission rates can be determined using a modification of the ASTM Standard Method D 3985-81 with an Ox-Tran apparatus (Mocon, Inc., Minneapolis, USA) where a coulometric detector detects the permeated oxygen in a stream of dry nitrogen circulating through the system. The carbon dioxide transmission rate is measured by a "dry ice method". PET bottles containing dry ice for the inside pressure of 0.27 MPa are kept at room temperature and measured weight regularly. The loss of carbon dioxide can be calculated from the change in weight.

4. DLC films as a barrier enhancement material for PET bottles

The gas barrier property of DLC films has not been sufficiently investigated, while other fundamental characteristics including high hardness and chemical inertness are well known. Recently, several reports have suggested high gas barrier properties of DLC films on plastic films [11,12]. Kirin

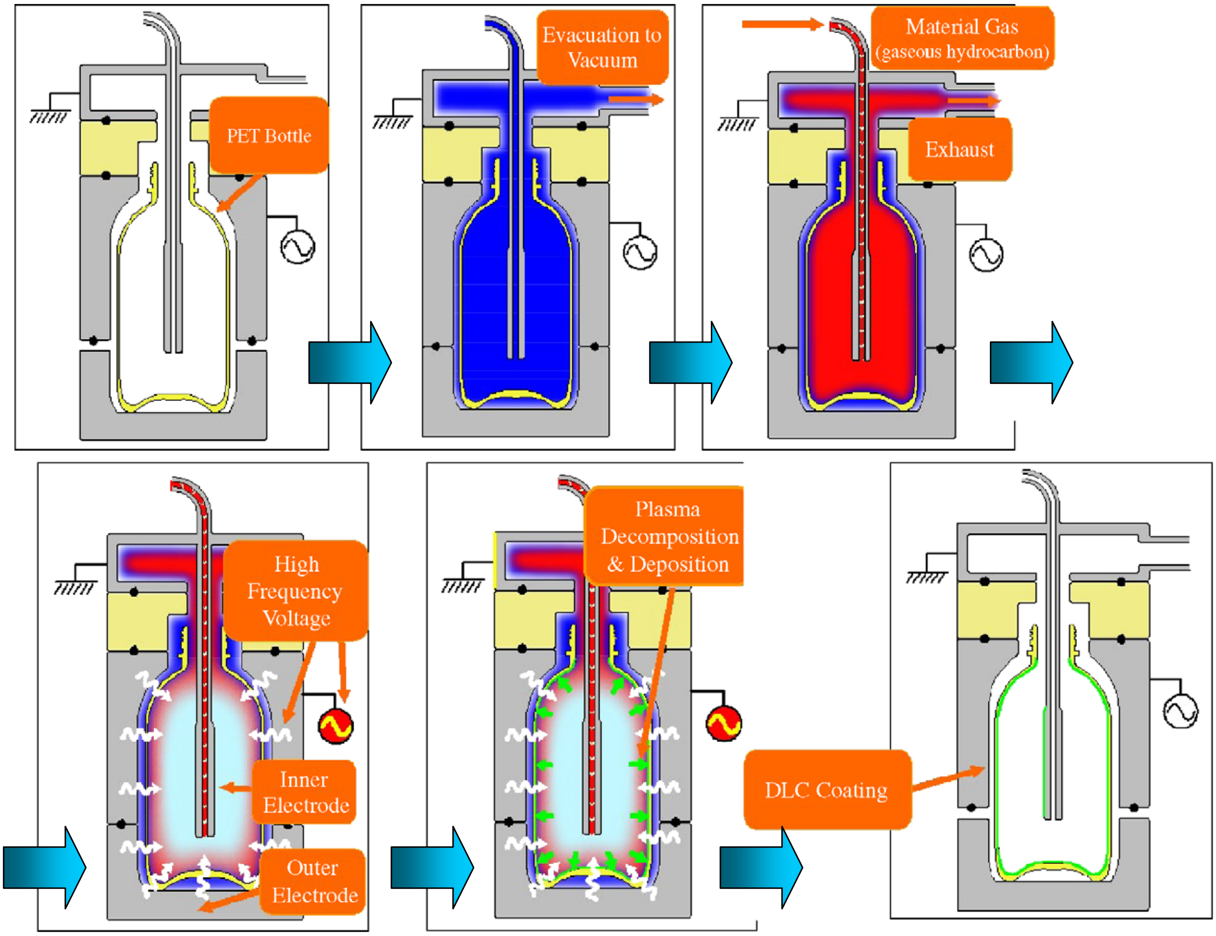

Fig. 3. Process for Kirin's DLC-coated PET bottle. A type of capacitively coupled plasma CVD process is used to coat the inside of PET bottles.

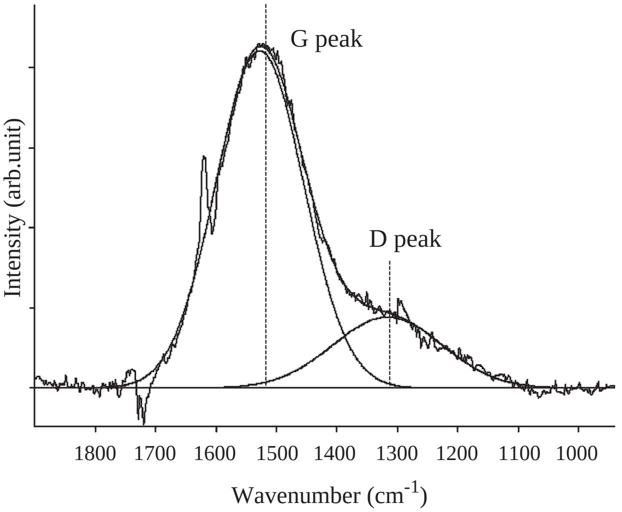

Fig. 4. Raman spectrum of DLC films (subtracted spectrum of DLC coated PET from uncoated PET) using Super LabRAM (Jobin Yvon Ltd.) with 514.5 nm Ar$^+$ laser. The thickness of DLC film was 200 nm.

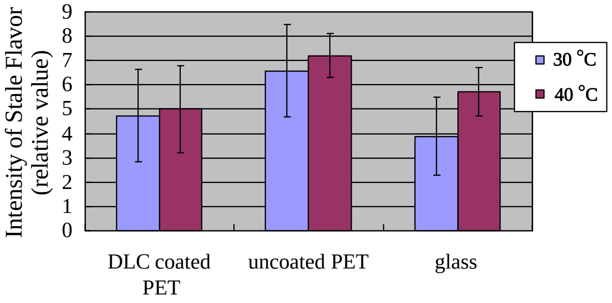

Fig. 5. Stale flavor of beer in DLC-coated PET bottles stored for 2 weeks at 30 °C and 40 °C. For the sensory measurement, the panel consisted of 12 members trained for beer flavor evaluation and scored the stale flavor on a scale from 0 (not perceptible) to 9 (very strong perceptible). The blind samples were assessed by the triangle scoring test. Bars represent standard deviation ($n = 12$).

Brewery Co., Ltd. has developed a unique technology using DLC coating for high gas barrier PET bottles since early 1990s, and succeeded in making the first high barrier DLC-coated PET bottles in 1994 in a cooperative process development with Samco International, Inc. (Fig. 2) [13,14]. The technology was based on a PECVD method under vacuum conditions. Since their first official presentation on the excellent properties of DLC-coated PET bottles in 1997, many machine manufactures have made extensive efforts for the commercialization of high barrier PET bottles using dry vacuum process, which had been formally regarded as an impractical and costly process [15–18].

Kirin's DLC coating process applies the deposition of a very thin DLC film to the inner surface of PET bottles by generating capacitively coupled plasma between specifically designed inner and outer electrodes. The inner electrode is grounded while the outer electrode is connected to the power supply. As schematically shown in Fig. 3, the first step of the process is to place a bottle in a vacuum chamber that functions as the outer electrode. Radio frequency power of 13.56 MHz is then applied to the outer electrode to generate a low temperature plasma state of hydrocarbons while acetylene (C_2H_2) gas is injected into the bottle. The ions and radicals react to deposit on the inner surface of the bottle in a negative self-bias potential over the outer electrode.

The advantages of the use of DLC film for PET bottles are primarily derived from its flexible nature along with its high gas barrier property and chemical inertness. The physical and chemical properties of Kirin's DLC coating are summarized in Table 1. The composition of Kirin's DLC coating was obtained in the combination of elastic recoil detection analysis (ERDA) and Rutherford backscattering analysis (RBS). The result shows relatively high hydrogen content for DLC films. This ensures excellent adhesion and crack resistance. The amorphous identity of Kirin's DLC was also confirmed in Fourier transform infrared absorption (FT-IR) measurement (data not shown) and transmission electron microscopy (TEM) observation (data not shown). These results indicate that the DLC coating obtained is basically composed of a three-dimensional amorphous carbon and hydrogen network [19,20]. Fig. 4 shows that a typical Raman spectrum of the DLC film consists of a relatively sharper peak at 1530 cm (the G peak) and a broad shoulder peak at 1350 cm (the D peak). The relatively low area ratio of a two Gaussian fit (the area of the G line over the area of the D line) and the lower shifted G position suggests that the DLC film has a mixture of sp^2 and sp^3 bonding structures [21–23]. Microscopic observation revealed the surface of the DLC film is smooth and the

Table 2
Thermal gas barrier properties of PET bottles

	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		0.0035		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/package·day·0.21 atm; CO_2TR g/package·day·atm.

[a] Barrier improvement factor (BIF) refers to the reciprocal ratio of transmission rate of DLC-coated bottle compared to uncoated bottle.

[b] Apparent activation energy for the permeation process.

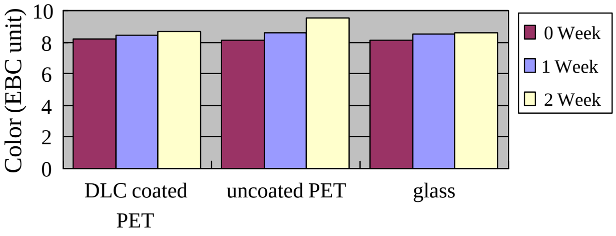

Fig. 6. Color of beer stored at 40 °C in DLC-coated PET bottles. The color of beer was measured by ultraviolet/visible spectrometry. The absorbance of 430 nm (A_{430}) was calculated to the EBC unit using the EBC standard method as follows [26]: Color (EBC units) = $A_{430} \times 25$.

Table 3
Coating conditions for Kirin's DLC-coated PET bottles

Pressure: 1–100 Pa
Power frequency: 13.56 MHz
Power input: 250–2500 W
Material gas: hydrocarbon gas
Gas flow rate: 30–300 sccm
Coating time: 0.5–5 sec
Bottle shape: practically any
Bottle volume: up to 3000 ml

thickness ranges from 10 nm to 30 nm for 2.0 sec of coating, depending on coating conditions.

5. Gas barrier property of DLC-coated PET bottles

Table 2 shows the oxygen transmission rate (OTR) and carbon dioxide transmission rate (CO_2TR) of DLC-coated bottles at different temperatures. Gas barrier properties of DLC-coated PET bottles were significantly improved as expressed in the numbers of barrier improvement factor (BIF).

As the temperature increased, DLC-coated and uncoated bottles showed lower barrier properties both for OTR and CO_2TR. This result shows that, although DLC coating is known as a thermally stable material, thermal molecular movement has an influence on the gas permeation property of the whole coated bottle [24]. Table 2 also shows the values of activation energy, E_p, determined in an Arrhenius plot, for the gas transmission, indicating that the DLC coating layer improved thermal stability to the barrier property of the whole bottle [25]. Since the DLC coating layer has a high thermal stability, the E_p values for the whole DLC-coated bottle were 50% to 70% of those for the whole uncoated bottle.

6. Evaluation of the food preservation performance of DLC-coated PET bottles

As indicated in Table 2, the DLC coating provided quite a high level of gas barrier enhancement, and the DLC-coated bottles were comparable to glass bottles in terms of quality protection against gas permeation. Based on the results of sensory evaluation and chemical analysis as shown in Figs. 5 and 6, respectively, the DLC-coated PET bottles proved an excellent quality retention performance comparable to glass bottles. This supports that the DLC coating can provide a sufficient property for the use of beer, one of the most sensitive product to oxygen permeation in the PET bottle market [27].

The coating of the DLC film on the inside surface of the PET bottle preserves fresh flavors of products because the film prevents the sorption and migration between bottle wall and contents. The sorption test using various aroma components showed that the sorption amount in DLC-coated PET bottles was only 5% to 10% of that in uncoated PET bottles [28]. As partially described above, the chemically inert nature of the DLC coating can provide safe and long shelf life with food and beverage.

7. Current commercialized coatings for high barrier PET bottles

In the commercial coating process using a PECVD method for PET bottles, a great number of process parameters related to each other must be controlled including raw material gas rate, gas pressure, input power, and dimensions of electrodes. These parameters are required to be set differently depending on the size and shape of bottles and the barrier requirement for

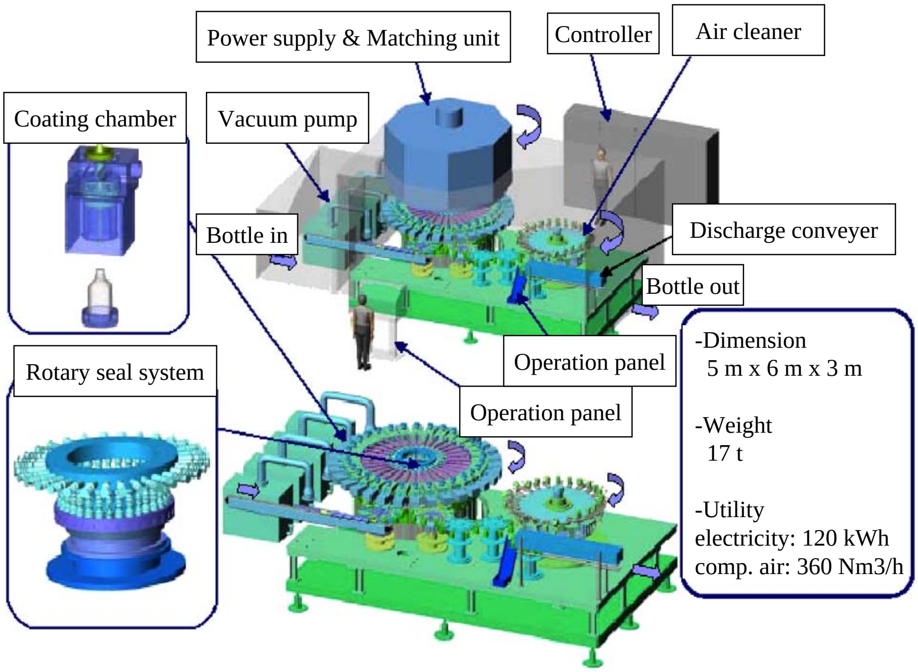

Fig. 7. Commercialized DLC coating machine for PET bottles. The machine components and arrangement are shown schematically for ease. The actual system coats 18000 PET bottles per hour.

products. Typical coating conditions of Kirin's DLC coating are shown in Table 3. A high-speed commercial DLC coating machine of this technology, manufactured by Mitsubishi Heavy Industries, Inc., is schematically shown in Fig. 7. This machine has a capacity of 18,000 bottles per hour and has been in operation. It automatically monitors the operating conditions including chamber pressure, input and scattered power profiles, gas flow rate, and photoemission in order to ensure product quality [29,30].

Sidel Inc. has developed another type of DLC coating technology: Actis (amorphous carbon treatment on internal surface) [17]. It also uses acetylene gas as a source of carbon coating. A microwave-assisted process excites the gas into plasma, which deposits a layer of carbon about 0.15 μm thick on the inside of the bottle. Sidel claims that Actis increases the carbon dioxide barrier of PET bottles by up to seven times. Toyo Seikan Kaisha Ltd., Toppan Printing Co., Ltd., and SIG Corpoplast GmbH Co. have developed silicon dioxide coatings using PECVD methods. Interestingly, all of these commercially successful coatings are applied to the inside of bottles, while several unsuccessful coating technologies have tried to coat the outside of them [16]. In this way, Kirin's DLC coating has derived into other practical high barrier coating technologies for food and beverage containers.

8. Diamond-like carbon coatings for medical applications

Biomedical devices have proven to be effective for treating diseases and organ insufficiencies in the aging population. 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 [31]. Carbon is generally well tolerated in the body. 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 [32]. Thrombogenic complications also remain as one of the main problems for blood-contacting devices, such as cardiovascular and interventional devices (stents, guide wires and catheters), and artificial organs. 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 hemocompatibility 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. Thus, there has been substantial interest in developing ways to modify the surfaces of metal and polymer implants to increase biocompatibility.

A number of promising results for the surface modification by DLC coatings have been obtained in vitro and in vivo preclinical studies. For examples, 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 [1,33–41] and in animal models [32,38]. DLC coating is therefore being considered for widespread use as a surface coating for coronary stents [42–44], heart valves [45] and orthopedic implants [38] in clinical situations.

One of the major limitations of this coating technology is micro-cracks on the surfaces [46]. In coatings with high internal stress, interface cracks can lead to the complete delamination of the coating. The flaking of DLC coatings was usually observed not on the polymer substrates, but especially on the metal substrates due to the poor adhesion and cracking. The crack spacing was observed to increase with thickness, tending to saturation beyond ~500 nm [47]. The DLC coatings must therefore be optimized in order to minimize the risk of film breakdown. Doping with some elements into DLC films or the use of a-Si:H/a-Si:C:H interlayer possibly helps minimize the risk of a 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 [33,48]. 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 [49]. It has been reported that the incorporation of fluorine into the DLC film greatly reduces its surface energy [50,51] and film hardness but largely preserves other DLC properties [52]. The elastic features of fluorinated diamond-like carbon (F-DLC) would be advantageous for coating three-dimensional medical devices.

Recently, we have reported quantitative and morphological studies on platelet adhesion to DLC films or F-DLC-coated silicon (Si) and bare Si substrates incubated in platelet-rich

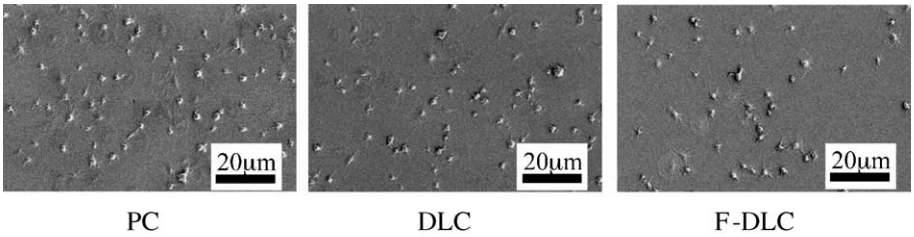

Fig. 8. Platelet adhesion and activation on PC (polycarbonate), DLC and F-DLC observed by SEM. Each material is incubated with human platelet-rich plasma (PRP) for 60 min under 5% of CO_2 at 37 °C.

plasma [53]. In that study, it was found that F-DLC showed the best antithrombogenicity among the tested samples. In addition, F-DLC coating reduced the number of platelets, and also inhibited platelet activation on the film surface with statistical significance. We have also confirmed the same tendency of platelet attachment and activation on DLC or F-DLC films deposited on polymers as when using Si substrates (Fig. 8). Our data demonstrate that F-DLC is a promising candidate coating material for blood contacting devices, such as cardiovascular interventional devices, artificial organs and pacemakers.

9. Conclusions

DLC films containing a certain amount of hydrogen can provide the following advantages to PET bottles.

1. Gas barrier properties: blocks oxygen and carbon dioxide passing through bottles.
2. Flavor barrier: blocks migration and sorption between bottles and products.
3. UV barrier: increase absorbance of ultraviolet ray.
4. Chemical inertness: chemical stability with no interaction with contents.
5. Recycleability: no obstacle to the recycling process for PET resin.
6. Others: maintaining existing benefits of PET bottles economically.

The future of DLC coatings for food and beverage containers can be considered in view of market needs and technical development. In both aspects, further use of DLC coatings seems promising. The potential market for high barrier PET bottles lies widespread and worldwide, including the large market of beer, juice, wine and carbonated soft drinks, and is estimated to be 10% of the whole PET bottle market, approximately 30 billion units. At present, in Japan, DLC-coated PET bottles for hot tea drinks have been sold in the market, and 50 million units of such bottles will come into the market in the year of 2005. Future market needs are also promisingly found in high barrier containers made of plastics instead of PET. The candidate plastics include polyethylene, polypropylene and biodegradable plastics. These plastics are used in large quantities; however, they often have poor barrier properties.

From the technical perspective, a DLC film less than 10 nm thickness is expected to achieve sufficient barrier improvement of PET bottles. This thin structure would exhibit much more colorless clarity than the current structure with slightly tinted color, which limits the applications of the current DLC products to some specific product categories [54]. The current vacuum process is another drawback in the present market since the achievement of process vacuum requires high capital investment, long process time (decreased throughput), and wide space occupation due to pumps and other systems. Atmospheric plasma treatment may solve this problem. In our laboratory scale trial, remarkably high barrier DLC coating was successfully obtained using an atmospheric plasma method (data not shown).

Thus, the future development of DLC coatings is expected to improve the performance and cost effectiveness, and subsequently to contribute towards broader applications of plastic containers for food and beverage.

The future use of DLC and modified DLC coatings seems promising in the medical field. The short-term data on DLC and modified DLC coatings obtained so far in in vitro and in vivo experiments indicate that their biocompatibility and hemocompatibility are excellent. The investigation of their long-term biological performance is further required before being able to use them in practical applications.

References

[1] L.A. Thomson, F.C. Law, N. Rushton, J. Franks, Biomaterials 12 (1991) 37.
[2] G. Dearnaley, Clin. Mater. 12 (1993) 237.
[3] D.H. Witte, Proceedings of Nova-Pack Europe 2003, Munich, 2003, p. 39.
[4] G. Bockner, Proceedings of Barrier PET Packaging, Brussels, 2004, p. 2.
[5] BDA, Inc., Barrier-Enhancing Technologies for PET and Polypropylene Containers and Closures, Packaging Strategies, West Chester, A, 2002, p. 8.
[6] G. Czeremuszkin, M. Latreche, M.R. Wertheimer, A.S. da Silva Sorbrinho, Plasmas Polym. 6 (1/2) (2001) 107.
[7] T. Krug, Society of Vacuum Coaters, Procedings of 33rd Ann. Tch. Conf., 1990, p. 163.
[8] T. Krug, R. Ludwig, G. Steiniger, Socs. of Vac. Coaters, 36th Annual Tech. Conf. Proc., 1993, p. 302.
[9] Commercial report from Eastapac Company, QLF Coating for Rigid Plastic, (1991).
[10] Toyo Seikan Kaisha, JP2003328131A2.
[11] S.P.J. Higsin, P.M. Vadgama, Anal. Chim. Acta 300 (1995) 77.
[12] D.S. Finch, J. Franks, N.X. Randall, A. Barnetson, J. Crouch, A.C. Evans, B. Ralph, Packag. Technol. Sci. 9 (1996) 73.
[13] Kirin Brewery, JP08053116A2.
[14] Kirin Brewery, Samco International, JP2788412.
[15] E. Shimamura, K. Nagashima, A. Shirakura, Proceedings of 10th IAPRI Conference, Melbourne, 1997, p. 251.
[16] THE COCA-COLA COMPANY, WO0008226A2.
[17] SIDEL, WO9949991A1.
[18] K. Matsuoka, T. Kakemura, H. Kashima, T. Seki, M. Tsujino, Proceedings of 12th IAPRI Conference, East Lansing, USA, 2004, p. 393.
[19] A. Shirakura, 6th Pan Asian PET Markets '99 Conference Proceedings, Singapore, 1999, p. 1920.
[20] A. Kimura, H. Kodama, T. Suzuki, J. Vac. Sci. Technol., A, Vac. Surf. Films 21 (2) (2003 Mar/Apr) 515.
[21] A.C. Ferrari, J. Robertson, Phys. Rev., B 61 (2000) 14095.
[22] M. Yoshikawa, G. Katagiri, H. Ishida, A. Ishitani, T. Akagi, J. Appl. Phys. 64 (1999) 6464.
[23] H.C. Tsai, D.B. Bogy, M.K. Kundmann, D.K. Veirs, M.R. Hilton, S.T. Mayer, J. Vac. Sci. Technol., A, Vac. Surf. Films 6 (1988) 2307.
[24] A. Shirakura, M. Nakaya, N. Yoshimura, T. Yamasaki, Proceedings of 13th IAPRI Conference, Stockholm, 2004, p. 29.
[25] D.W. Van Krevelen, Properties of Polymers, Elsevier, 1990, p. 457.
[26] Analytica-EBC, 4th ed., 8.3, (1987), E131.
[27] M. Nakaya, World Brewing Congress Proceedings, San Diego, USA, 2004, p. 143.
[28] K. Hosoe, T. Matsui, M. Shimoda, Y. Osajima, E. Shimamura, A. Shirakura, The 44th Proceedings of Japan Food Engineering Society, 1997, p. 146.
[29] Packaging Strategies, October 15, 2003, p. 7.
[30] A. Shirakura, T. Shono, Proceedings of Nova-Pack Europe 2003, Munich, 2003, p. 275.

[31] J.M. Anderson, Probl. Gen. Surg. 11 (1994) 147.
[32] M. Mohanty, T.V. Anilkumar, P.V. Mohanan, C.V. Muraleedharan, G.S. Bhuvaneshwar, F. Derangere, Y. Sampeur, R. Suryanarayanan, Biomol. Eng. 19 (2002) 125.
[33] R. Hauert, Diamond Relat. Mater. 12 (2003) 583.
[34] L. Lu, M.W. Jones, R.L. Wu, Biomed. Mater. Eng. 3 (1993) 223.
[35] R. Lappalainen, H. Heinonen, A. Anttila, S. Santavirta, Diamond Relat. Mater. 7 (1998) 482.
[36] A. Schroeder, G. Francz, A. Bruinink, R. Hauert, J. Mayer, E. Wintermantel, Biomaterials 21 (2000) 449.
[37] C. Du, X.W. Su, F.Z. Cui, X.D. Zhu, Biomaterials 19 (1998) 651.
[38] M. Allen, B. Myer, N. Rushton, J. Biomed. Mater. Res. 58 (2001) 319.
[39] S. Affatato, M. Frigo, A. Toni, J. Biomed. Mater. Res. 53 (2000) 221.
[40] M. Allen, F. Law, N. Rushton, Clin. Mater. 17 (1994) 1.
[41] S. Linder, W. Pinkowski, M. Aepfelbacher, Biomaterials 23 (2002) 767.
[42] I. De Schroerder, M. Szilard, H. Yanming, X.B. Ping, E. Verbeken, D. Neerinck, E. Demeyere, W. Coppens, F. Van de Werf, J. Invasive Cardiol. 12 (2000) 389.
[43] K. Gutensohn, C. Beythien, J. Bau, T. Fenner, P. Grewe, R. Koester, K. Padmanaban, P. Kuehnl, Thromb. Res. 99 (2000) 577.
[44] 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, C. Di Mario, Am. J. Cardiol. 93 (2004) 474.
[45] H.S. Tran, M.M. Puc, C.W. Hewitt, D.B. Soll, S.W. Marra, V.A. Simonetti, J.H. Cilley, J. DelRossi, J. Invest. Surg. 12 (1999) 133.
[46] Z.-H. Xu, D. Rowcliffe, Surf. Coat. Technol. 161 (2002) 44.
[47] P.D. Maguire, J.A. McLaughlin, T.I.T. Okpalugo, P. Lemoine, P. Papakonstantinou, E.T. McAdams, M. Needham, A.A. Ogwu, M. Ball, G.A. Abbas, Diamond Relat. Mater. 14 (2005) 1277.
[48] A. Dorner-Reisel, C. Schurer, G. Irmer, F. Simon, C. Nischan, E. Muller, Anal. Bioanal. Chem. 374 (2002) 753.
[49] J.Y. Ho, T. Matsuura, J.P. Santerre, J. Biomater. Sci., Polym. Ed. 11 (2000) 1085.
[50] A. M.Grischke, F. Hieke, H. Morgenweck, Diamond Relat. Mater. 7 (1998) 454.
[51] M. Grischke, K. Bewilogua, K. Trojan, H. Dimigen, Surf. Coat. Technol. 74–75 (1995) 739.
[52] R. Memming, Thin Solid Films 143 (1986) 279.
[53] T. Saito, T. Hasebe, S. Yohena, Y. Matsuoka, A. Kamijo, K. Takahahi, T. Suzuki, Diamond Relat. Mater. 14 (2005) 1116.
[54] S. Yamamoto, H. Kodama, T. Hasebe, A. Shirakura, T. Suzuki, Diamond Relat. Mater. 14 (2005) 1112.