A Thesis for the Degree of Ph. D. in Engineering

Application of gas barrier thin films to three-dimensional polymer packages

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Abbreviation

3APTMS:	3-aminopropyltrimethoxysilane
BIF:	barrier improvement factor
Cat-CVD:	catalytic chemical vapor deposition
cc (STP):	cubic centimeter at standard temperature and pressure
CVD:	chemical vapor deposition
DLC:	diamond-like carbon
ERDA:	elastic recoil detection analysis
FTIR:	Fourier transform infrared spectroscopy
HMDSN:	hexa-methyl-di-silazane
HMDSO:	hexa-methyl-di-siloxane
MAP:	modified atmospheric packages
OTR:	oxygen transmission rate
PACVD:	plasma-assisted chemical vapor deposition
PE:	poly(ethylene)
PET:	poly(ethylene terephthalate)
PLA:	poly(lactic acid)
PP:	poly(propylene)
PVD:	physical vapor deposition
sccm:	cubic centimeter under standard temperature and pressure per minute
SEM:	scattering electron microscope
SiOC:	thin film(s) composed of silicon, oxygen, carbon and hydrogen
SiN_x:	silicate nitride (x refers to number.)
SiO_x:	silicate oxide (x refers to number, often somewhere between 1.5 and 1.8.)
TEM:	transmission electron microscope
VS:	vinylsilane
XPS:	X-ray photoelectron spectroscopy

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Chapter 1

Preface

1.1 Packaging

A definition of packaging is a coordinated system of preparing goods for transport, distribution, retailing and use [1)], and packages can be defined as specific materials for the system. Because this system is used in numerous industries and products, the common functions of packages are categorized in several manners [1-3)]. Containment and preservation are, however, always among the most important functions, along with transportation, communication, etc. Fig. 1-1 shows the package examples of beer industry [4)].

Fig. 1-1. Example of beverage packages.

The containment and preservation of beverage and food are essential for human daily life, which is supported by the fact that ancient cultures had already used specific packages for beverage and foods with their accessible techniques. While a wide variety of the materials and formats of packages are used based on the nature of products and their supply chains, modern beverage and food packages mainly tend to employ polymer (plastics), metal, glass, and paper materials [5)] as shown in Fig. 1-2.

Fig. 1-2 also shows that beverage and food packages can be categorized into rigid and flexible packages. The former is often composed of three dimensional containers and closures in contact with the contents of beverage and food. The reasons of the use of rigid packages can be found in anti-pressure strength required for carbonated beverages, and also in fast and economical production. Even though metal cans are able to provide a higher throughput in today's industry, polymer containers, especially made of poly(ethylene terephthalate) (PET), are also widely used based on unique properties of polymer materials, such as high shapeability, transparency, and softness for sealing and unbreakable performance. Based on these properties, the usage of polymer packages has been in a growing trend, leading to the increase of their importance.

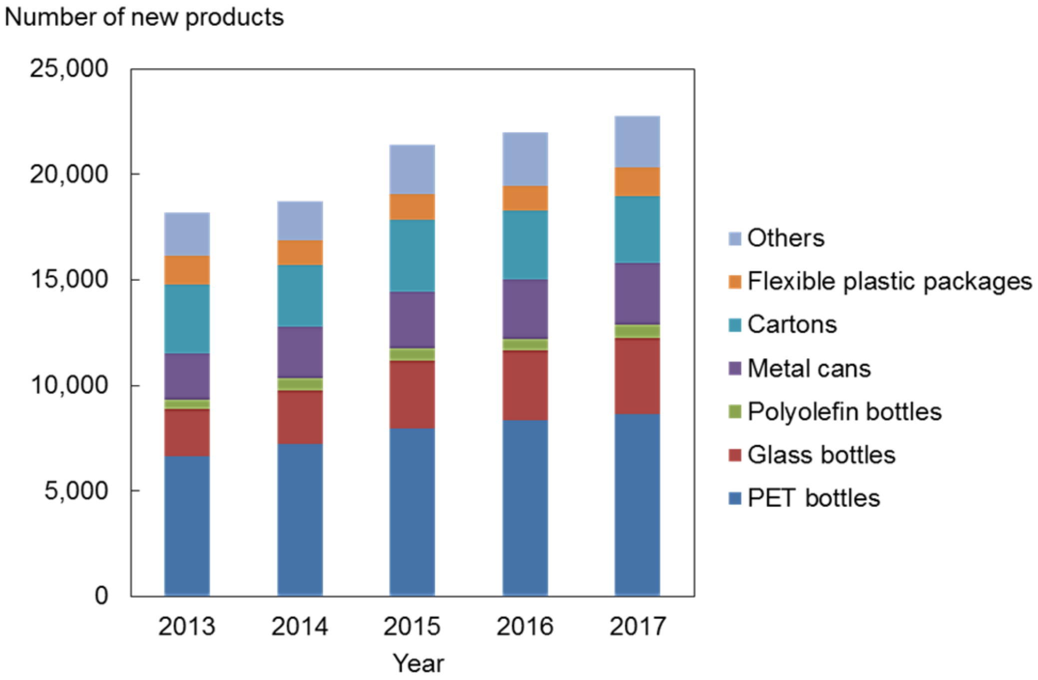


Fig. 1-2. Global new products of packaged beverage by materials (statistical data provided by courtesy of Mintel Japan, Inc.)

1.2 Permeation and polymer packages

In beverage and food preservation, permeation is a significantly important phenomenon for polymer rigid packages as well as polymer flexible packages. Due to the nature of polymeric matrix, even a continuous polymer film or container allows gas molecules to pass from one side to another as long as the difference in the concentration of the gas species exits between both sides.

While a high permeability of gas molecules is not necessarily harmful for beverages and foods in polymer packages as seen in modified atmospheric packages (MAP) 6), a low permeability is often aimed in rigid containers because the passage of oxygen, carbon dioxide, and water vapor (and sometimes flavor components) through polymer materials tends to deteriorate the quality of the contents of beverage and food.

In this context, the property for inhibiting the passage of gas molecules is called gas barrier property, and an intended result through a specification or treatment for a higher gas barrier property is called gas barrier enhancement.

1.3 Goals of gas-barrier-enhanced polymer packages and thin film approach

One major goal of the gas barrier enhancement of polymer packages is to achieve the above-mentioned performance. The gas barrier property of the package must satisfy requirements for the quality of a product, for example, satisfactory flavor for consumers and sufficient shelf-life for retailers.

Another major goal also lies in sustainability. For a sustainable use of product, the products need to use technologies which are acceptable from social, environmental, and economical standpoints. For instance, the social acceptance includes an available recycling infrastructure and scheme, and the environmental acceptance demands material savings and so-called eco-friendly/recyclable materials along with the economical acceptance.

In order to achieve these goals, thin film formation for gas barrier polymer packages is considered as the most promising approach. As described later, quite a small amount of thin film materials used in the whole polymer materials in the finished packages provide a unique position to this approach, where a high functional improvement, a high recyclability, and a low material cost can be expected to a degree that other types of approach cannot follow, especially in rigid polymer packages.

1.4 Function of thin films on gas barrier polymer packages

While the primary target of thin film formation in this paper is gas barrier enhancement of three dimensional polymer packages, it should be noted that other types of modification to polymer properties can be expected through the use of thin films on polymer materials.

An example can be found in PET bottles. Fig. 1-3 shows typical interactions between a PET bottle and its beverage product [7)]. In addition to gas permeation, sorption tends to cause flavor loss from the contents of beverage and food. An enhanced anti-sorption property inhibits the sorption of the content molecules onto the inner surface of the bottle and the closure, leading to a higher flavor stability of the product, along with an impact on gas permeation. Migration also tends to cause off-flavor to the contents of beverage and food. Because polymer materials usually involve by-products in their synthetic processes and intentional additives, thin films can inhibit the migration of these substances into the content.

Another example can be found in a flexible package where an aluminum thin film not only increases gas barrier, but also shields light transmission.

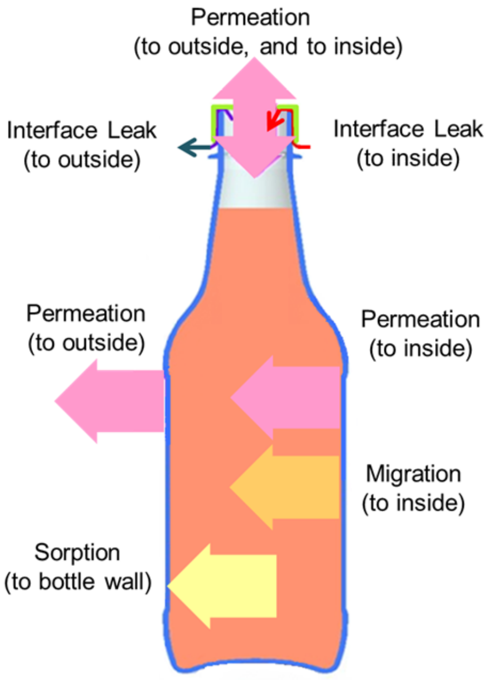


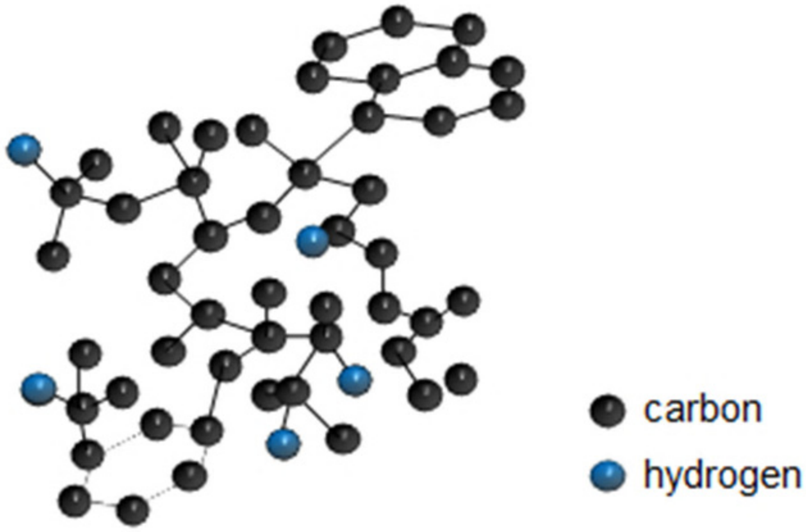
Fig. 1-3. Typical interactions between a PET bottle and its beverage product.

1.5 Methodology of thin films applied to polymer packages

A thin film used for a polymer package is usually formed as a coating, that is, the surface of polymer substrate was exposed to thin film formation treatment after the preparation of the polymer substrate.

The treatment can be classified into (A) physical vapor deposition (PVD) and (B) chemical vapor deposition (CVD) techniques. A typical example of PVD for gas barrier packages is electron beam evaporation 8). Also, a typical example of CVD is plasma-assisted chemical vapor deposition 9). It should be stressed that while various techniques both of PVD and CVD can be seen in flexible packages, quite limited techniques can be seen in rigid packages such as PET bottles. This is because direct coating onto three dimensional objects involves a technical difficulty in fast and evenly distributed deposition, compared to coating onto flat substrates. Coating techniques for rigid packages are, however, highly demanded with the spread of blow molding processes 10)

As described later, only PACVD technologies are available for coating polymer containers in today's beverage and food industry. In these technologies, carbon (often called diamond-like carbon, DLC) 11, 12) and silicon oxide (SiO_x) 13, 14) thin films (see Figs. 1-4 and 1-5) are applied to PET bottles. With a gradual spread of products using these thin film applications, further technical advancements leading to more product variety and improved cost performance are expected among this industry.



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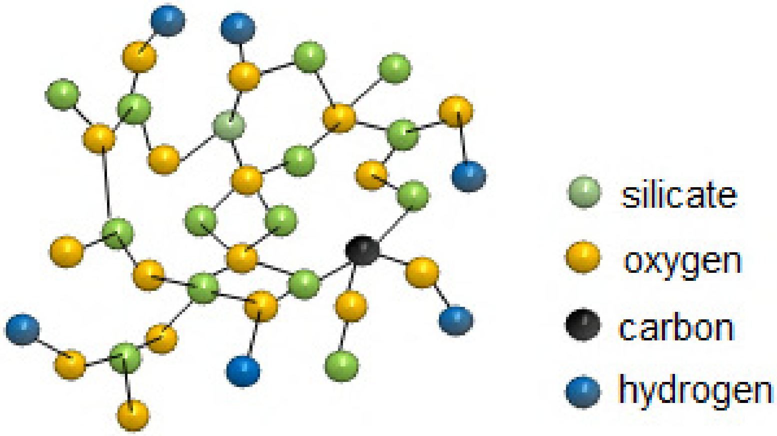

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1.6 Purpose of this paper

Based on the technical and market background as describe above, new technical methods were studied to widen the practical applications of thin film coating to polymer rigid packages. In this study, most of description in this paper was focused on PET bottle format for beverage because of the industrial scale of this format. Discussions of this study are, however, not limited to the bottle format nor the beverage category, and can be generally applied to other package formats and categories such as food containers.

In chapter 2, a general view of the state-of-art in coated polymer rigid packages is described. Also, issues for further practical applications are mainly discussed on the expected target (i.e. colorless and physico-chemically stable) of novel thin films for gas-barrier-enhanced PET bottles, and on approach to form gas barrier thin films on polymer substrates other than PET packages. Especially, new findings on DLC thin films formed on different polymer films are described based on the result of positron annihilation analysis. The result suggested homogenous coatings were formed on all of the used films in spite of their significant difference in the performance of gas barrier improvement.

In chapters 3 and 4, advanced coating conditions using conventional DLC thin films are studied. Chapter 3 describes the methodology to optimize power frequency applied to electrodes for the generation of plasma in the inside of a bottle. The results of the combination of elastic recoil detection analysis (ERDA) and positron annihilation analysis indicated the homogeneity of DLC thin films among the used different power frequencies. Also, the results of the measurement of oxygen transmission rate and coloring of the coated PET bottles indicated power frequency caused change in spatial distribution of plasma inside the bottle, probably due to balance between primary and secondary electrons generated with different frequencies. Chapter 4 describes the reason of the demand for gas barrier enhancement of polymer closures used with gas-barrier-enhanced PET containers, and a practical methodology to form a high gas barrier DLC thin film onto the inner surface of a polyethylene (PE) closure is described.

In chapters 5 and 6, a novel approach to the above-mentioned target (gas barrier coating with colorless and physico-chemically stable thin films) was attempted. A unique method to coat a PET bottle using a hot wire CVD technique and the evaluation of the obtained thin films composed of silicon, oxygen, carbon and hydrogen (SiOC thin films) were described. Interestingly, these films showed the respective advantageous properties of both DLC and SiO_x coatings on PET bottles, where the oxygen and carbon dioxide barrier properties and stability in contact with water of these films were equivalent to DLC films while appearance was virtually colorless like SiO_x films. Chapter 5 describes the first attempt to apply a hot wire CVD technique specifically for coating the inner surface of PET bottles. The resultant thin film was characterized from the viewpoints of performance for PET bottles. The Chapter 6 describes the procedure and result of screening experiments for useful combinations of wire and material gas species. As a result, molybdenum or tantalum wire and vinylsilane gas was selected as the candidate combination for the mass production of coated PET bottles.

In chapter 7, possible advancement of both DLC and SiOC coatings studied in this paper is discussed from the viewpoints of the advantages of each performance and corresponding machinery. For the recent demand of the gas barrier enhancement of relatively large polymer containers like PET kegs, the DLC coating is considered favorable because the use of plasma is likely to provide more efficient means, and the tint of the coated containers is less important for products filled in the containers of this size. For typical personal size polymer containers like PET bottles, economical machinery and colorless appearance facilitate the spread of SiOC coating in the beverage and food industry. From a standpoint of coating to various polymer substrates, a novel approach to successive wet undercoat with organic silicon as an instance and thin film topcoat using either a PACVD or hot wire CVD technique is another target of further study.

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Chapter 2

General Review and Future Technical Targets in Gas Barrier Thin Film Coatings on PET Bottles in Beverage and Food Applications

2.1 Introduction

2.1.1 General introduction

Polymer materials have unique properties, such as being easy to shape, and are elastic to physical impacts compared to other types of materials, like metal, glass, and ceramics, and nowadays quite a wide variety of plastic containers are seen in the food and beverage industry. For example, poly(ethylene terephthalate) (PET) bottles are the most widely used package format in the soft drink segment and further use of PET bottles is expected both inside and beyond the soft drink segment 1,2).

From the view of package performance, light-weight, unbreakable, and transparent properties are favorable advantages of common plastic containers. To the contrary to these consumer benefits, gas permeability is a remarkable disadvantage of plastic containers compared to metal and glass containers 3), which virtually eliminate gas permeation, except sealing parts where polymer materials are usually used. It should be mentioned that, in this paper, the term of weight is used for expressing the mass of packages.

Especially, the permeation of oxygen and carbon dioxide molecules often limits the shelf-life of sensitive products. One of the most sensitive products to gas permeation is beer. Beer is quite sensitive to oxidation, and also sensitive to carbon dioxide release. From the view point of shelf-life extension, the degree of gas barrier improvement is often expressed by BIF (barrier improvement factor) 4). The value of BIF can be calculated based on the gas transmission rate of normal container(s) divided by that of barrier improved container(s). Although this calculation provides a relative value, the result is often expressed in time(s) in this field, for the perceptual ease of the possible extendable period of product shelf-life. In this paper, BIF values are expressed as relative values. Empirically, PET bottles of single serve size require 10 or more oxygen barrier in BIF for a realistic shelf-life of beer. Furthermore, they require seven or more carbon dioxide barrier in BIF if the equivalent shelf-life in glass bottles is demanded.

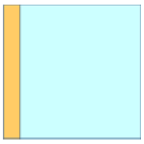
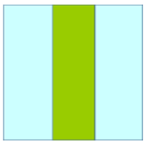
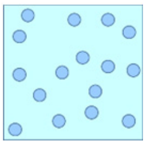
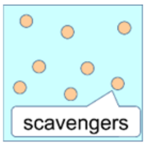
Since these sensitive products are seen quite often in our daily diet, like in juice, tea, seasoning, edible oil, and wine, as well as beer, significant effort has been made for improving the gas barrier performance of plastic containers. Among rigid containers used in the food and beverage industry, PET bottles are the most intensive category of plastic containers for gas barrier enhancement study because of their industrial scale of use. It should be stressed that the demand for high gas barrier PET bottles has been increasing because of the global trend in weight reduction, where thinner bottle walls show less gas barrier performance 5), and of a gradual increase of the applications of PET bottle formats.

Based on these backgrounds, this paper reviews the past and recent progress of gas barrier enhanced PET bottles, especially gas barrier thin film coated bottles.

2.1.2 Approach to the gas barrier enhancement of PET bottles other than thin film coating

Major technologies to enhance the gas barrier property of PET bottles used in today's industry can be roughly classified into four categories, that is, (i) coating, (ii) multi-layer, (iii) blending, and (iv) oxygen scavengers, as illustrated in Table 2-1 6,7). It should be noted that different approaches can be combined together. For example, the core layer explained below in the multi-layer approach may include oxygen scavengers, or the blending additives explained below are added in PET layers of multi-layer walls.

Table 2-1. Rough classification of the current major gas barrier technologies for PET bottles.

Technology	Coating	Multilayer	Blending	O_2 Scavengers
Schematic Image				
O_2 Scavengers	High	Middle	Middle	High
Other gas barrier	High	Middle	Middle	Low
Recyclability	High	Middle	Middle	Middle
Installation cost	High	High	Low	–
Operation cost	Low	High	High	High

The multi-layer approach employs at least one core layer with higher gas barrier properties placed between PET layers. The core layer(s) provides the majority of the gas barrier property of the whole bottle. Some specific grades of polyamides are often used for core layer materials, even though other materials had been attempted [3, 8)]. While the multi-layer approach is widely used in many industrial fields and its process control has been well established, economics due to the use of specific injection machines for multilayer preforms and of relatively expensive core-layer materials are the barrier to further distribution in the PET bottle industry. From a technical standpoint of view, the core layers are usually adjusted to occupy several percentages of the whole bottle weight to shape the bottle properly, and the core layers of a bottle usually do not exist near the mouth part and the center of the bottom part. These factors limit the maximum oxygen barrier property of multi-layered bottles compared to oxygen scavengers and coating approaches. In Japan, the market share of barrier PET bottles based on this approach has been decreasing.

In the blending approach, higher gas barrier materials are added into melted PET resin before the shaping process. The additives increase the gas barrier property of the whole bottle depending on the concentration in the PET matrix. Some specific grades of polyamides are often used for additive materials [9)], even though other materials had been attempted [3, 10)]. Due to the cost of additives and limited barrier performance compared to other approaches, the use of this approach is limited in these days in Japan. Additionally, in some countries such as Japan, possible mass use of polyamide additives is a concern for their recycling systems.

Oxygen scavengers are a type of additive which reacts with the oxygen permeant and results in restricting the passage of oxygen molecules through the bottle wall. The addition of a certain polyamide and transition metal complex into the PET matrix is an example of this approach [11)]. In ideal conditions, this approach can inhibit the increase of dissolved oxygen in the liquid content of the bottle. However, it makes it difficult for bottle manufactures to control the quality of their products as additive concentration and shaping conditions of bottles affects to each other. Some application may not accept the tint and haze due to typical types of scavenger additives.

2.1.3 Current thin film coatings for the gas barrier enhancement of PET bottles

Coatings in this context refer to techniques which form thin films on the surface of PET bottles. Dense structures of the thin films, typically several tens of nanometers in thickness, behave like glass or ceramics, and block the passage of gas permeants. The current approach generally uses two types of thin film species, that is, (A) carbon thin films, often described as diamond-like carbon (DLC) or a-C:H [3, 4)], or (B) silicate oxide thin films, often described as SiO_x, where x is a number and often somewhere between 1.5 and 1.8 3, 12).

While each approach described in the previous chapter has its own advantages and disadvantages, the use of coating is an expanding trend, or is expected to expand 13). At least in the Japanese market, the trend is remarkable in recent years 14). One of the advantages in the coating approach lies in the possibility of the relatively high gas barrier enhancement of various gas components including oxygen, carbon dioxide, water vapor, and flavors. This favors the quality retention of beverages where quite complex combinations of flavors contribute to unique taste and mouth-feeling, for example, seen in wine and beer 15-17). Another advantage lies in high recyclability. While other categories of the gas barrier enhancement approach of PET bottles usually require several percentages of foreign materials in the PET matrix in terms of weight, the foreign materials derived from coating amount to be, at most, several parts per million in terms of weight. As a result, coated bottles are usually no problem in recycling of normal PET bottles even in the case of mass use. From an economic point of view, relatively high capital cost to install coating machines is disadvantageous to coating, and this can explain the cause of the relatively slow increase of the use of coated bottles. On the other hand, relatively low operation cost is advantageous, and, in the case with high operational efficiency, coating is expected to require the lowest operation cost 6-8). In brief, in the case where a remarkable increase of barrier PET bottles happens, especially involved with the mass use in beer and carbonated soft drinks, coating approaches are most likely to be accepted from the viewpoint of bottle performance, social systems, and economics. In other words, at present, coating can be considered to have the largest growth potential among the barrier enhancement technologies of PET bottles.

2.1.4 Current methodology to thin film formation onto PET bottle surface

While various techniques are known to form thin films on substrates, plasma-assisted chemical vapor deposition (PACVD) techniques are currently available for mass production machinery for gas barrier thin film coating of PET bottles. These techniques meet the requirements for food and beverage containers. At least several requirements are essential, as summarized in Table 2-2.

Table 2-2. Basic requirements for thin film coating to PET bottles.

No.	Property	Reason	Corresponding Process Design
1	High gas barrier	For the flavor quality of the bottle content	Special configuration in coating chambers
2	Flexible	To withstand bottle deformation	Limited coating thickness and/or use of adhesion layer(s)
3	Thin and clear	For recycling and bottle appearance	Limited coating thickness
4	Physically and chemically stable to the bottle content	For safety to human and the flavor quality of the bottle content	Choice of thin film species in case of inside coating
5	Short process time	Economics	Optimization between barrier enhancement and throughput

One of major conceivable reasons of the use of PACVD lies in low heat load to the substrate. The deformation of the containers is likely to occur when the temperature of the substrate increases above its glass transition temperature which, in the case of polyester-based plastic containers like PET and poly(lactic acid) (PLA) bottles is 70–80°C, and 60–70°C, respectively [18)].

A second conceivable reason is that plasma can relatively readily occur inside a bottle. While coating may be applied to the outer surface of a bottle, these types of technologies involve some difficulty to protect the physical damage to the coating during production in filling lines and transportation to retailers, and also to control coating conditions along with accumulating coating dusts inside vacuum chambers. On the other hand, in the case of coating on the inner surface of a bottle, the thin film is protected with the bottle wall from physical impacts from the outside of the bottle, and most coating dusts can be deposited inside the bottle and removed from the vacuum chamber. Physical impacts may be a concern even with the internal coating due to known “abuse”, while typical production and transportation processes seem harmless to the barrier performance of the coating inside the bottle, as far as coated bottles were observed in Japanese market. Additionally, it should be noted that dust control is significantly important for continuous production which might last 20 hours or longer. In the case of coatings over the inner surface of containers, thin films tend to come in contact with food and beverages, and are required to have physico-chemical stability which secures the safety to human diet.

The third reason is the relatively short process time for thin film formation. Usually, thin films of 10–100 nm in thickness are used in current technologies. Coating thickness is determined, depending on thin film species, based on economics and the optimal thickness for gas barrier properties [2, 12)].

It should be noted that an excessively thin film lacks in barrier property, and an excessively thick film decreases in visual and barrier quality due to the occurrence of cracks [2, 19)].

As a result, based on the deposition rates of roughly 2–10 nm per second, 1–5 s are taken for thin film deposition under vacuum conditions, such as 1–20 Pa before coating and 5–30 Pa during coating. The whole process time ranges from 6–30 s per one bottle coating, depending on coating conditions and machine configurations. These process conditions are summarized in Table 2-3.

Table 2-3. Summary of plasma-assisted CVD techniques used for PET bottle coating.

No.	Coating process/device	Variations
1	Power frequency	2.45 GHz, 13.56 MHz, or 6.0 MHz
2	Thin film species	Carbon (DLC) or SiO_x
3	Material gas	Acetylene, HMDSO, HMDSN
4	Coating chambers	With electrodes (capacitive systems), or without electrodes (inductive systems)
5	Vacuum pressure	Around 10 Pa
6	Coating time	Around 1–5 sec
7	Coating surface	Inside of bottles

Note: HMDSO and HMDSN refer to the abbreviation of hexamethyldisiloxane and hexamethyldisilazane, respectively.

As a result, high throughput machines with a capacity of up to 40,000 bottles per hour have been in operation in soft drink and beer segments based on industrially realistic economics. Fig. 2-1 and Table 2-4 show an example of high throughput machine and details on coating process and performance, respectively, based on Kirin's proprietary DLC coating method [20].

Fig. 2-1. Example of high throughput rotary coating machine for PET bottles (photo provided by courtesy of Mitsubishi Heavy Industry Machinery Systems, Ltd., Japan).

Table 2-4. Typical process conditions for DLC coating to PET bottles.

Process Parameter	Conditions
Power frequency	13.56 MHz, or 6.0 MHz
Power outlet	300–2500 W
Material gas	Acetylene
Gas flow rate	10–300 sccm (*)
Vacuum pressure	5–10 Pa
Coating time	1–2 sec
Resultant Properties	**Performance**
Deposition rate	Around 10 nm/sec
Gas barrier improvement	Oxygen, carbon dioxide, water vapor, and flavor components
Applicable container	1–5000 mL
Applicable filling manner	Aseptic to hot filling

(*) sccm: cubic centimeter at standard temperature and pressure per minute

Although differences in processes for coating bottles can be found among the current PACVD technologies, they have the basic process concept in common, that is, (i) to place a bottle into a vacuum chamber, and to vacuum the chamber; (ii) to supply material gas into the bottle; (iii) to apply electromagnetic wave to the inside of the bottle so that the material gas is decomposed into a plasma state; (iv) to allow the plasma to form a thin film on the inner surface of the bottle; and (v) to release the chamber to the atmospheric pressure, and to remove the coated bottle (as summarized in Fig. 2-3). Obviously, these processes can be repeated continuously.

Figs. 2-2 and 2-3 show an example of the coating system and the coating processes of Kirin’s proprietary DLC coating method, respectively. In this system, an outer electrode functions as a part of vacuum chamber. Moreover, its internal shape similar to the bottle shape enables evenly distributed coating over the entire part of the bottle, based on that distance between the inner surface of the outer electrode and the bottle can control the voltage of the bottle surface and the resultant plasma distribution.

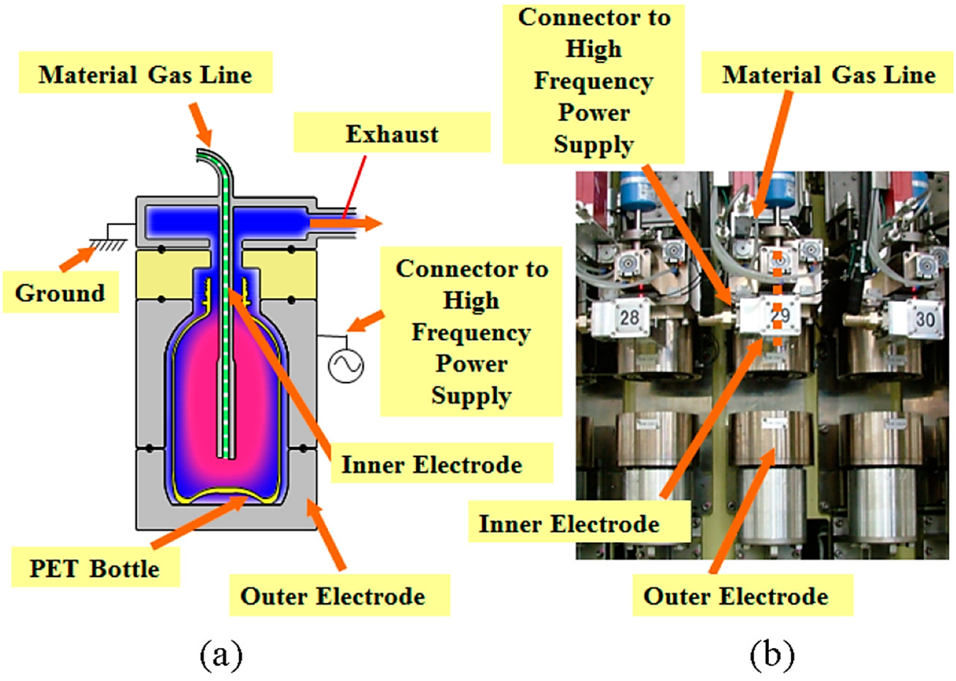


Fig. 2-2. Example of the components of coating system for PET bottles: (a) schematic model; and (b) the corresponding part of the production machines (photo provided by courtesy of Mitsubishi Heavy Industry Machinery Systems, Ltd., Japan).

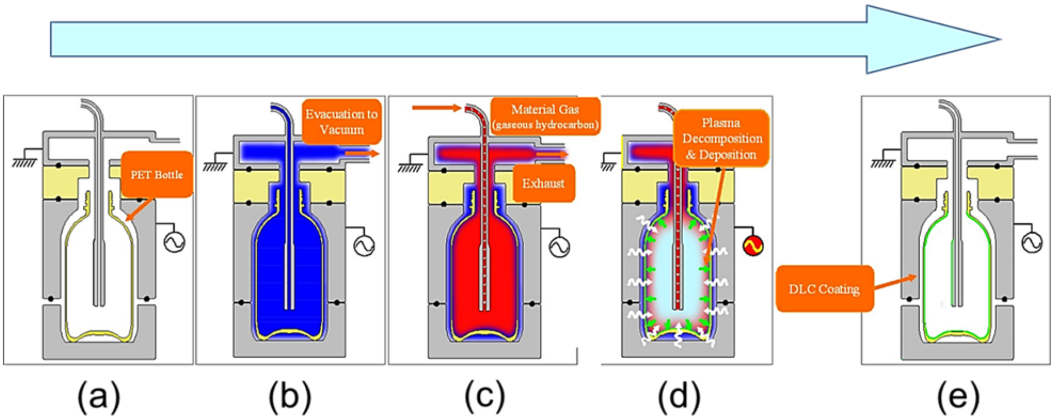


Fig. 2-3. Schematic plasma CVD process for coating plastic bottles in case of Kirin's DLC coating. (a) bottle placement into the coating chamber and vacuuming; (b) material gas supply; (c) power application to the coating chamber; (d) thin film deposition; and (e) pressure release and bottle removal from the coating chamber.

This basic process concept for hollow containers was seen at least as early as the 1980s, and some coating machines intended for commercial use were introduced early in the 1990s [21, 22], and various process conditions, including different material gas species, have been tried. As a result, the main difference of the processes among the current coating technologies for PET bottles, in general, lies in the material gas species and the frequency of power used to create plasma states.

Nowadays, types of metal oxides and nitrides, as well as carbons, are known to be possible to function as gas barrier thin films [23]. Carbon and silicate oxide thin films are, however, only two thin film materials available for mass production technologies for gas barrier enhanced PET bottles. The major reasons for the use of carbon and silicate oxide thin films for PET bottle applications lie in safety in food contact, the availability and relatively easy handling of material gas, and the economics to achieve sufficient gas barrier performance. Although aluminum and aluminum oxide thin films have a long history of use for the gas barrier enhancement of film and sheet applications [24], appropriate material gas species and coating processes for container applications have not yet been found.

In addition, the current PACVD processes which are practical in the mass production can be found in vacuum conditions. Although it has been proved that certain atmospheric PACVD techniques can form gas barrier carbon and silicate oxide thin films based on dielectric barrier discharge techniques [25], their technical problems, such as dimensional limits, remain yet unsolved for the application of three-dimensional objects like PET bottles.

2.1.5 Difference in and between carbon and silicate oxide coatings

The current commercial carbon thin films have a slight, brownish to golden, tint [26]. Although this may restrict applicable product categories of carbon coated PET bottles, from the viewpoint of the visual quality of products, the degree of the tint appears to position within the scope of consumer acceptance, based on the commercial products of white wine (Fig. 2-4) and edible oil categories in the Japanese market.

Fig. 2-4. Example of DLC coated bottles for wine.

In case of beverage and liquor market in Japan, carbon coating is more often seen than silicate oxide coating in spite of the abovementioned disadvantage to carbon coating. The reason might be found in that carbon thin films are readily applicable to various product categories because carbon coating is inert to food and beverage solutions as long as the PET substrate is stable. On the other hand, some more remarkable limits in applicable product properties is known in typical silicate oxide coating. The gas barrier property of silicate oxide coatings may be decreased in contact with some solutions, for example, beverages of pH close to neutral 27).

Acetylene (C_2H_2) is the main material gas for carbon thin films for gas barrier-enhanced PET bottles. Derived from the hydrogen contained in acetylene molecules, the resultant carbon thin films contain hydrogen components up to 40% in atomic percentage. Elastic Recoil Detection Analysis (ERDA) analyses showed oxygen components up to 10% may be present in the carbon thin films [4, 28)], which is considered to be mainly derived from water vapor from PET substrates. The advantage of the use of acetylene lies in high deposition rates and economics, while methane (CH_4) is used in many studies [4, 26)]. At least carbon thin films formed with acetylene contain the carbon bonding of *sp*3, *sp*2, and *sp*1, based on X-ray photo spectrometry (XPS) and Fourier transform infrared spectroscopy (FTIR) studies [22)]. In the Japanese market, commercial carbon-coated PET bottles are derived from the technologies of Kirin's DLC and Sidel's Actis™ [14)].

Hexamethyldisiloxane (HMDSO) and hexamethydisilazane (HMDSN) are the main material gases for silicate oxide thin films with aid of the controlled supply of oxygen. Based on the ratio in the mass flow of the material gas to oxygen and other conditions, the resultant thin films have different components consisting of silicate, carbon, oxygen, and hydrogen [29)]. The components have impacts on gas barrier properties and stability in contact with beverage solutions, and sometimes also on tint. In the case with commercial gas barrier silicate oxide, thin films are totally colorless in visual observation.

In the Japanese market, silicate oxide-coated PET bottles can be mainly seen in domestic edible oil and wine products, and rarely seen in imported carbonated water. Those bottles are derived from the technologies of Toyo Seikan's Sibird™, Toppan's GL-C™, and KHS's Plasmax™ [14)].

From the viewpoint of the frequency of power used to cause the plasma states of material gas supplied, radio frequency (13.56 MHz) and microwave (2.45 MHz) are used in commercial technologies. The use of radio frequencies usually leads to a bi-electrode system, in other words, a type of capacitively-coupled plasma system, where sheath voltage and the resultant ion impact over the surface of the substrate can be controlled relatively precise manner [28)]. It can be expressed that the use of these systems involves both merits and demerits to machine users. Examples of the merits are possible improvement in the performance of coating and stable application to relatively small or large containers, while those of the demerits are the possible increase of the change of mechanical parts for the application to containers of different shapes and sizes.

2.1.6 Recent advancement in commercialized technologies for coating plastic containers

In spite of the different nature of carbon and silicate oxide thin films as described above, it can be said that the difference between the two thin films is decreasing in the recent technical advancement.

It is obviously conceivable that the optimization of process conditions in parallel to the improvement in machinery has been performed in each technology, and as a result, deposition time has been shortened while the barrier properties of PET bottles coated are maintained or even improved. It is supposed that typical process conditions, including vacuum pressure, gas flow rate, and power application have been optimized. As a result, carbon coating has been less colored, and widened its applications (as shown in Fig. 2-4). In the same way, silicate oxide coating has clarified and mitigated its limitation in applications, and widened its applications. In the case of the Japanese market, the use of coating technologies has been rapidly increased in recent years, and at present coating is the most abundant among technologies, compared to other gas barrier enhancement technologies applied to PET bottles 14).

An example of technological advancement has been found in the appropriate use of dielectric materials along electrodes in Kirin's DLC coating technology 30), and the modification of power frequency as described later in detail (see the chapter 3 of this paper). Conventionally, this technology employed 13.56 MHz for power frequency and outer electrodes made of metal (conductive materials) parts only. Recently, power frequency was confirmed as one of the significant process parameters 28). The use of 6 MHz for power frequency and outer electrodes fully or partially covered with dielectric material parts has been proposed in order to facilitate finding the appropriate process conditions for high gas barrier coatings in addition to a decreased change of electrode parts for bottles of different shape and size. The results of the observation of coating thickness and plasma light emission indicate that the reason why 6 MHz power frequency showed the lowest gas barrier performance lies in the optimized spatial distribution of plasma. Compared to plasma produced with 13.56 MHz, where the plasma tends to concentrate around the neck part of the bottle, it seems that plasma with a lower frequency provides higher ion impacts to the PET substrate and the resultant secondary electrons modify the spatial distribution of the plasma to the direction of the bottom part of the bottle.

Another example has been found in the modification in the manner of material gas and oxygen supply during the coating process of KHS's Plasmax™. This technology is called Plasmax Plus™. Due to an extra carbon-rich layer formed on the conventional silicate oxide layer, the resultant coating can be stable in contact with solutions of pH close to neutral, which deteriorates the performance of coating based on the conventional process. Interestingly, the new coating manner requires no machinery modification 27).

2.1.7 Targets for near future advancements in this field

2.1.7.1 Gas barrier coatings to various polymer substrates, especially polyolefins

The above description in this review mainly covered a brief history of gas barrier enhancement of PET bottles through PACVD techniques. On the other hand, a lot of effort has been made to other types of plastic containers and novel approaches to gas barrier enhancement.

Although the current era where PET bottles are the most abundant package format of rigid plastic containers is likely to last in this and the following decades because of their industrially-favorable balance between performance and economics, other plastic materials also have demands for functional thin film coating. Some polyolefins, such as polyethylene (PE) and polypropylene (PP), with large industrial demands compared to PET, are quite useful materials while the lack of oxygen and other barrier properties limits their benefits. For possible example, coated PP bottles or jars could keep the flavor quality of filled contents for certain extended periods of time in addition to high heat resistance, compared to PET containers, which are limited in applications below the boiling temperature of water.

A distinctive commercial benefit of gas barrier coatings onto PE can be found in enhancing the oxygen and carbon dioxide barrier of closures used in gas barrier enhanced PET bottles. While PE provides economical sealing parts of closures, the enhancement of these gas barrier and anti-sorption properties is demanded in the beverage industry, especially for beer products in PET containers, as described in detail in the chapter 4 of this paper. Other commercial benefits can be found in packages sterilized in the boiling temperature of water and above, including medical packages.

2.1.7.2 Novel approach to lower machinery economics and advanced thin film properties

As summarized in Table 2-1, thin film coatings onto PET bottles involve advantageous aspects in comparison with current competitive approach. Relatively a high installing expenditure for the machinery of PACVD processes, however, inhibits the further spread of this approach over the industry.

Also, Table 2-2 and the comparison between the current commercialized thin films to PET bottles, that is, carbon (DLC) and SiO_x coatings, lead to a concept of novel thin film species like a colorless carbon coatings. In the thin film species, it is demanded that appearance looks like SiO_x, and also that a single material gas species can form a high gas barrier and physico-chemically stable coating like DLC.

The chapters 5 and 6 of this paper propose a novel approach to gas barrier thin film coating, where a hot wire or catalytic CVD technique is applied to bottle coating in an attempt to achieve decreased installing expenditure based on the simple configuration of coating machines compared to that of conventional PACVD machines. Furthermore, the application of this technique can produce unique gas barrier coating to PET bottles, like an intermediate between carbon and silicate oxide thin films.

2.2 Experiments

Even with the advent of a colorless and physico-chemically stable coating mentioned above, polymer substrates are still one of the most important process conditions. As described in 2.1.7.1, gas barrier coatings onto substrates made of various polymer materials are demanded, and the difference in polymer properties is likely to affect the growth of the formed thin films and the resultant functions. However, little is known on the influence of the diversity of polymer substrates.

In order to confirm the fundamental issues to form gas barrier thin film coatings onto various polymer substrates, the author compared the degree of oxygen gas barrier enhancement with DLC coating formed on various kinds of plastic film substrates, and discussed its difference based on the result of the performed positron annihilation study.

2.2.1 DLC film formation onto different polymer substrates

Commercial plastic film products as listed in Table 2-5 were used for polymer substrates. Each sample was cut to 40 mm square size, and placed on the inner surface of the center of the body part 500 mL PET bottle.

DLC coating was performed based on Kirin’s proprietary method for PET bottles illustrated in Fig. 2-2 [20, 25]. Each sample film of ca. 50 mm square was placed on the inner surface of a commercial 500 mL PET bottle and vacuumed to 5.0 Pa. Then, acetylene gas was supplied at a flow rate of 80 cubic centimeter at standard pressure and temperature per minute (sccm), followed by the application of 1000 W of 13.56 MHz radio frequency power for 2.0 sec.

Table 2-5. List of plastic materials used for comparing the degree of gas barrier enhancement with DLC coating.

Material	Abbreviation	Manufacturer	Type	Thickness
Linear low-density polyethylene	LLDPE	Toyobo Co., Ltd	L6102	30 µm
Low-density polyethylene	LDPE	–	Type S-1	40 µm
High-density polyethylene	HDPE	Mitsui-Toatsu Pleatec Co., Ltd	Hiburon	25 µm
Cast polypropylene	CPP	Toyobo Co., Ltd	P1128	18 µm
Retortable cast polypropylene	rCPP	Toyobo Co., Ltd	P1153	40 µm
Oriented polypropylene	OPP	Toyobo Co., Ltd	P2108	40 µm
Oriented polystyrene	OPS	Toyo Chemical Co., Ltd	Hallen L	25 µm
Poly(vinyl acetate)	EVA	Kaito Chemical Industry Co., Ltd	Type E-30	30 µm
Poly(ethylene)-poly(vinyl acetate)	EVOH	Kuraray Co., Ltd	Eval EF-F	30 µm
Oriented polyamid	ONY	Toyobo Co., Ltd	N1100	30 µm
Poly(acrylo nitril)	PAN	Mitsui-Toatsu Pleatec Co., Ltd	Zecron	20 µm
Poly(lactic acid)	PLA	Mitsubishi Plastics Co., Ltd	–	50 µm
Oriented poly(ethylene terephthalate)	PET	Toyobo Co., Ltd	ES100	12 µm

2.2.2 Measurement of oxygen transmission rate and calculation of barrier improvement factor

As a nature of polymeric materials, polymer chains pack together to a more or less degree based on their different composition. Between polymer chains, the thermal motion allows clearance of a several nm order. The total distribution of the clearance at a specific time affects the free volume of materials, which is conceived as the pathway of gas molecules dissolved in the matrix 31). In a typical case, the dissolved gas molecules, occurred based on Henry's law, diffuse in the matrix based on Fick's second law. The total phenomenon is called permeation, and the rate of the passage of gas molecules per unit time is called transmission rate.

As a result, the permeability of a polymer material can be expressed as below:

$P = Q \cdot d / A \cdot \triangle p \cdot t$, where

P: permeability in $\mathrm{cc \cdot mm/m^2/day/atm}$
Q: permeated gas in cc (STP)
d: thickness of polymer material in mm
A: area of polymer material in $\mathrm{m^2}$
$\triangle p$: differential gas pressure in atm
t: unit time for permeation in day (=24 hr).

In this Chapter, as an index of gas barrier performance, oxygen transmission rate (OTR) was used based on room conditions, where measurement temperature is 23°C and a pressure difference of oxygen is 0.21 atm (ca. 0.021 MPa) derived from 21% oxygen concentration in air. Because this experiment aims to show the degree of oxygen gas barrier enhancement with DLC coating, the thickness of each sample was not considered in the expression of OTR, and, as a result, OTR in this experiment was expressed in the unit of cc (STP) /$\mathrm{m^2}$/day.

OTR was measured with Oxtran 2/21, Mocon Co., Ltd., USA, for 5 hours under the conditions of 23°C and 90% relative humidity, based on ASTM D3985 method 32). With this device, a steady pressure and volume method was employed, where each side of film sample was exposed either to pure oxygen or to pure nitrogen flow. As a result, the latter nitrogen flow contained permeant oxygen through a window of 5 $\mathrm{cm^2}$ area, and was supplied to a coulometric detector as shown in Fig. 2-5.

As described above, barrier improvement factor (BIF) is often used in the beverage and food industry in order to facilitate to infer the degree of the extension of product shelf-life. BIF is calculated based on

BIF = OTR of uncoated samples / OTR of coated samples.

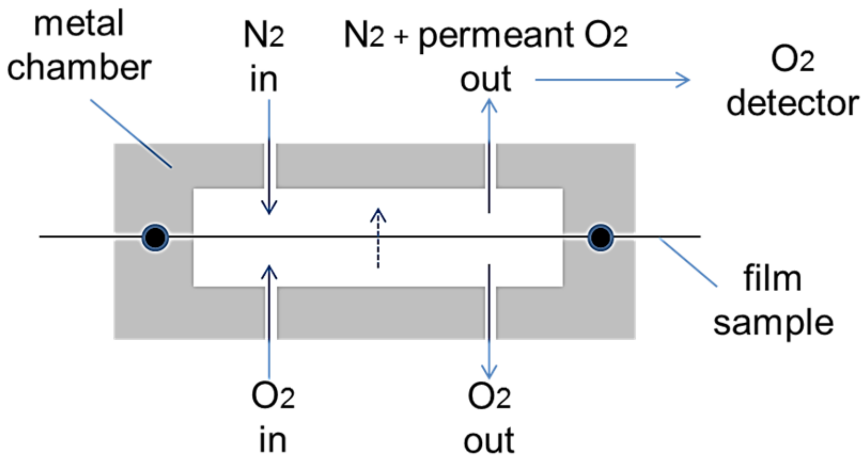
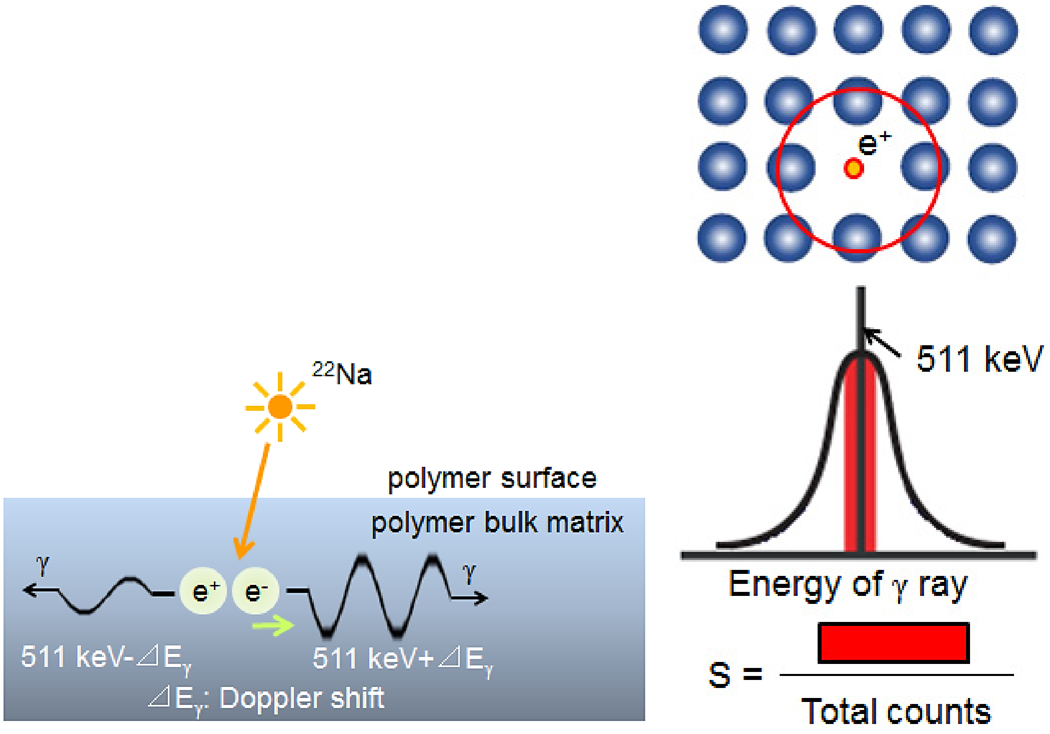


Fig. 2-5. Schematic configuration of the measurement of the oxygen transmission rate of polymer film samples.

2.2.3 Detection of free volume in polymer and thin film matrix

The positron annihilation method [33)] is based on a phenomenon where positrons implanted into a condensed matter annihilate with an electron and emits two 511-keV γ quanta. The spectra of γ energy, including the Doppler shift, are characterized by the S parameter (see Fig. 2-6) [34)], which mainly reflects changes due to the annihilation of positron-electron pairs with a low-momentum distribution. For amorphous materials, positronium (Ps: a hydrogen-like bound state between a positron and an electron) may form in open spaces. As a result, smaller S parameter, as well as shorter positron lifetime, shows denser structure in terms of free volume [35, 36)].

The S parameter of the DLC coating and substrate polymer of each sample was detected through a positron annihilation using ^{22}Na. For details, see the method described in a previous paper written by Uedono *et. al* [37)].



(a) (b)

Fig. 2-6. Schematic illustration of (a) positron annihilation and γ quanta emission, and (b) the definition of S value as the ratio of quanta counts within the Doppler shift range over the total counts.

2.3 Results and Discussion

A remarkable difference in the degree of oxygen gas barrier enhancement with DLC coating formed on various kinds of plastic film substrates, as seen in BIF values shown in Fig. 2-7. Although all of polymer substrates showed the increase of BIF, that is, the decrease of OTR, the values of BIF varied in a range from 1, that is, almost no decrease in OTR, to 12, significant decrease in OTR. In detail, while relatively higher BIF values were obtained in PET and polystyrene samples, relatively lower BIF values were seen over types of PE and PP samples.

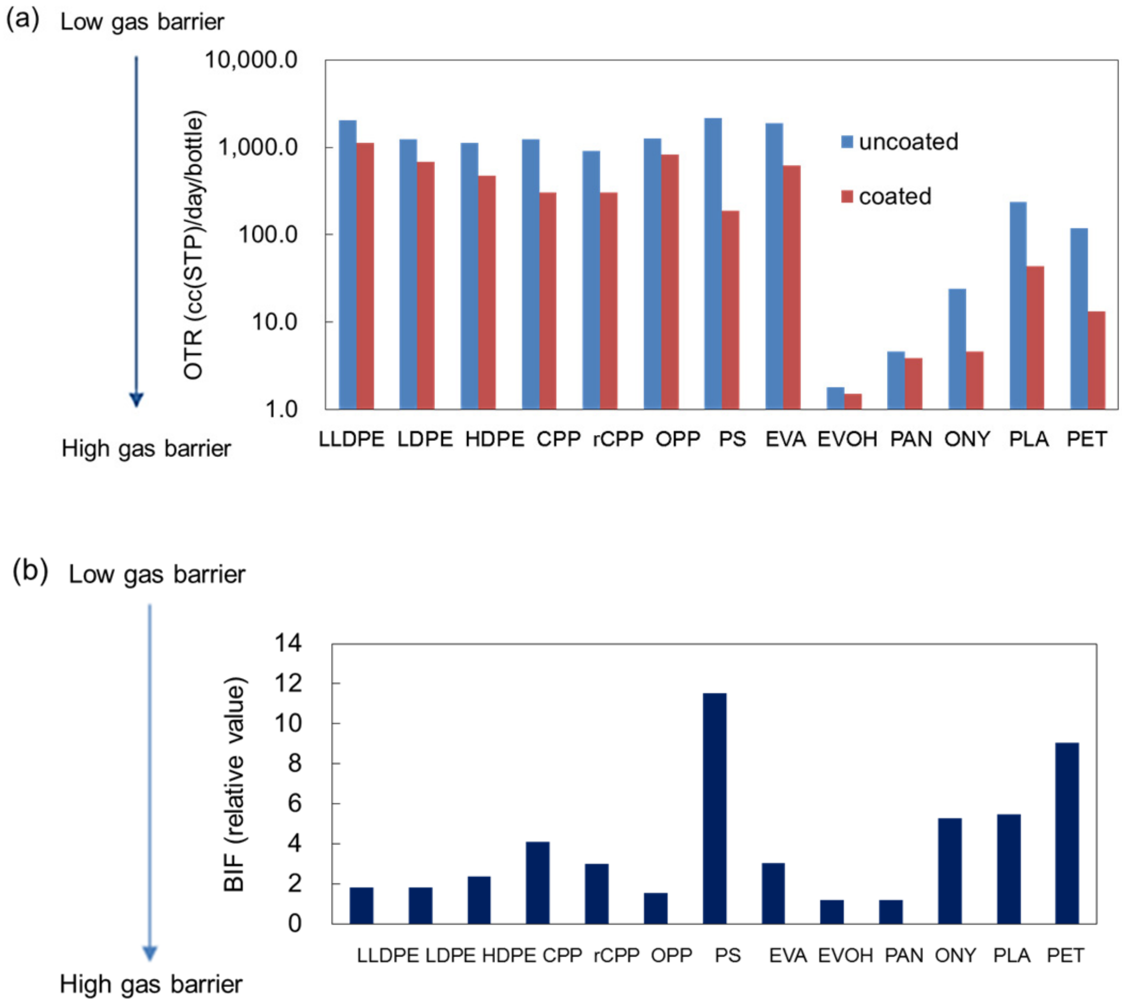


Fig. 2-7. Comparison of (a) the oxygen transmission rate (OTR), and (b) BIF of DLC coating on different plastics films. For abbreviations of these plastics, see Table 2-5.

However, the performed positron annihilation indicated that, on these substrates, DLC coatings were formed homogeneously in terms of free volume, as shown in Fig. 2-8. In this figure, it is clearly shown that DLC films, with positron energy of less than 1 keV, has a small S parameter, compared to polymer substrates, with positron energy of more than 3 keV, and that thin films of small free volume function as barriers against gas permeation.

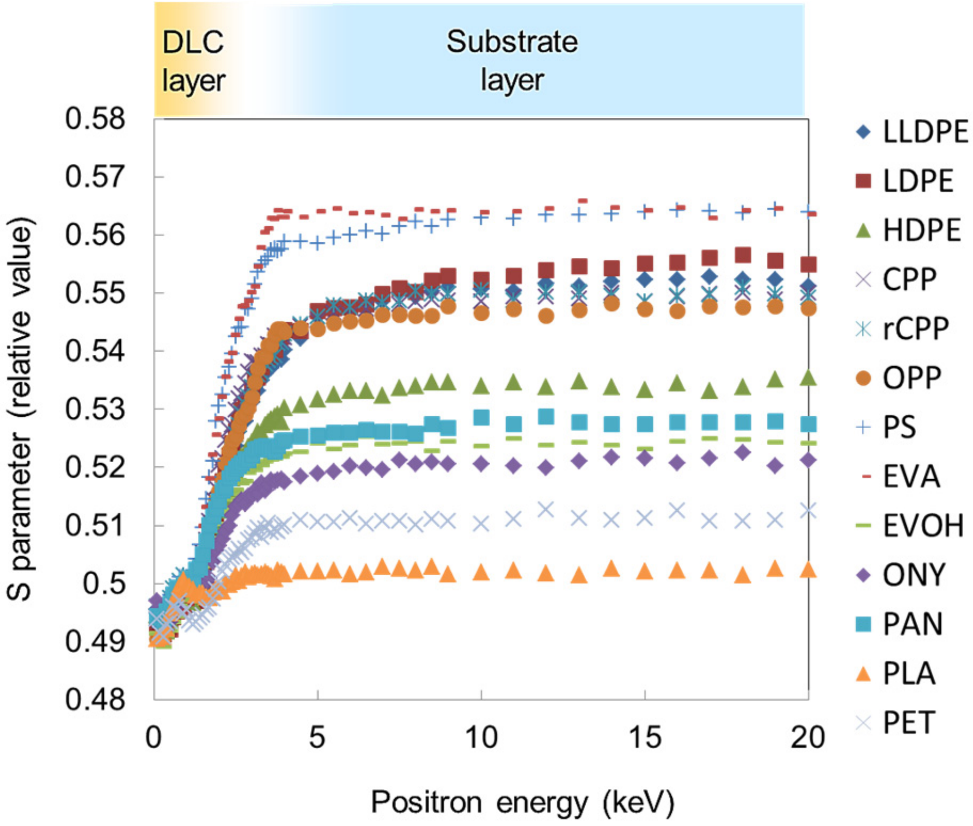


Fig. 2-8. Depth profile of the positron annihilation of DLC coated samples. The S parameter of DLC coating (see the region of less than 1.5 keV) and plastics substrates (see the region of more than in 5.0 keV) was measured. For abbreviations of these plastics, see Table 2-5.

Empirically, packages made of PE and PP tend to have relatively rough surface, and rough surface is considered to lead to significant defects in coating. When the surface of them and PET bottles is observed using an atomic force microscopy, the R_a of 1 μm square is usually 30–100 nm and less than 1 nm, respectively. A result of wet coating approach in which the author previously engaged 38) supports this concept, where a specific type of organosilane materials placed between DLC thin films and PP substrates remarkably enhanced oxygen barrier property, even though the organosilane layer itself did not have a significant barrier property to the PP substrate. It should be noted that, when the surface of the organosilane layer is observed with an atomic force microscopy, the R_a of 1 μm square is usually around 1 nm. In this case, the smoothed surface with an increased anti-crack property due to the organosilane layer caused the enhancement of the gas barrier performance of the coating.

It should be also noted that a similar behavior was observed in a recent approach with ultraviolet curable resin both for under- and top-coating, also in which the author engaged [39)], and seems to occur without the existence of cracks in DLC thin films. A supporting report indicates that although any cracks and other defects were not observed in the formed thin films, some structural difference sensitive to plasma etching had a correlation to gas barrier enhancement [40)].

These results suggest the interface between thin films and substrates plays a crucial role on the enhancement of gas barrier property with dense thin film coating, leading to a concept similar to cavity model by Inagaki [41)]. Technologies for surface conditions are considered to be a key for the future commercialization of coated containers made of various plastics such as PE and PP.

2.4 Conclusions

This chapter reviewed the current situations and high potentials surrounding gas barrier thin film technologies for PET bottle applications, and depicted the issues for the advancements of this approach as below:

(a) to improve plasma control inside bottles for faster and higher gas barrier coatings, leading to enhanced performance to product quality including shelf-life and appearance, and economics in gas barrier enhanced bottles.

(b) to provide appropriate substrate surface for various kinds of polymer materials, leading to expand applications not only within but also beyond beverage containers.

(c) to develop a novel coating methodology for improved machinery economics and/or performance compared to current carbon or SiO_x coatings.

Especially regarding the issue (b) above, a fundamental study was made in an attempt to confirm how DLC coating can enhance the oxygen barrier property on different kinds of polymer materials, based on the combination of OTR (BIF) and positron annihilation behavior. As a result, (1) OTR based BIF values of DLC coated substrates were remarkably different from one polymer material to another. (2) In spite of this behavior, S values obtained in positron annihilation indicated virtually homogenous DLC thin films were formed in the various substrates.

These results lead to a conclusion that the interface between a thin film and its substrate has a key function to express the gas barrier enhancement effect in coated polymer packages. In specific cases with PE sealing parts of closures for PET bottles, direct coating onto these parts is likely to require surface modification for gas barrier enhancement.

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Chapter 3

Impact and Optimization of the Difference in Power Frequency on Diamond-Like Carbon Thin Film Coating over Three-Dimensional Objects

3.1 Introduction

Diamond-like carbon (DLC) refers to materials consisting of amorphous carbon (and hydrogen) network 1, 2). This material has inert and stable physico-chemical properties, and is used in a wide range of industrial applications such as mechanical tools and medical devices. As described in the previous chapter, the nano-layer of DLC is also applied to polymer packages for beverage and food. In these applications, DLC thin films can function as gas barrier coatings, and decrease gas transmission rate through plastic materials. In cases of poly(ethylene terephthalate) (PET) bottles, the enhanced gas barrier properties can be used for the extension of the shelf life of products sensitive to gas permeation, such as beer, wine, and carbonated soft drinks 3, 4). The coatings for three dimensional objects like PET bottles require different devices from those for flat (two dimensional) substrates like wafers and sheets.

One method to coat the inner surface of PET bottles with DLC is to employ a capacitively-coupled PACVD technique by using a specially designed device for this application, as described in the previous chapter 3). In its early applications, the high frequency power of 13.56 MHz was supplied to produce plasma to form DLC layers. Another industrially known method is an inductively-coupled PACVD technique, where microwave (2.45 GHz) is used to produce plasma 4). Similar techniques have been invented to coat other three dimensional objects such as tanks, vials, and syringes, and therefore the importance of this kind of plasma techniques has increased in the industrial applications.

It is generally known that, in capacitively-coupled PACVD techniques, power frequency applied to the electrodes has an impact on the deposition rate and properties of the obtained thin films 5). In case of PET bottle application, questions arise in what power frequency will provide the optimized industrial performance such as gas barrier, bottle appearance, and coating adhesion, and also in what kind of difference lies in DLC formed with varied power frequency. From the standpoint of safety issue in medical and food/beverage applications, another more important question arises in how the homogeneity of DLC can be clarified in case the power frequency is slightly different among devises and the resultant applications. If the homogeneity can be maintained, the use of different frequencies would be easy to spread in these industries.

The difference in DLC formed in different frequencies may exist in physical structure and chemical composition. To infer the micro-structure of DLC, positron annihilation is considered to be the most appropriate technique, because it is an established technique for investigating point defects in materials 6, 7), including carbon thin film 8). This is a non-destructive and very sensitive technique to detect difference in the structure of nano-layers, and applicable to detect the existence of free volume 9). Free volume is considered to provide the pathway of gas molecules which permeates through the matrix of polymers and thin films, and known to be measurable with positron annihilation techniques 10, 11).

It is known that PACVD can employ various power frequencies to generate plasma, from kHz to GHz 4, 12, 13). Difference in frequency affects ion-bombardment, and secondary electron scattering. This may lead to plasma with significantly different characteristics, and change in the resultant structure of DLC films.

In this study, different power frequencies were used to form DLC thin film on the surface of PET bottles, and the important properties of coated bottles such as oxygen transmission rate and tint were compared, especially to the case with 13.56 MHz power frequency. Because this frequency is used in conventional capacitively-coupled PACVD devices including the industrial coating machines for PET bottles, enhanced properties with different frequencies lead to improvement in industrial performance. Positron annihilation and other analyses were employed in order to confirm the homogeneity of DLC coating over the different power frequencies, and to infer the reason of the improved properties.

3.2 Experiments

3.2.1 Preparation of PET bottles

PET bottles were produced using typical commercial PET resin. PET preforms of 29 g in weight were produced using an injection machine, KS100T, Kata System Co, Ltd., Japan. The resultant preforms were formed into PET bottles of 500 mL in volume (Fig. 3-1) with an averaged thickness of ca. 0.035 mm.

Fig.3-1. Appearance of PET bottles used. The shape of the bottle is typical for carbonated soft drinks. The bar represents 10 mm.

3.2.2 DLC coating

DLC nano-layer was formed on the surface of sample bottles with a device, PNS-1, Youtec Co., Ltd., Japan, specifically designed for PET bottle coating [3)]. As shown in Fig. 3-2, each bottle sample was placed onto the bottom part of the outer electrode in order to be enclosed in the vacuum chamber, parts of which were consisted of the outer electrode, and to be subjected to subsequent processes for PACVD. The vacuum chamber was closed and vacuumed to 5.0 Pa. For the material gas of DLC, acetylene was supplied into the bottle at a rate of 80 cubic centimeter at standard pressure and temperature per minute (sccm). High frequency power of 1000 W was applied with a power supply to produce acetylene plasma between the inner and the outer electrodes. The plasma was maintained for 2.0 seconds. For 13.56 MHz input, a power supply, RFK30-UT1, Kyosan Electric Manufacturing Co., Ltd., Japan, was used. For 2.50-7.00 MHz input, a power supply with frequency-variable function, NR1.5F5-7M-01., Noda RF Technologies, Co., Ltd., Japan, was used. Consequently, DLC coating was formed over the inner surface of the sample bottles.

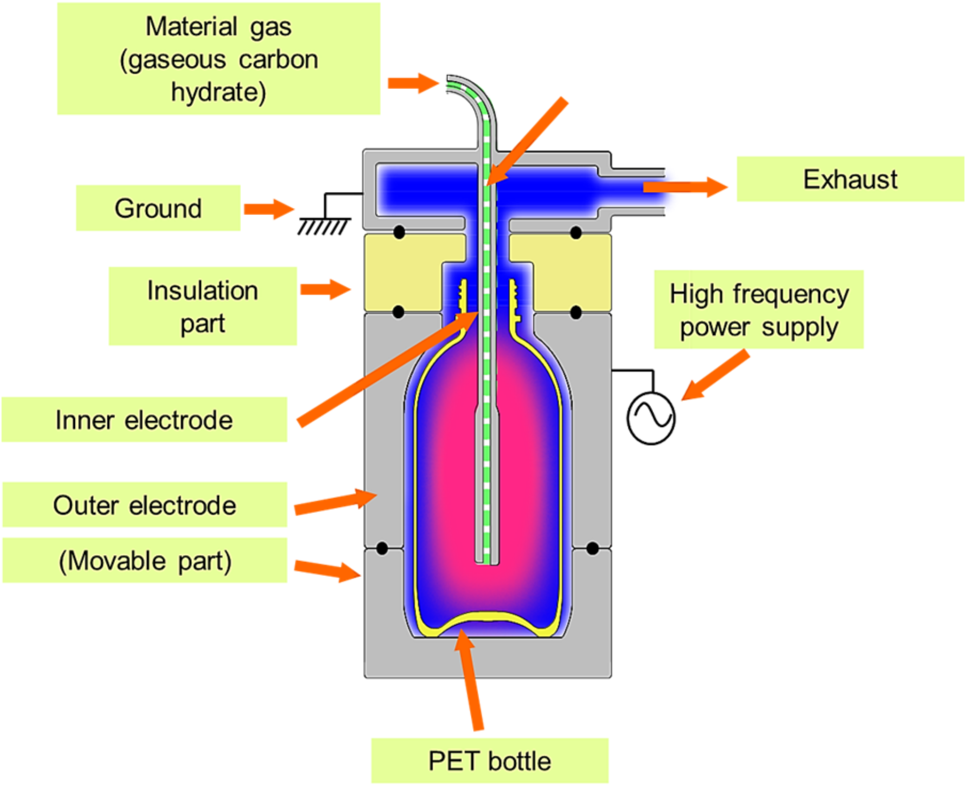

Fig. 3-2. Basic components of DLC coating system. The outer electrode functions as an electrode for plasma occurrence and a part of vacuum chamber. The bottom part of the outer electrode is movable for placing the bottle into the chamber and removing it out of the chamber.

3.2.3 Measurement of the gas barrier property of PET bottles

To represent gas barrier property, the oxygen transmission rate (OTR) of uncoated and coated bottles was measured basically in the same manner as that of polymer films described in the previous chapter (for details applied to containers, see ASTM F-1307) using an Oxtran 2/21 device, Mocon Co, Ltd., USA, under conditions of 23°C and 90% relative humidity.

Barrier improvement factor (BIF) was used as an index of barrier enhancement with DLC coating, which is calculated by the following formula:

$$\text{BIF} = \text{OTR of uncoated bottle} / \text{OTR of coated bottle}$$

3.2.4 Detection of free volume in DLC coating

Free volume in DLC coating on each sample was detected through a positron annihilation using ^{22}Na based on a method described in a previous paper written by Uedono *et. al* 14).

Samples were cut from the body part of coated PET bottles as shown in Fig. 3-3. The body part had a cylindrical side wall, and was located in the middle of the upper part tapering to the mouth opening and the bottom part tapering to the bottom base.

The degree of free volume was represented in S parameter, where lower value indicates denser electron cloud in DLC and PET matrix, and thus indicates the denser DLC structures 14).

3.2.5 Analysis of composition and structure of DLC

The chemical composition of DLC was measured with the combination of high resolution Rutherford backscattering spectrometry (HR-RBS) and elastic recoil detection analysis (HR-ERDA) using HRBS500, Kobe Steel Ltd, Japan.

The chemical structure of DLC was measured with X-ray photoelectron spectroscopy (XPS) using MgKα radiation with JPS-9000MC, JEOL, Japan. The peak position of C1s spectral regions was calibrated based on the C1s peak of 284.6 eV. The ratio of sp^2 and sp^3 fractions of carbon were calculated based on the deconvolution of C1s core-level spectra through peak fitting using Spec XPS, where the binding energies of 284.5 eV and 285.3 eV correspond to energy derived from graphite (sp^2) and diamond (sp^3), respectively.

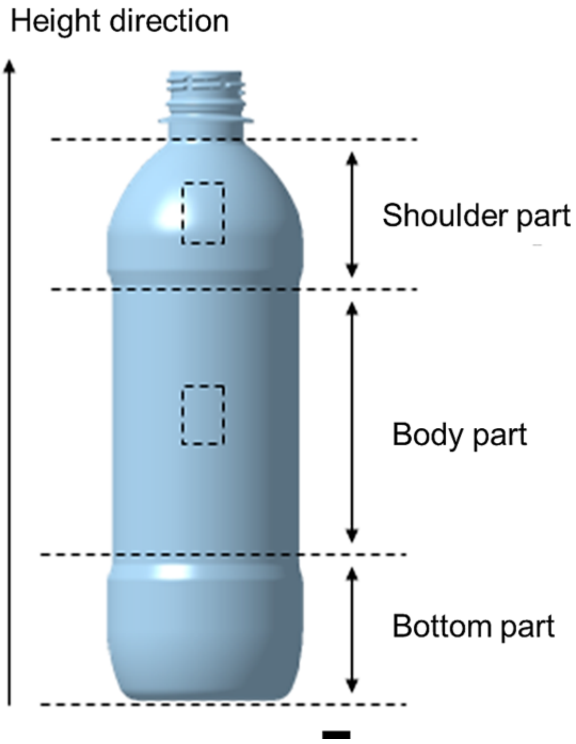

Fig. 3-3. Schematic model of a PET bottle and its portion for sample cutting. Each sample was cut from the middle of each part in terms of height direction. The bar represents 10 mm.

3.2.6 Measurement of deposition rate of DLC coating

The deposition rate of thin film formed in the above mentioned manner was measured as described in our previous study [12)]. Partially masked silicon wafers placed on the inner surface of the center of the sealing part of closures, and the difference in height between the unmasked and the masked parts is detected using a contact-type thickness meter, α-step, KLA-Tencor Corporation, USA.

3.2.7 Measurement of tint caused by DLC coating

The color tint of PET bottles caused by DLC coating was quantified based on the increase of b* value (⊿b value) in the L-*a*-b* color quantifying system 15). DLC has its own metallic golden or yellowish tint caused by light absorption at various wavelength due to the amorphous nature of DLC matrix (mainly due to the various bond-length between adjourning carbon atoms). As a result, the ⊿b* value is effective to compare the thickness of the tint of DLC coatings formed with different frequencies, because the positive b* value represents the degree of yellowish tint.

To measure the ⊿b* value, each sample cut from PET bottles was placed in a spectrometer, U-3900, Hitachi High-Technologies Corporation, Japan, and b* value was calculated based on the light transmission of each wavelength ranging from 380 nm to 780 nm. Samples were cut from the shoulder and body parts shown in Figure 3-3. The difference of ⊿b* values between both parts was examined in order to observe the uniformity of color tint over the bottle, because the uniformity has an industrial value for PET bottles.

3.2.8 Examination of adhesion stability between DLC coating and PET substrate

Adhesion stability between DLC coating and PET substrate was quantified based on anti-caustic resistance. When a PET bottle is filled with a caustic solution, PET causes hydrolysis where longer polymer chains chemically break into shorter polymer segments. Caustic treatment leads to the loss of adhesion of DLC layer to PET surface. A simple explanation to this loss of the adhesion is that, as polymer chains break, residual stress inside the DLC layer gradually exceeds adhesion force along the interface between the DLC layer and the PET substrate, leading to cracks in the DLC layer, and finally to the physical separation of the DLC layer (and some PET segments) from the PET substrate.

For this purpose, 0.01% sodium hydroxide (NaOH) solution was prepared. Each bottle samples was filled with the prepared solution, and stored at 65°C. The duration of coating adhesion was determined based on daily visual observation, and the occurrence of visible flakes of DLC coating in the solution was judged as the loss of adhesion.

3.3. Results and Discussion

3.3.1. Homogeneity of DLC layers formed at different power frequency

As shown in Table 3-1 and Fig. 3-4, DLC coating formed at any power frequency ranging from 2.50 MHz to 13.56 MHz remarkably enhanced the barrier property of PET bottles. As the used frequency was increased from 2.50 MHz to 6.00 MHz, the obtained OTR was gradually decreased. The use of higher frequencies had an increasing trend of OTR. As a result, the minimum OTR and consequently the maximum BIF was obtained at 6.00 MHz.

Table 3-1. OTR of uncoated bottles and coated bottles using different power frequencies.

Frequency (MHz)	OTR (cc(STD)/day/bottle)	BIF (relative value)
Uncoated	0.0314	1
2.50	0.0038	8.3
3.00	0.0035	9.0
3.50	0.0033	9.5
4.00	0.0028	11.2
4.50	0.0023	13.7
5.00	0.0020	15.7
5.50	0.0017	18.5
6.00	0.0015	20.9
6.50	0.0021	15.0
7.00	0.0020	15.7
13.56	0.0023	13.7

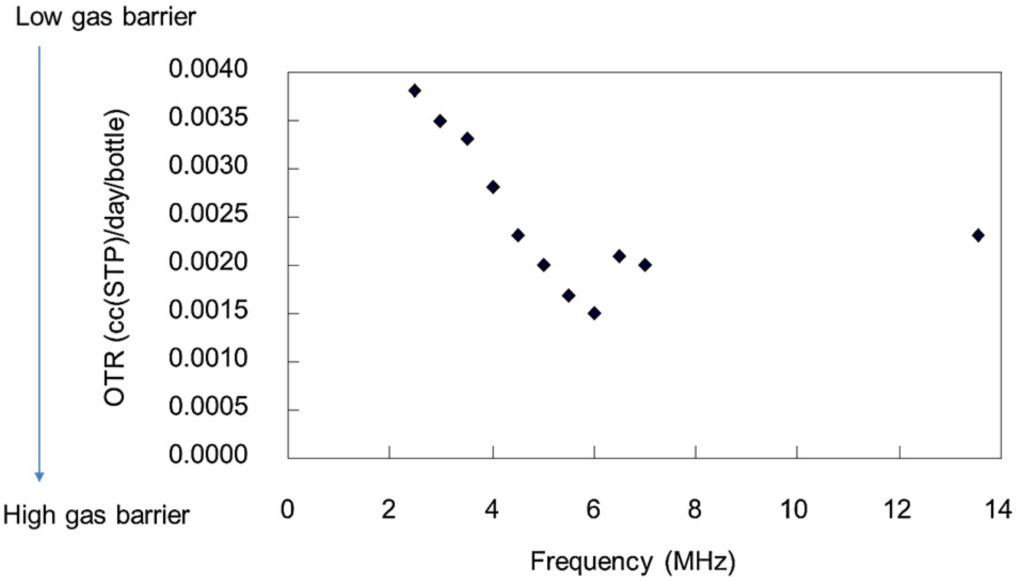

Fig. 3-4. OTR as function of power frequency ranging from 2.50 MHz to 13.56 MHz. PET bottles were coated with DLC using different power frequency. The same conditions of material gas supply and plasma deposition time were used.

In Fig. 3-5, the horizontal axis of positron energy represents the relative depth of samples from the DLC coated surface because the DLC coated surface was placed to face the positron source, and the positron energy determines how deep positrons enter into the DLC coating and its substrate. The positron energy of less than and more than ca. 3.0 keV was considered to provide the S values of DLC coating and its substrate, respectively, because two regions of remarkably different S values were distributed above and below this energy in all the samples examined.

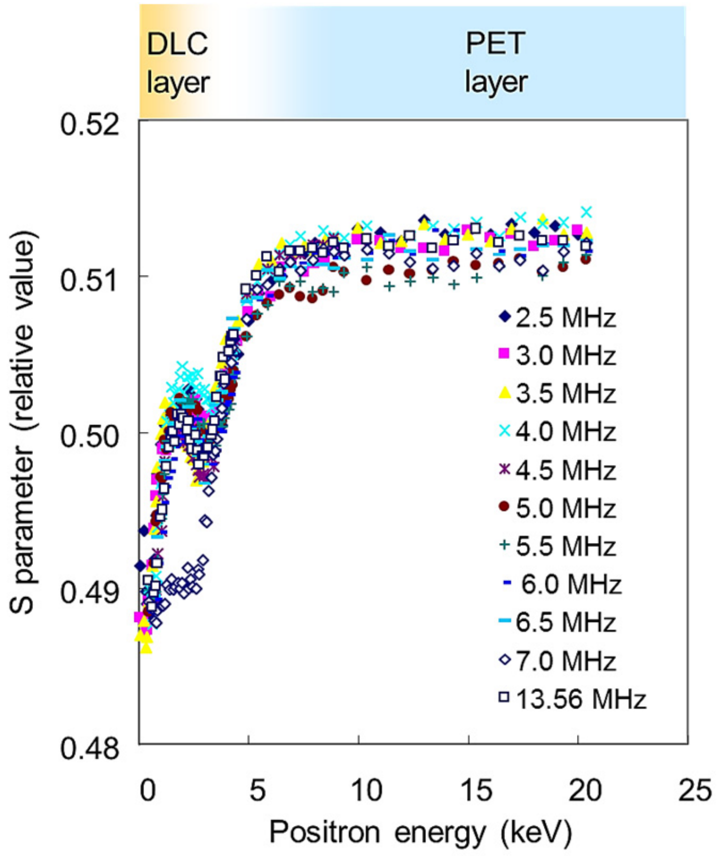

Fig. 3-5. S parameter profile of coated PET. PET bottles were coated with DLC using different power frequency. The same conditions of material gas supply and plasma deposition time were used. The interface between DLC layer and PET substrate is considered to be located around 3 keV.

In the substrate region, the S values of ca. 0.51 refer to the relative free volume of PET substrate, that is, biaxially-oriented PET matrix for bottle shaping. The positron annihilation technique was accurate enough to provide the equal S value of the PET substrates for all examined samples. It is considered that the small variance of S values among PET samples was caused by the difference in the crystalline parts of PET, often due to the degree of orientation in the bottle blowing process. In the DLC coating region, the behavior of positron annihilation was virtually same, indicating the formation of homogeneous DLC thin films, among the samples of any power frequency except that of 7.00 MHz. Except this power frequency, the S value of the DLC layer formed on the inner surface of sample bottles was interpreted to be ca. 0.50, which were given in the lowest value in the peak between the surface and the PET substrate positions. It should be noted that the decrease of the S values near the uppermost surface of DLC layers is considered to be caused by the positrons which moved and annihilated in the outside of the DLC layers. It is also considered that the decrease of the S values between the DLC and PET layers was caused by the occurrence of mixing layers (PET layers including DLC components). The different positron annihilation behavior in the case with 7.00 MHz suggests unknown structural difference. However, its details were yet to be describable. Fig. 3-6 shows the result of positron annihilation of different positions of the sample bottle, indicating that the exceptional S values were not due to a positional effect, but to unique to the power frequency of 7.00 MHz.

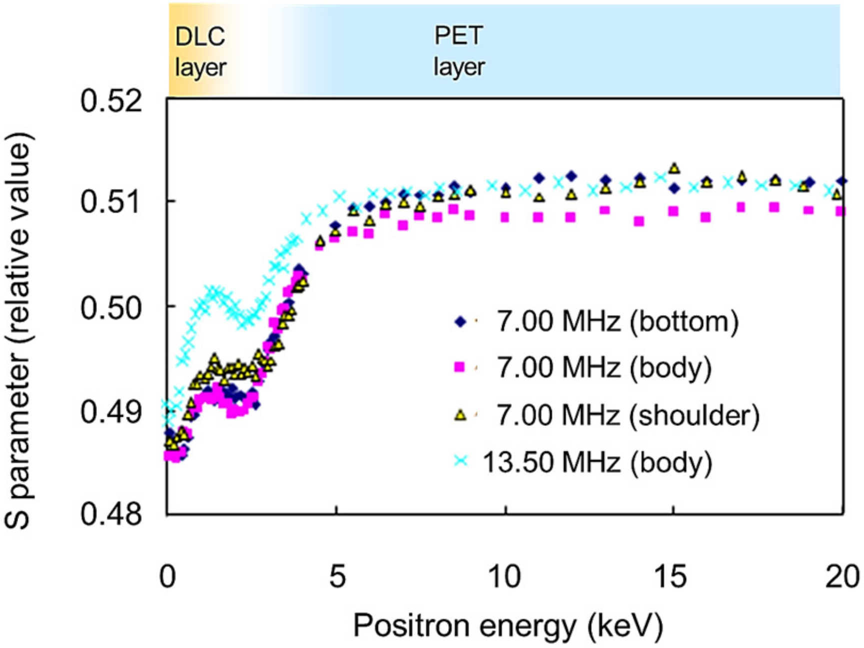

Fig. 3-6. S parameter profile of bottle parts coated with DLC thin films. The sample bottle was coated with DLC using 7.00 MHz, and each portion was cut to compare with one coated using 13.56 MHz in terms of S parameter, in order to observe positional impact on the value of S parameter inside the bottle.

Table 3-2 supports the result of the homogeneity of DLC coatings mentioned above, from the viewpoint of chemical composition. DLC thin films formed both with 13.56 MHz and 6.00 MHz were mainly composed of ca. 70 atomic percentages of carbon and almost 30 atomic percentages of hydrogen, and their compositions were not significantly different.

Figs. 3-7 and 3-8 also provided support data, from the viewpoint of chemical and physical properties, respectively, where both XPS spectra and sp^3/sp^2 ratio were not significantly different along the examined frequencies.

Table 3-2. Chemical composition of DLC coating.

Frequency:		6.00 MHz	13.56 MHz
Atomic %:	C	72.9	69.3
	H	26.3	28.1
	O	0.8	2.6
	N	not detected	not detected

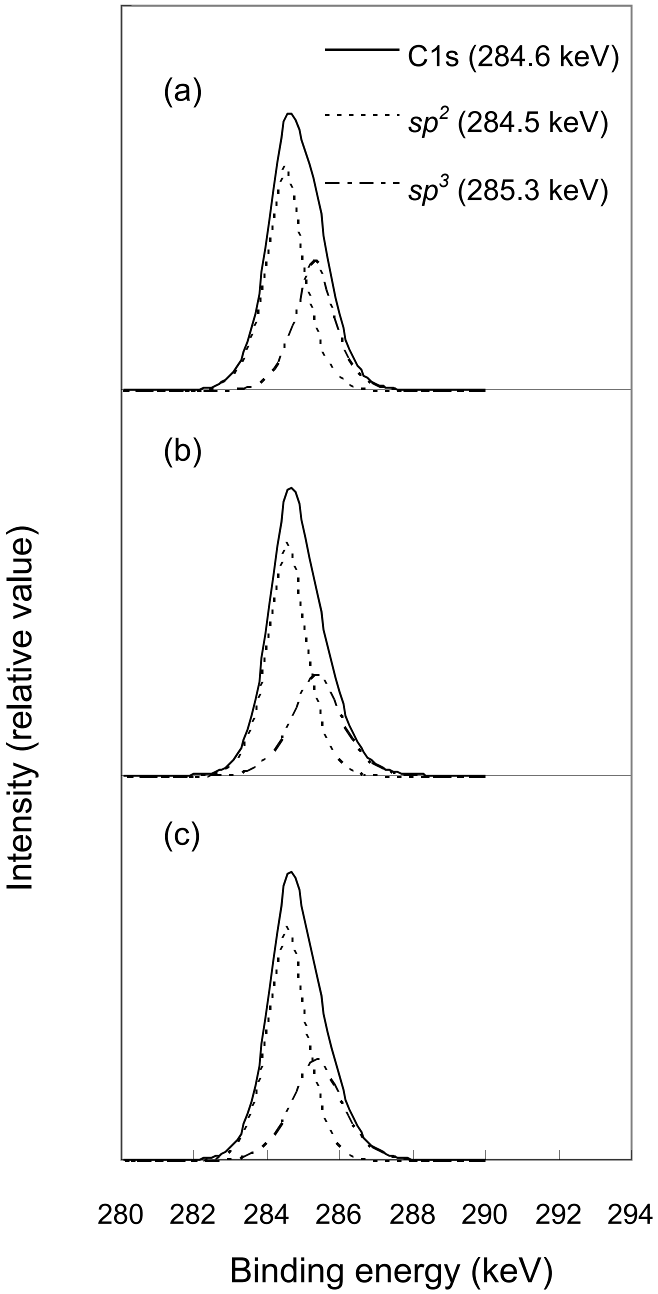

Fig. 3-7. XPS spectra on C1s core level of DLC coating. Examples of the spectra of DLC coatings on PET bottles using the power frequencies of (a) 13.56 MHz, (b) 6.00 MHz, and (c) 3.00 MHz were shown.

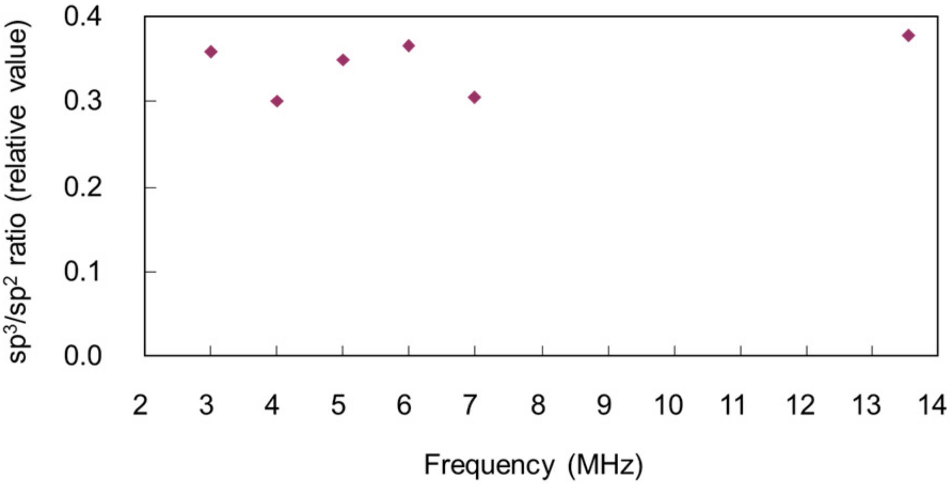

Fig. 3-8. Ratio of sp^3/sp^2 vs frequency. For the reference of chemical and physical properties of DLC coating on PET bottles, sp^3/sp^2 ratios correspondent to the power frequency ranging from 3.00 MHz to 13.56 MHz were calculated.

It should be mentioned that the peaks in at the positron energy of ca. 3 keV in Fig. 3-5 were found in close positions among different frequencies except 7.00 MHz. This indicates that coating thickness is almost same over all the examined frequencies, probably including 7.00 MHz. The almost equivalent thickness of DLC layers was supported by the result of measurement with a contact-type thickness meter, as shown in Fig. 3-9. For reference, the thickness of DLC coated with 13. 56 MHz was 19 nm.

These results indicate that the combination of positron annihilation, ERDA and XPS techniques was turned out to be a powerful method to infer the physical and chemical identity of carbon-based materials such as PET and DLC. The results obtained in this study also indicated that DLC layers formed at different power frequencies ranging from 2.50 MHz to 13.56 MHz were basically homogeneous in terms of structure for gas permeation and chemical composition, except 7.00 MHz..

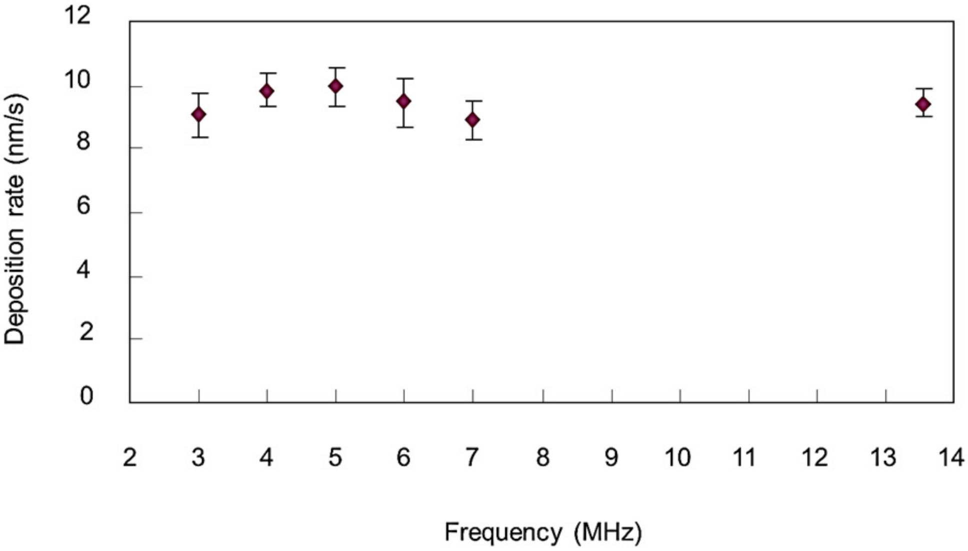

Fig. 3-9. Deposition rate of DLC coating. Partially masked silicon wafers on the inner surface of PET bottles were coated with DLC using different power frequencies. The same conditions of material gas supply and deposition time were used. The resultant surface profile of coated and un-coated areas on the wafers was used for the calculation of the deposition rate. Bars represent standard deviation.

3.3.2. Background of optimization through power frequency

Regarding gas barrier enhancement, it can be explained that the higher gas barrier property obtained at around 6.00 MHz power frequencies was caused by the appropriate distribution of plasma between the inner and outer electrodes of the coating machine. Theoretically, in the plasma occurrence conditions used in this study, a lower frequency leads to less primary electrons in the plasma due to the decrease of electro-magnetic oscillation, and more secondary electrons due to increase of the ion impact to the substrate [5)]. It is likely that secondary electrons are produced at the inner surface of a PET bottle and therefore that more secondary electrons force the plasma to concentrate, that is, to increase electron density, inside the bottle. On the other hand, it is also likely that less secondary electrons, for example in the case with 13.56 MHz power frequency, lead to plasma concentration in the middle of the inner and outer electrodes, that is, the space close to the bottle mouth and shoulder parts. A schematic image of this positional shift of plasma concentration inside a bottle was drawn in Fig. 3-10. The shift in the concentration of plasma along with power frequency was at least partially observed in light emission through transparent windows placed along with the exhaust line of the coating machine.

It should be noted that high electron density and ion impact are one of factors to form dense DLC structure. Based on both factors, we can assume a trade-off relation to enhance the barrier property of DLC coated containers, where a higher power frequency favors higher electron density while a lower power frequency favors higher ion and impact and more even plasma distribution inside the substrate containers.

This assumed trade-off relation is supported by the results of color tint and adhesion stability described later. Thinner tint of the shoulder part of the sample bottles can be interpreted as the occurrence of less concentrated plasma around the mouth and the shoulder part, as shown in Fig. 3-11.

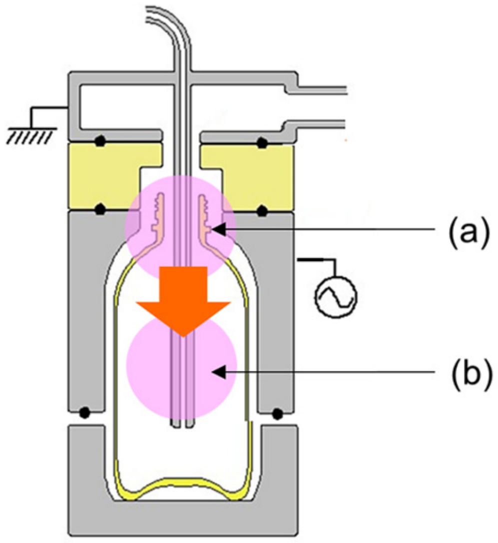

Fig. 3-10. Schematic image of plasma concentrated position with power frequency of (a) 13.56 MHz and (b) 6.00 MHz.

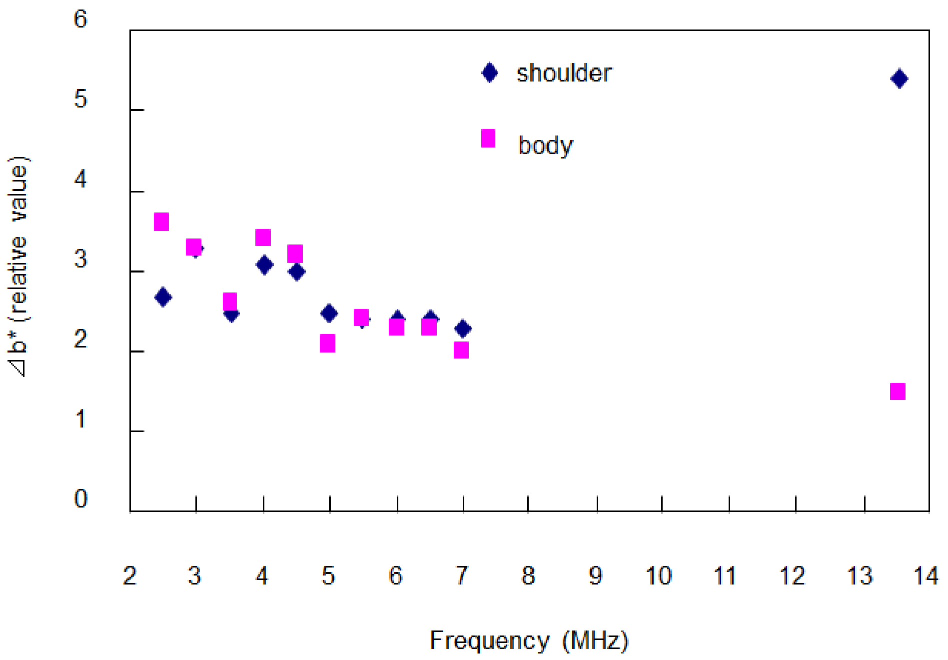

Fig. 3-11. Tint of PET bottles. As an indicator of tint, b* value in the L*-a*-b* system was used. The shoulder and body parts were used to represent the degree of even distribution of coating thickness.

Furthermore, it is considered that the thicker tint of the body part in lower frequency was caused by higher ion impact, because higher ion impact may cause the increased occurrence of graphite structure, which is likely to enhance the tint of DLC [16)]. As shown in Fig. 3-12, the duration of the adhesion of DLC coating in contact with NaOH caustic solution had a decreasing tendency as the used power frequency decreased. It is considered that the earlier loss of the adhesion of DLC coating obtained in the case with a power frequency less than 5.50 MHz was caused by the occurrence of higher ion impact, because higher ion impact more likely breaks polymer chains to weaken the adhesion stability of DLC coating. However, it seems that the polymer breakage due to ion impact cannot be clearly shown in the results of this study. The resultant change in free volume in the interface region between DLC layer and PET substrate may be too small to be detected with the used positron annihilation technique. In other case, higher residual stress in DLC coating due to higher ion impact may be the reason for the weakened adhesion stability.

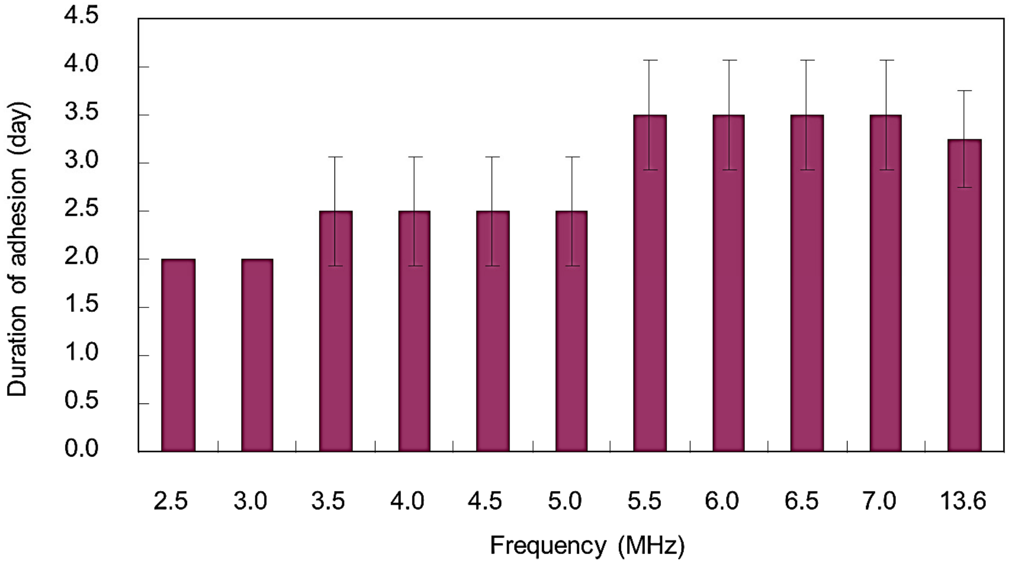

Fig. 3-12. Duration of the adhesion of DLC coating to PET substrate. Sample bottles were filled with 0.01% sodium hydroxide, and daily observed for the adhesion of DLC layer to PET bottle wall. Bar represents standard deviation.

3.3.3. Significance in practical use of optimized power frequency

From the industrial standpoint of view, compared to the use conventional power frequency of 13.56 MHz, the use of the power frequency of 6.00 MHz for DLC coating on PET containers was turned out to enable favorable gas barrier, tint, and adhesion stability when the above-mentioned capacitively-coupled PACVD technique was employed. Similar optimization of power frequency with lower frequency than widely used 13.56 MHz can be applied to other capacitively-coupled PACVD systems and the resultant coated three dimensional objects in various industrial applications.

For beverage and food polymer containers, this optimization can be used for quality improvement in terms of shelf-life extension and/or bottle appearance. Also, the optimized coating conditions for gas barrier enhancement can be utilized for a shorter coating time, leading to an improved economics.

3.4. Conclusions

In this study, the optimization of the power frequencies of a capacitively-coupled PACVD machine was conducted to enhance the gas barrier property of DLC layers on the inner surface of PET containers.

Power frequencies ranging from 2.50 MHz to 13.56 MHz were used. As the used frequency was increased from 2.50 MHz to 6.00 MHz, the obtained OTR was gradually decreased, and the use of higher frequencies had an increasing trend of OTR. As a result, with the use of power frequencies between 5.00 MHz and 7.00 MHz, decreased OTR was obtained, compared to the use of conventional 13.56 MHz (OTR: 0.023 cc (STP)/day/bottle). Especially, the use of 6.00 MHz provided the minimum OTR, 0.015 cc (STP)/day/bottle.

The results of the obtained positron annihilation property, chemical composition, and chemical structure indicated that virtually homogeneous DLC coatings were formed with the examined frequencies, except that the power frequency of 7.00 MHz provided somewhat different positron annihilation property. As a result, the combination of positron annihilation, ERDA and XPS techniques showed a powerful manner to infer the physical and chemical identity of carbon-based materials. It is expected, for instances, that the use of these techniques can facilitate to secure food safety and to execute quality control.

Tint caused by DLC coatings and the adhesion property of DLC coatings in contact with caustic solution were also examined. The use of power frequency of 6.00 MHz provided the minimum difference in tint between the shoulder and body parts of coated PET bottles. The use of higher and lower frequencies had tendencies of thicker shoulder and body, respectively. Also, the duration of adhesion had a decreasing tendency as the used frequency decreased. These results support that the modification of power frequency causes a shift of spatial distribution of plasma concentration inside the PET container.

Form the industrial viewpoint, the power frequency of 6.00 MHz provided the most optimized properties for DLC coated PET containers in terms of gas barrier, tint and adhesion stability. These properties can be utilized for the improvements of product quality and cost performance.

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Chapter 4

Gas and Flavor Barrier Diamond-Like Carbon Thin Film Coating to Plastic Closures

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4.1 Introduction

4.1.1 Required properties of plastic bottles for beer

As mentioned in the previous chapters, poly(ethylene terephthalate) (PET) bottles are the most intensive polymer packages for gas barrier enhancement study [1, 2)], the application of diamond-like carbon (DLC) coating is used to reduce gas permeation of PET bottles in beverage and food industry. The use of coating enables practical shelf-life extension for beer and other sensitive products [3)].

The potential huge market of DLC coated PET bottles lies in beer, and both gas and flavor barrier properties are required for its containers. Beer is known as extremely sensitive to oxidation, and oxygen permeation through polymer packages accelerates the oxidative deterioration in terms of taste quality. When normal PET bottles are used for typical packaged products in retailers, the occurrence of off-flavor caused by beer oxidation leads to a quite limited shelf-life [4)]. This is the reason why DLC coating and other equivalent applications for gas barrier enhancement [1, 5-8)] are demanded for the practical shelf-life of these products. Furthermore, beer is also a type of carbonated beverage, and the decrease of carbon dioxide content caused by permeation may lose the total flavor balance of the product. Also, in the brewing process of beer, ingredients with strong flavor such as hops, herbs, and fruits, are used. The use of these ingredients sometimes leads to the requirement of barrier property against flavor components, so-called anti-sorption property, for beer containers. Sorption is highly related to flavor scalping [9)], and relates to permeation through and dissolution into polymer packages. Because sorption can cause the loss of subtle balance among various organic compounds in beer, it affects the flavor quality of the product.

Juice is also widely packaged in gas-barrier-enhanced PET bottles, because the permeation of oxide (and, in case with carbonated juice, carbon dioxide) deteriorates the flavor of juice products. Sorption also affects the flavor quality of packaged juice products.

4.1.2 Increasing demand of plastic closures with high gas and flavor barrier properties

As the performance of PET bottles is enhanced, the performance of plastic closures used with PET bottles has been more important to determine the overall performance of the package. Thin film coatings can provide the effective inhibition of both gas permeation through PET bottles and sorption into PET bottle wall. On the other hand, the sealing parts of the most of these plastic closures are made of polyethylene (PE) due to its suitable rigidity and shapeability. In some cases, perforated PE sealing parts with PET uppermost layers or poly(vinyl chloride) sealing parts, which may perform with effective anti-sorption functions, are used. The use of these closures was, however, quite limited in today's industry because of increased production cost or environmental concern with the use of chloride. The enhancement of gas barrier and anti-sorption properties of PE is, therefore, the key for extended shelf-life and quality extension of sensitive products in a PET bottle

In attention to anti-sorption property as well as gas barrier property, the attempt in this paper was made to form practical DLC thin film coating to the inner surface of PE sealing parts. It should be stressed that the gas barrier enhancement of PE with thin film coating is a challenging effort because of the rough surface and/or weak adhesion properties of substrates shaped with PE, derived from the nature of this polymer material. To the contrary, Tashiro *et. al.* reported that, for the oxygen barrier enhancement of PE and other polymeric films, use of specific organic silane compounds as a undercoat of DLC coating was effective in enhanced adhesion and gas barrier enhancement 10). In this report, DLC coating was formed in 35 second to about 80 nm thickness, and, therefore, a shorter and thinner coating demanded in today's industry is still a challenging effort. Because one of these organic silane compounds, 3-aminopropyltrimethoxysilane (3APTMS), is known as a relatively safe compound, the author applied a modification of this technique to plastic closures in order to enhance the overall performance of the package composed of a coated PET bottle with a PE closure.

4.2 Experiments

4.2.1 Package components

4.2.1.1 PET bottles

For manufacturing 500 ml PET bottles of typical shape and weight (34 g) for carbonated soft drinks as shown in Fig. 4-1, a preform injection machine, KS100T Kata System Co., Ltd., Japan, and a blow molding machine, FRB-1, Frontier Co., Ltd., Japan, were used. The resultant bottles had ca. 190.4 mm in height, ca. 66 mm in diameter, and 0.035 mm in thickness.

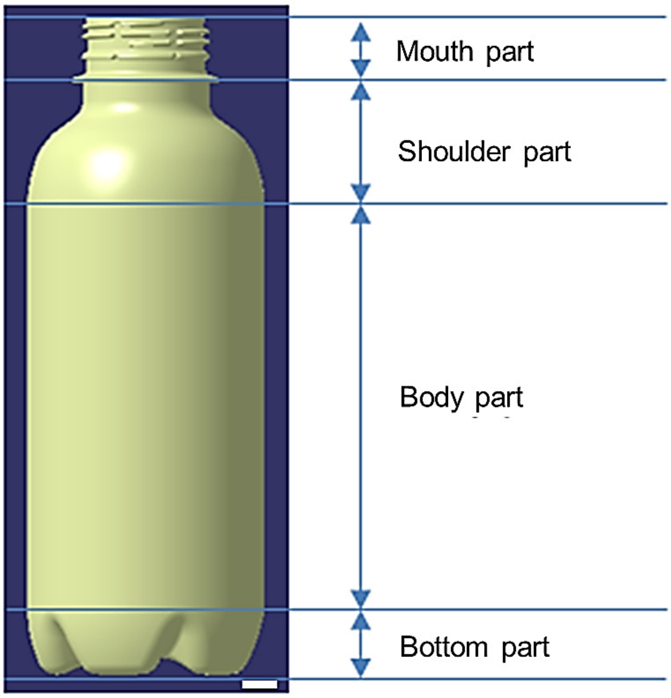


Fig. 4-1. Appearance and parts of PET bottles. The bar represents 10 mm.

4.2.1.2 Plastic closures

A variation of commercial two-piece plastic closures developed for PET bottles for beer products were used as shown in Fig. 4-2. These closures were designed to fit to the PET bottle mouth part which had 33.1 mm in outer diameter, and were composed of PE sealing parts (1.19 g per one part) and polypropylene shell parts as shown in Fig. 4-2. The inner area of the inner ring of the sealing part had 27.4 mm in diameter and 1.1 mm in thickness.

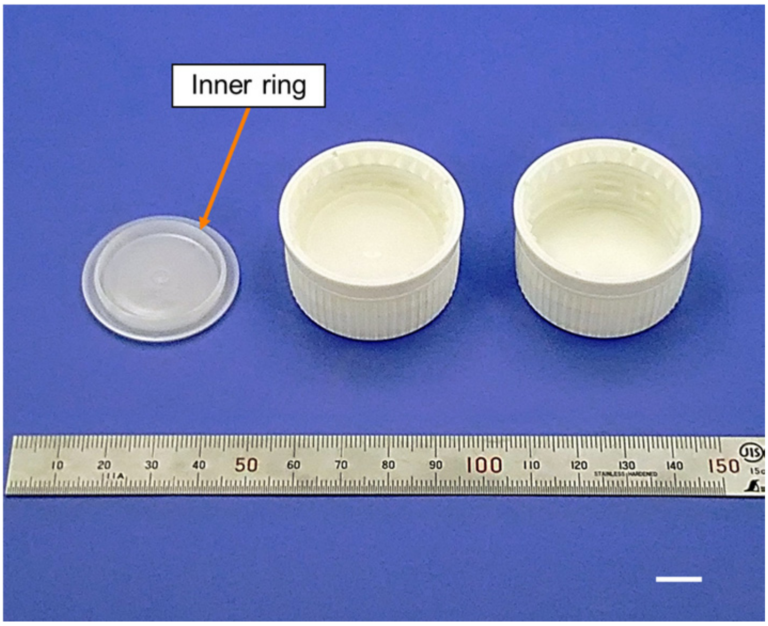


Fig. 4-2. Appearance of a two-piece closure. A sealing part, assembled sealing and shell parts, and a shell part are shown from left to right. The bar represents 10 mm.

4.2.2 DLC and its pretreatment coating to package components

4.2.2.1 DLC coating to PET bottles

In order to clearly observe the performance of plastic closures and evaluate the overall performance of packages composed of closures and bottles, DLC coated PET bottles were used. It should be mentioned DLC coating provides enhanced anti-sorption property as well as gas barrier property to coated plastic substrate [11)].

DLC coating to PET bottles was performed as described in the previous chapter of this paper [12)]. DLC thin films were formed on the inner surface of PET bottles or PE sealing parts with a device, PNS-1, Youtec Co., Ltd., Japan, specifically designed for PET bottle coating. Fig. 4-3 (a) shows an example of coating to a PET bottle. Each bottle sample was placed onto the bottom part of the outer electrode in order to be enclosed in the vacuum chamber, and to be subjected to subsequent processes for a type of PACVD technique. The vacuum chamber was closed and vacuumed to 5 Pa. Acetylene gas was supplied into the bottle at a rate of 80 cubic centimeters at standard pressure and temperature per minute (sccm). 13.56 MHz high frequency power of 1000 W was applied to the outer electrode so that acetylene plasma was produced between the inner and outer electrodes. The plasma was maintained for 2.0 seconds.

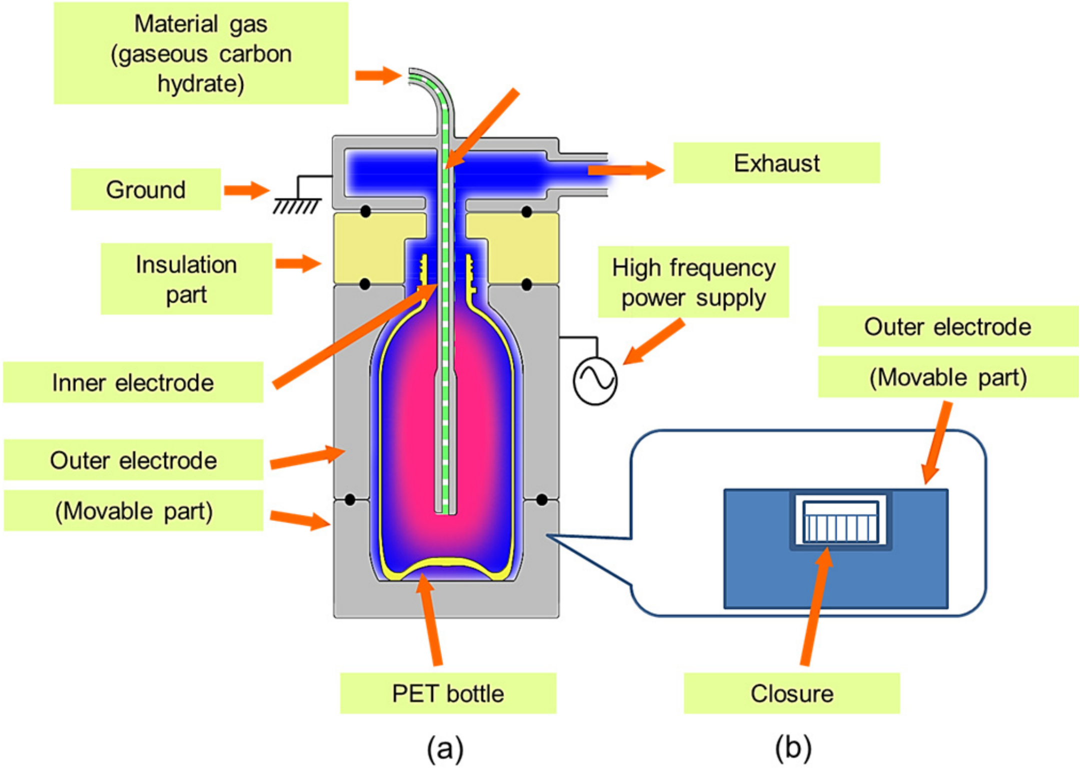


Fig. 4-3. Schematic illustration of DLC coating devices for (a) PET bottles and (b) plastic closures. The exchange of outer electrodes enables coating to different bottles and closures in a single device. The above Fig. 4-3 (b) illustrate a closure can be coated with a specific movable part of the outer electrode. It should be mentioned that outer electrodes function as a part of vacuum chambers and the movement of the movable parts of the outer electrodes enables the introduction and removal of uncoated and coated substrates, respectively.

4.2.2.2 DLC coating to plastic closures

DLC coating to plastic closures were performed basically in the same manner as that to PET bottles, and applied to the inner surface (the surface in contact with the content of PET bottles) of sealing parts. In order to coat a sealing part of closure, the bottom part of the outer electrode was modified to fit the shape of the closure as shown in Fig. 4-3 (b).

For the pretreatment of 3APTMS undercoating, 70 μL of 3APTMS, supplied by Shin-Etsu Silicon Chemicals Co., Ltd., Japan, was dropped to the center of the inner ring of a sealing part and distributed over the surface based on a spin-coating technique using 3000 rpm in a draft chamber under 23°C. The resultant 3APTMS undercoating was dried at a room temperature around 23°C or immediately applied to DLC coating without any specific drying process.

4.2.3 Measurement of oxygen barrier property of package components

4.2.3.1 Oxygen barrier property of PET bottles

Oxygen transmission rate (OTR) was measured with Oxtran 2/21. Mocon Co., Ltd., USA, for 72 hours under the conditions of 23°C and RH 90%, based on ASTM F-1307 method [13]. ASTM F-1307 is a type of a constant pressure and volume method for the measurement of oxygen permeation through containers.

In this method, the mouth part of a sample bottle is hermetically sealed to a metal pipe system with two ends. One end is connected to the source of nitrogen carrier gas source, and another end is connected to the oxygen detector of the device. With a steady carrier gas flow, the inside of the sample bottle has virtually no oxygen except permeant oxygen through bottle wall, and the outside is surrounded by air. The surface area and the wall thickness of the sample bottle, and oxygen pressure difference are kept constant. The oxygen detector detects the permeant oxygen concentration in the steady carrier flow and converts into the OTR through the bottle sample.

4.2.3.2 Oxygen barrier property of plastic closures

The OTR of plastic closures was measured basically in the same manner as that of PET bottles. Instead of that bottle samples were sealed to the metal pipe system, closure samples were hermetically screwed to a metal thread port which was shaped into the same dimension as the mouth part of PET bottles. Because clearance between the sealing and shell parts of a closure was large enough in terms of permeation, the oxygen detector detected only the permeant oxygen through the sealing parts and the interface between the sealing and mouth parts.

4.2.4 Measurement of deposition rate on closures

The deposition rate of thin films formed in the manner mentioned above was measured, as described in the previous chapter of this paper [12)]. Partially masked silicon wafers placed on the inner surface of the center of the sealing part of closures, and the difference in height between the unmasked and the masked parts is detected using a contact-type thickness meter, α-step, KLA-Tencor Corporation, CA, USA. The average of deposition rate obtained from three samples was adopted. It should be noted that above-mentioned coating conditions for PET bottles resulted in the deposition of DLC thin films of ca. 19 nm thickness in the center of the body part, leading to the deposition rate of ca. 9.5 nm/sec.

4.2.5 Measurement of surface roughness

The surface roughness of substrate or coating was measured based on Ra over the square area of 10 μm × 10 μm using an atomic force microscopy, AFM5100N, Hitachi High-Technologies Co., Japan.

4.2.6. Chemical characterization of thin film

In order to confirm the formation of DLC over 3APTMS undercoat, Raman spectroscopy was performed using a Raman spectrometer, LabRAM HR Evolution, Horiba, Ltd., Kyoto, Japan, in conditions of a photo excitement at 532 nm under room temperature. For this analysis, DLC coating was deposited to 80 nm on sample substrates. It should be noted that in an attempt to apply thicker DLC coating in order to avoid the influence of substrate chemical structures, DLC coatings tend to be spontaneously cracked with the thickness of 100 nm and more. The deposition of 80 nm thickness was, therefore, employed for this experiment.

To complement the above Raman spectrometry, XPS analysis was also performed. The depth profile of the chemical composition of the coated surface was analyzed using a scanning XPS microprobe, Quantera II, Physical Electronics, Inc., OR, USA, with the AlKα radiation (1486.6 eV) was used for the spectral regions of Si2p, O1s, and C1s. N1s was omitted in consideration of the previous results with no detection of nitrogen in DLC coatings [6)]. For samples of this analysis, thin films of ca. 20 nm in thickness were formed on the sealing parts of plastic closures.

4.2.7 Sorption test

4.2.7.1 Sample preparation

1.00 mL of commercial orange juice including 29.2 μg d-limonene ($C_{10}H_{16}$) / ml was dropped to the inside of the inner ring of a sealing part, and stored at 35°C for 24 hours, assuming product storage and distribution at a high temperature season. Three each of (1) uncoated, (2) DLC coated, and (3) 3APTMS (undercoat) and DLC (top coat) coated samples were prepared. After the storage, each sample was gently rinsed with distilled water, and dried at room temperature.

4.2.7.2 Quantitative analysis of d-limonene

As an index of the sorption of d-limonene to the sealing part of a plastic closure, the total amount of d-limonene released from a sealing part sample detected in a gas chromatography system with a flame ionization detector, GC-2010 AF, Shimadzu Corporation, Japan. Each sample containing fragments of an individual sealing part in a glass vial was hermetically transferred to the detector controlled at 250°C, using helium for a constant carrier gas flow. Before the measurement of these samples, it was confirmed that blank samples (empty or containing fragments of a fresh sealing part) did not show any significant detection of d-limonene above the background level. The content of d-limonene in the orange juice was measured in the same manner.

4.2.8 Sample description

In this paper, the coated sealing part samples prepared were described in the following manner. PE, PE/DLC, PE/3APTMS, PE/3APTMS/DLC refers to uncoated samples, sealing parts directly coated with DLC thin films, sealing parts coated with 3APTMS, and sealing parts coated with 3APTMS followed by DLC thin films, respectively.

4.3 Results and discussion

4.3.1 DLC coating to closures and resultant OTR

It was observed in plastic closures that a gas-barrier-enhanced performance of DLC coating was achieved when 3APTMS undercoating was applied. Fig. 4-4 shows the visual appearance of each sample. Because of slight flow lines from the center to the peripheral directions caused by the spin-coating of 3APTMS, the appearance of PE/3APTMS/DLC was slightly white, compared to PE/DLC. 3APTMS and DLC layers. The thickness of the 3APTMS and DLC layers was measured as 1.3 μm, and 21.6 nm, respectively.

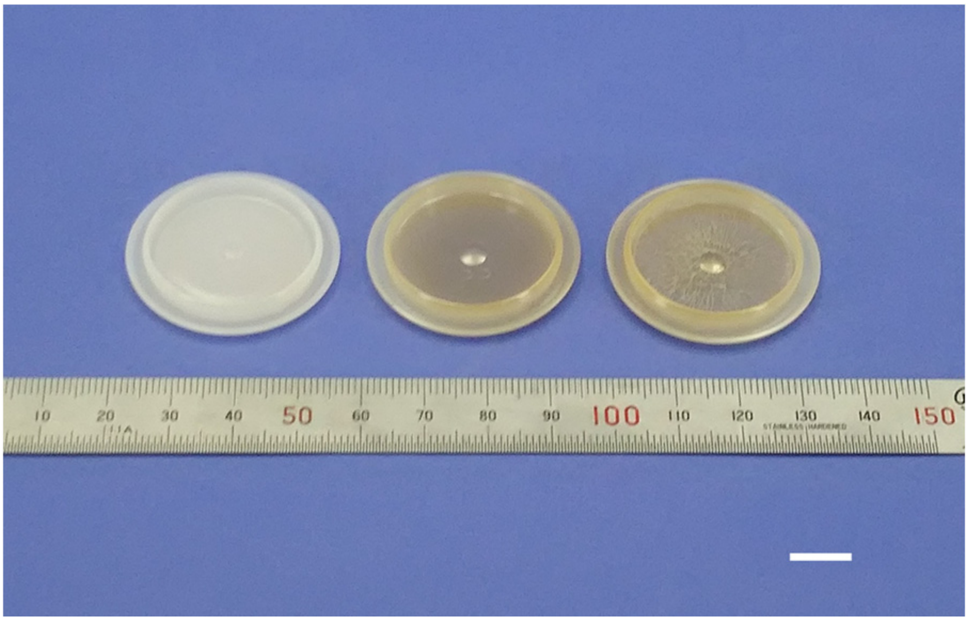


Fig. 4-4. Visual appearance of coated and uncoated sealing parts of plastic closures. Samples of PE, PE/DLC, and PE/3APTMS/DLC were shown from left to right. The bar represents 10 mm.

The OTR of the prepared samples were shown in Fig. 4-5. The abbreviation of cc (STP) represents cubic centimeter at standard temperature and pressure. For PE/DLC and PE/3APTMS samples, OTR was slightly decreased, from 0.011 cc (STP) / closure / day (PE samples) to 0.009 cc (STP) / closure / day (PE/DLC samples) and 0.010 cc (STP) / closure / day (PE/3APTMS samples), respectively. On the other hand, the OTR of the closure was decreased by about two thirds, to 0.003 cc (STP) /closure / day (PE/3APTMS/DLC samples) with the introduction of the 3APTMS undercoating layer.

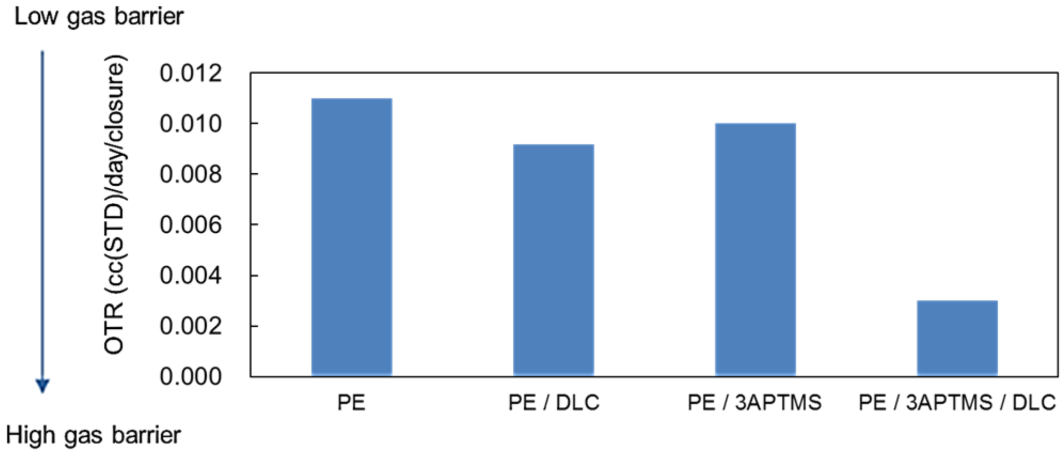


Fig. 4-5. Oxygen transmission rate of uncoated and coated closures.

The overall OTR of the package composed of a bottle and a closure was calculated. For the OTR of uncoated and DLC coated PET bottles, 0.0375 and 0.0030 cc (STP) / package / day, respectively, was employed. As shown in Fig. 4-6, compared to the set of uncoated bottle and closure, the OTR was remarkably reduced for the set of the coated bottle and uncoated closure. In the latter set, the majority of oxygen permeation occurred through the closure part. On the other hand, compared to the set of coated bottle and uncoated closure, the majority of the OTR of the set of coated bottle and closure occurred through the bottle part. In other words, the overall OTR of the package composed of the coated bottle and closure was decreased by about one half, compared to the case with the uncoated closure and DLC coated bottle (from 0.014 to 0.006 cc (STP) / package / day). With this oxygen barrier enhancement, a corresponding significant shelf-life extension and quality improvement against the oxidation of the content of the package can be expected.

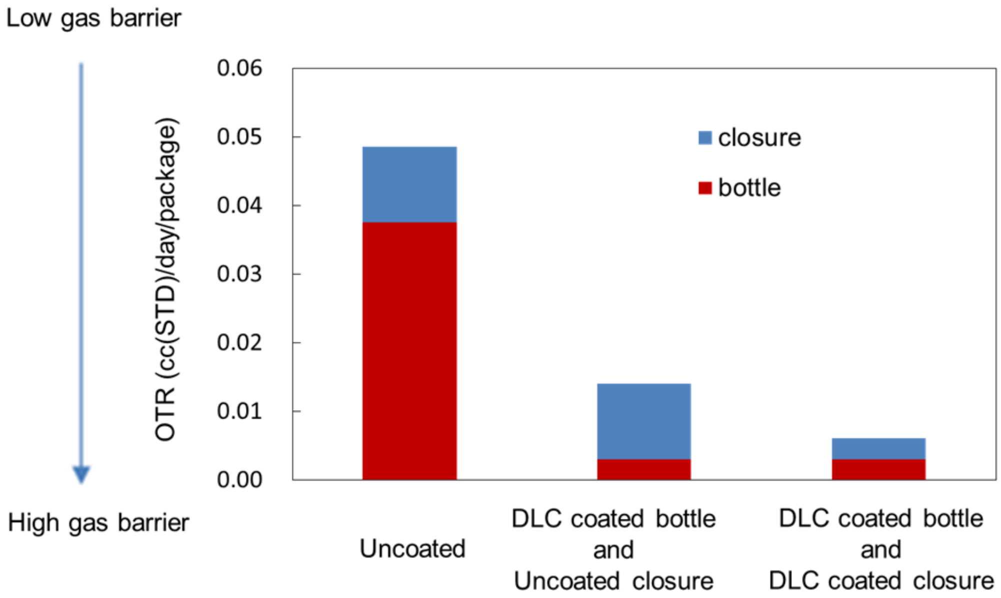


Fig. 4-6. Calculated total oxygen transmission rate of the whole packages. Compared to a set of uncoated bottle and closure, the OTR of a set of DLC coated bottle and uncoated closure was decreased to about 34%. Also, the OTR of a set of DLC coated bottle and closure was decreased to about 15%.

4.3.2 Mechanism of enhanced gas barrier property with 3APTMS undercoating

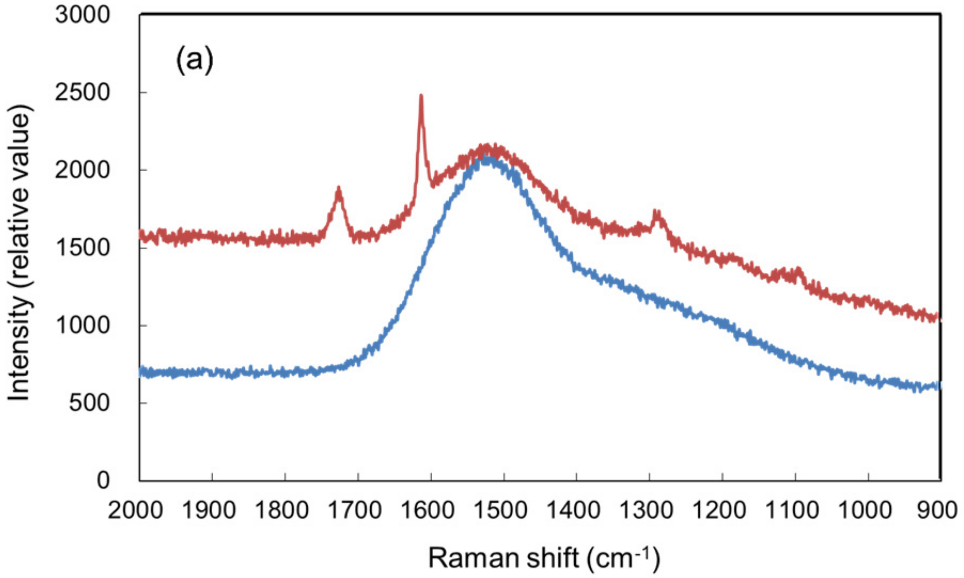
The reason of enhanced gas barrier performance of PE/3APTMS/DLC closure samples was studied from the viewpoint of surface roughness and the chemical structure of DLC layers.

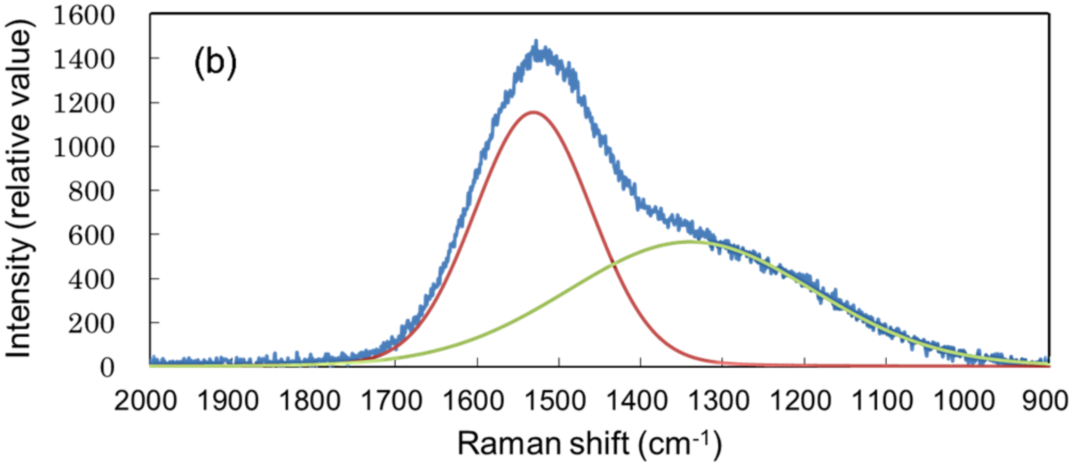
As summarized in Table 4-1, it was observed that DLC coating directly applied to PE surface was deposited basically along the surface morphology of the substrate. Interestingly, 3APTMS undercoating had a significant effect to increase surface roughness, and did not show any leveling effect. Despite of the rough undercoating, the oxygen barrier was enhanced with DLC coating on the 3APTMS layer.

Table 4-1. Surface roughness of uncoated and coated sealing parts of closures.

Sample	Surface roughness (*Ra*, nm)
(1) PE	21.15 ± 3.93
(2) PE/DLC	13.27 ± 2.21
(3) PE/3APTMS	192.73 ± 32.45
(4) PE/3APTMS/DLC	61.10 ± 6.85

As an analysis to the chemical structure of DLC layers, Raman spectrometry was conducted for the PE/3APTMS/DLC sample in comparison with a PET bottle sample treated with the same DLC coating. Because the spectrum obtained appeared to contain the influence of substrate as shown in Fig. 4-7 (a), especially with the sample using PET, the fitting of G and D peaks were calculated without the influence of peaks around 1730 cm^{-1}, 1610 cm^{-1}, and 1290 cm^{-1}. The resultant spectrum of G and D peaks was shown in Figs. 4-7 (b) and (c), and the ratio of these peaks indicates equivalent DLC coating was formed as shown in Table 4-2.





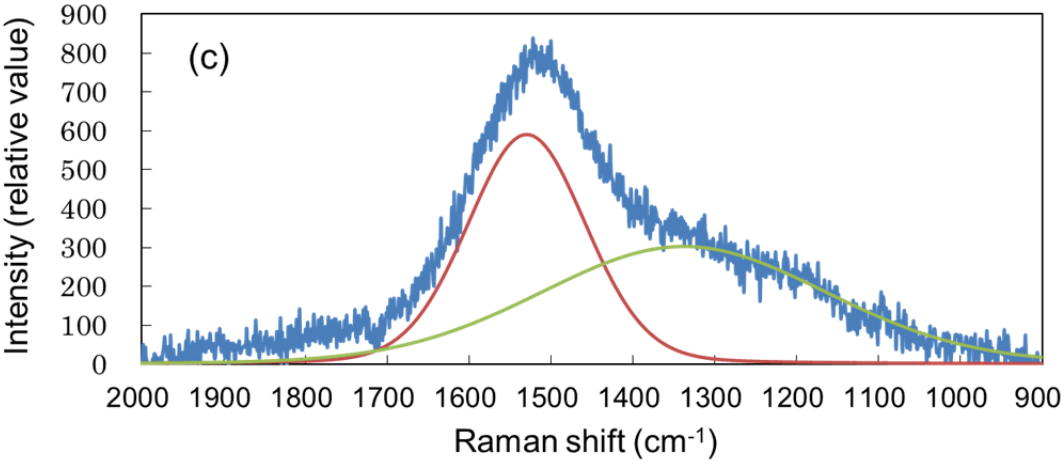


Fig. 4-7. Raman spectra of DLC coatings, (a) formed on PET (red line) and PE/3APTMS (blue line), (b) formed on PET (blue line), fit to G and D bands (red and green lines, respectively), and (c) formed on PE/3APTMS (blue line), fit to G and D bands (red and green lines), respectively.

Table 4-2. Ratio of G and D band peaks.

Sample	Peak position of bands (cm^{-1})	Height (relative value)	Ratio (relative value)
(1) PET/DLC	G: 1531.2	1155	0.49
	D: 1339.1	567	
(2) PE/3APTMS/DLC	G: 1529.8	590	0.51
	D: 1337.9	303	

It is considered that similar DLC coatings were formed on the samples of PET/DLC and PE/3APTMS/DLC, because the ratio of G and D band peaks was 0.49 and 0.51, respectively.

In order to confirm whether the atomic composition of the DLC layer formed on PE/3APTMS/DLC samples was affected by the components of 3APTMS layer, the surface depth profile of the DLC layer was analyzed with an XPS technique. Fig. 4-8 clearly shows that one layer composed of carbon only was formed on another layer containing carbon, silicon and oxygen. In this figure, the purple line for silicon is almost overlapping on the blue line for oxygen, except the uppermost depth. Although the accurate depth or etching rate of different layers was unknown, the carbon layer was empirically deduced to be around 20 to 30 nm in thickness based on the conducted XPS analysis conditions, and also matched with the deposition rate of DLC coating mentioned above.

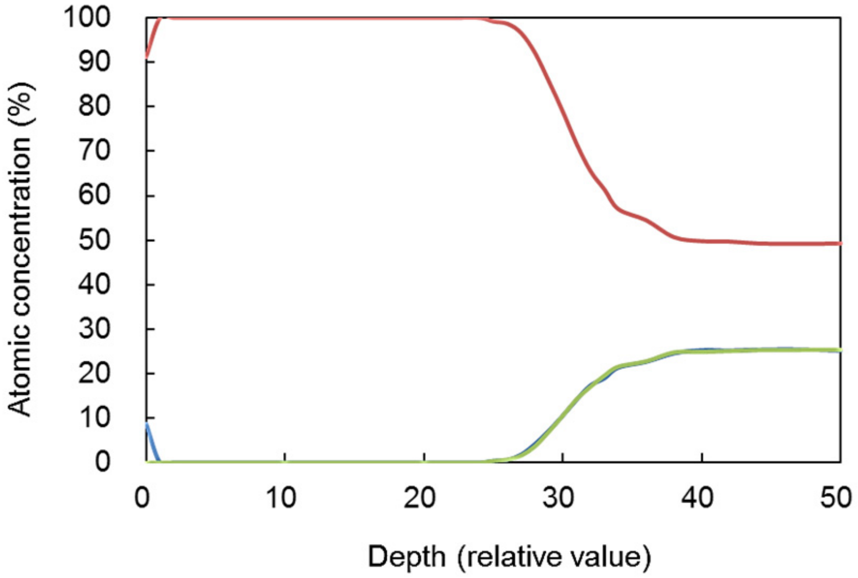


Fig. 4-8**.** Depth atomic profile of PE/3APTMS/DLC. From left to right, the uppermost surface of DLC coating (to be in contact with the content of the package) to the interface with 3APTMS was shown. Blue, red, and purple lines represent oxygen, carbon, and silicon, respectively. It should be noted that the purple line for silicon is almost overlapping on the blue line for oxygen, except the uppermost depth.

In this study, the combination of Raman spectrometry and XPS was employed to observe the possible homogeneity of DLC thin films, in consideration of a previous report which indicated silicon or nitrogen doped into DLC thin films affected the resultant Raman spectrometry [14)]. Based on the conducted Raman and XPS analyses, it can be concluded that homogeneous DLC thin films were formed either on PET or 3APTMS substrates. Interestingly, in spite of the fact that in the PE/3APTMS/DLC, DLC layers were formed on wet substrates, the dense structure of DLC thin films was formed in similar to the cases with other solid polymer substrates.

The quite limited oxygen barrier enhancement of the PE/DLC samples indicated the importance of interface conditions between polymers and DLC thin films for restricting permeation. The rough surface of the 3APTMS layers indicates that the principle of gas barrier enhancement with the DLC coating was different from the typical effect of undercoating, that is, the leveling of surface. It should be added that the surface of PE / 3APTMS or PE / 3APTMS / DLC was empirically rough enough to obtain little gas barrier enhancement with thin film formation. Tsuji *et. al* [15, 16)] reported that plasma treatment using such as oxygen or nitrogen modified the surface of 3APTMS layers into high gas barrier structures. It was reported that this plasma-assisted chemical modification caused the relative increase of silicon and oxygen contents in the uppermost surface layer. Even though the conducted XPS analysis showed the examined surface region was mainly composed of carbon at any depth, and any significantly silicon or oxygen rich layer was not observed, similar gas barrier enhancement through some chemical affinity, for example, dense chemical bonds, between DLC and 3APTMS layers appeared to occur. The reason of the missing silicon or oxygen rich layer probably lies in the PACVD technique used. A possible explanation is that the modification was not clear in the obtained XPS profile because a quite thin layer of 3APTMS was modified due to a shorter exposure to plasma. Slightly fluctuated curves in the depth between 35 and 40 in the profile shown in Fig. 4-8 may be the result of the modification, and provide an effective interface for gas barrier enhancement using DLC coating.

4.3.3 DLC coating to closures and resultant anti-sorption property

Table 4-3 shows d-limonene amounts detected from three different sample groups of sealing parts stored in contact with the orange juice used under the same conditions. A significant decrease of d-limonene was observed with PE/3APTMS/DLC samples, compared to uncoated PE samples (from 2.1×10^3 to 2.8×10^2 ng / sealing part). Interestingly, another coated samples of PE / DLC also showed a significant decrease of d-limonene detection (to 4.3×10^2 ng / sealing part), in spite of its quite limited oxygen gas barrier enhancement as mentioned above (from 0.011 to 0.009 cc (STP) / closure / day). This highly suggests that permeation and sorption can proceed differently, even though these phenomena are likely to have some principles in common such as dissolution and diffusion. A possible explanation is that large and polarized molecules of limonene compared to oxygen molecules are difficult to enter into the matrix of DLC layer, and, as a result, defects of DLC coating allow the passage of oxygen molecules while these defects still significantly restrict the entrance of limonene molecules into DLC and subsequent substrate layers.

Table 4-3. Sorption of d-limonene to the sealing parts of plastic closures.

Sample	Detected d-limonene (ng / sealing part)
(1) PE	2.1×10^3
(2) PE / DLC	4.3×10^2
(3) PE / 3APTMS / DLC	2.8×10^2

In total, it was suggested that the package composed of the DLC coated closure and bottle significantly inhibited the sorption of d-limonene, leading to an effective quality improvement against the scalping, for example, of hops or fruit flavors. The importance of this kind of quality improvement lies especially in consideration of substituting a PET bottle format for other package formats such as glass bottles and aluminum cans.

Because 3APTMS is known to be a useful sealant adhesive for food packages, it can be expected that the combination of 3APTMS and DLC can be used for food and beverage packages in safe manners.

In brief, thin film coatings can be considered as promising practical means to enhance the gas and flavor barrier property of plastic closures, like in the cases with existing coatings onto PET bottles. Especially from a standpoint where both gas and flavor barrier enhancement can be achieved, approach with thin film coating can be expected to be advantageous over other conventional types of approach such as the use of perforated PE sealing parts laminated with thin PET sheets, multilayer, oxygen scavengers, in terms of performance and economics.

4.3.4 Possible further quality and economical improvements

The technique of this study is applicable to functional coating onto two or three dimensional objects because the results of this study suggest approaches to coatings with little defects over typical rough objects. In this study, DLC coating was used in consideration of direct contact with food and beverage, while 3APTMS coating treated with nitrogen or oxygen plasma [15)] has an advantage in requiring virtually a single material and a simple process in machinery.

While several technical approaches are proposed to form a smooth surface of molded materials such as hot and cool molding [17, 18)], these appears to be difficult to perform in an economical manner required for such as plastic closures for beverage products, daily necessities, and expendable parts. Wet undercoating is, therefore, likely to provide more universal approach. Other combinations of wet and dry process can be also expected, for instances, through the use of coupling agents or photo hardening compounds, and plasma or radical treatments, respectively.

4.4 Conclusions

DLC coating was applied to plastic closures used for PET bottles. When the coating was applied directly onto the surface of PE sealing parts of the closures, oxygen gas barrier property was not significantly enhanced (the OTR of closures was decreased from 0.011 cc was 0.009 cc (STP) / closure / day). On the other hand, the anti-sorption property of d-limonene, a representative substance in the study of sorption to polymer materials, was significantly enhanced (the detected concentration from sealing parts was decreased from 2.1×10^3 to 2.8×10^2 ng / sealing part). Also, a significant enhancement of oxygen gas barrier property as well as anti-sorption property was achieved with the aid of undercoating using a type of organosilane, 3APTMS (the OTR of these samples was 0.03 cc (STP) / closure / day). The large and polarized molecules of d-limonene, compared to oxygen molecules, were considered to involve difficulty to enter the matrix of DLC matrix. It is also considered that the difference in the difficulty of the entrance into DLC matrix caused the different behavior between gas permeation and sorption. In order to confirm the chemical structure of the formed DLC thin films on 3APTMS layer, Raman spectrometry analysis was conducted. The result indicated that equivalent DLC thin films were formed on the surface of 3APTMS and PET layers. The conducted XPS profile analysis also confirmed that silicon and oxygen was not contained in the DLC thin film formed on the surface of the 3APTMS layer.

Both with gas and flavor barrier enhancement function of DLC coated plastic closures with 3APTMS, it was expected that corresponding quality improvement and shelf-life extension to products filled in gas barrier enhanced PET bottles such as beer.

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Chapter 5

Novel Gas Barrier SiOC Coating to PET Bottles through a Hot Wire CVD Method

5.1 Introduction

As stated in chapter 2, thin film coatings are one of technical approach for the sensitive food and beverage products in poly(ethylene terephthalate) (PET) bottles. The advantages of thin film approach lie in the relatively high degree of gas barrier enhancement and the relatively wide coverage of product categories as well as the relatively high degree of the recyclability of PET bottles, compared to other approaches such as multi-layer [1-4)]. On the other hand, relatively high capital expenditure for the installment of specific machines based on plasma-assisted chemical vapor deposition (CVD) processes is the disadvantage of current coating technologies. In these situations, a novel process for thin film coating which provides possible reduced capital expenditure as well as conventional gas barrier performance is demanded.

The author conceived that one possible approach to the novel process was an application of a hot wire CVD technique. With this technique, relatively simple device configuration can be expected because some expensive and complex components, for examples, frequency power supplies, matching boxes, and electromagnetic shield parts, used in plasma-assisted CVD devices are not needed,

The key technique in the hot wire CVD lies in the combination of wire and material gas species [5)]. As some of hot wire CVD processes are called catalytic CVD (CAT-CVD), when hot wires have catalytic behavior [6)], the choice of wire species is important for the decomposition of material gas. Also, the choice of material gas species has an important influence on the consequent decomposed species for thin film formation. Some proposals have been made in hot wire techniques such as the combination of tungsten and silane gas [7)], and tungsten and hexametyldisilazane [8, 9)]. However, the explosive nature of silane gas involves the practical difficulty in use inside the factories of typical PET bottle manufactures in terms of safety and related legal restrictions [10)]. Also, PET bottles lack in the heat resistance required or sufficient deposition rate, for the formation of the barrier coating based on the tungsten and hexametyldisilazane approach mentioned above. As a result, a novel combination of hot wire and material gas species which is applicable to PET bottles in a safe manner is demanded in the hot wire CVD approach.

For a novel process, coatings with improved performance is demanded, compared to carbon [1, 4, 11-13)] and SiO_x [1, 4, 14, 15)] coatings synthesized with the current plasma-assisted CVD techniques. Because these coatings are formed on the inner surface of transparent PET bottles, both visual appearance and stability in direct contact with filled beverage liquids have impact on the quality of coated bottles. The carbon coating has a certain metallic carbon color tint, which may lead to the avoidance of use due to psychological impact on container appearance, while it is stable in contact with typical beverages. Also, the SiO_x coating, while it is colorless, tends to show a certain limited barrier performance and the resultant limited applications, because of instability in contact with some beverage liquids close to the neutral in terms of pH [16)]. Some types of tea are example of these liquids. In brief, a novel coating technique is demanded for a thin film which is colorless and physico-chemically stable in contact with various beverage liquids.

In this context, the author empirically conceived a possible gas barrier coating with colorless and physico-chemically stable properties can be found in a type of thin film composed of the mixture of silicon, carbon, and oxygen and hydrogen. This type of thin films is often shortly described as SiOC in the industry. In the matrix of SiOC, silicon and carbon are expected to provide a basic skeleton of dense structure, oxygen is expected to reduce the absorption of visible light, and carbon is expected to increase the stability in contact with beverage liquids.

For the material gas for the synthesis of SiOC thin films, organosilane is often used. A useful type of organosilane for this study is neither highly explosive nor poisonous, and can form gas barrier thin films with appropriate hot wire. The author conceived the use of vinylsilane for material gas in consideration of the modification of the chemical structure of silane. As shown in Fig. 5-1, vinylsilane has a silyl function in the molecule, and in this sense, a similar chemical structure to mono-silane, a known material gas for remarkably high gas barrier films, for example, SiN_x, as mentioned above. The vinyl function in vinyl silane, however, can increases chemical stability, and provides no explosive nature under atmospheric conditions. This chemically more stable nature of vinylsilane is practically expected to enable a safe operation in PET bottle manufacturing factories. We paid attention to these characteristic aspects and attempted to form a gas barrier thin film onto a PET bottle.

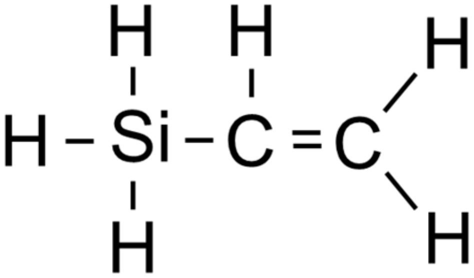


Fig. 5-1. Chemical structure of vinylsilane.

For wire species used in this study, useful hot wires can be heated to decompose material gas, and is not poisonous. Because of a heat resistance up to 2200°C and the general safe properties observed in medical applications 17), tantalum was chosen.

5.2 Experiments

5.2.1 Preparation of PET bottles

500 mL PET bottles of typical shape and weight (29 g) for carbonated soft drinks were manufactured using a preform injection machine, KS100T Kata System Co., Ltd., Japan, and a blow molding machine, LB01E, KHS, Germany. The resultant bottle had ca. 210 mm in height, ca. 66 mm in diameter, and ca. 0.035 mm in thickness. Fig. 5-2 shows the appearance of the bottles manufactured, which is the same picture used in the chapter 3 of this paper 18).

As mentioned in chapter 1, the term of weight is used for expressing the mass of packages in this paper.

Fig. 5-2. Appearance of PET bottles used in this study. The bar represents 10 mm.

5.2.2 Thin film formation onto a PET bottle

Tantalum wire of 0.5 mm in diameter supplied by Pransee Japan Co., Ltd., was cut to be a pair of 420 mm and 440 mm in length. The wire pair was set to a coating device originally designed for PET bottle coating (Fig. 5-3). Inside a bottle, each wire was supported in an insulated state with a gas inlet pipe made of ceramic (alumina) of 6.0 mm in the outer diameter and of 4.0 mm in the inner diameter, and crossly placed to each other in a non-contact manner, so that the wire surface is placed in a position generally 20 mm apart from the most parts of the bottle inner bottle wall. The bottle substrate, the wires, and the gas inlet pipe were set inside the vacuum chamber connected to vacuum pumps, EH500IND and E2M80, Edwards Co., Ltd., USA.

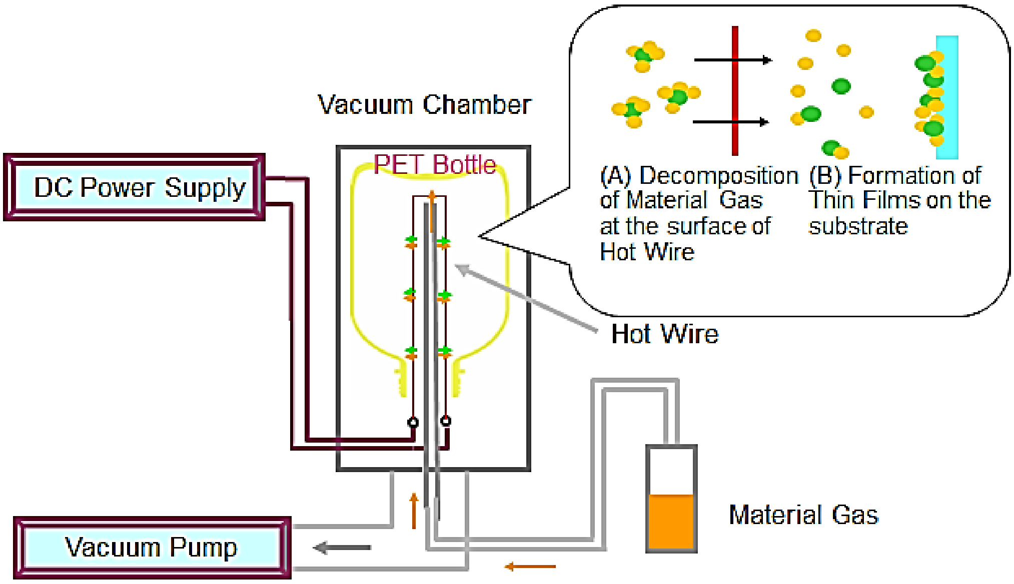


Fig. 5-3. Schematic structure of the coating device used in this study. Inside a bottle placed in a vacuum chamber, hot filaments connected to a power supply were fixed along a gas supply pipe connected to a material gas container. (A) Supplied material gas is decomposed in contact with the hot wire, and (B) the decomposed molecules form a thin film on the inner surface of a PET bottle.

Vinylsilane ($H_3Si\text{-}CH{=}CH_2$, Fig. 5-1), which is gaseous under the atmospheric pressure or below at room temperature, was synthesized by Japan Advanced Chemicals Co., Ltd., Japan. The flow rate of gas was controllable through a mass flow controller in cubic centimeter under standard temperature and pressure per minute (sccm) unit, which is installed in the middle of the gas inlet pipe and a gas cylinder.

Thin film was formed through heating the wires with a DC power supply, HX0500-30, Takasago Ltd., Japan. The temperature of the heated wires was measured with a handy radiation thermometer, TR-630A, Konica Minolta Inc., Japan, through a window made of Pyrex® glass which forms a part of the chamber.

For thin film formation, the vacuum chamber including a PET bottle and tantalum wires was vacuumed to 5.0 Pa. The wires were then heated inside the PET bottle to ca. 2000°C using a radiation thermometer. The supply of vinylsilane to the inside of the bottle was adjusted using a mass flow controller to a flow rate ranging from 30 cubic centimeter at standard temperature and pressure per minute (sccm) to 90 sccm, and kept for 6.0 seconds, followed by the termination of the heating of the wires and the vacuuming of the chamber.

When the resultant bottle was removed from the chamber after the pressure release of the chamber, no tangible deformation was observed in the shape of the coated PET bottles, in spite of vacuuming and heating processes described above.

The formation of a thin film coating was confirmed through visual observation based on a slight golden tint.

5.2.3 Measurement of deposition rate

The deposition rate of the thin film formed in the above mentioned manner was measured using partially masked silicon wafers placed on the inner surface of the center of the body part of PET bottles as described in a previous study 18). The difference in height between the unmasked and the masked parts was detected using a contact-type thickness meter, α-step, KLA-Tencor Corporation, USA.

5.2.4 Measurement of oxygen barrier property of PET bottles

The oxygen transmission rate (OTR) of a PET bottle was measured based on ASTM F-1307 using an Oxtran 2/21 device, Mocon Co., Ltd., USA, under conditions of 23°C and 90% relative humidity. This is a type of a constant pressure and volume method for containers. In this method, the mouth part of a sample bottle is hermetically sealed to a metal pipe system. One end of the system is connected to the nitrogen gas source, and the other is connected to the oxygen detector of the device. Because pure nitrogen constantly passes through the inside of the bottle, the sample volume (including the surface area and the wall thickness) and the difference of oxygen pressure between the inside and outside of the sample are controlled to be constant. The resultant OTR, therefore, reflects oxygen permeation through the bottle only. It should be mentioned that the degree of gas barrier enhancement is often expressed in barrier improvement factor (BIF), as previously described in the chapter 2 of this paper. The value of BIF is calculated based on the OTR of an uncoated bottle divided by the OTR of a coated bottle to that of an uncoated bottle, from the view of shelf-life extension of commercial products.

5.2.5 Morphological characterization of thin film coating

The surface images of the thin film formed on the PET substrate was observed with a scanning electron microscope, JSM-7600F, JEOL Ltd., Japan. The samples were cut from the center of the body part of PET bottles, and coated with vaporized osmium. To observe the surface images, the magnification was set to 100,000 times under the condition of 5 kV for the electron acceleration.

5.2.6 Chemical characterization of thin films

For the chemical composition and structure of thin films, X-ray photoelectron spectroscopy (XPS) analysis was performed. Samples were cut from the center of the body part of coated PET bottles, and the spectral regions of Si2p, O1s, C1s, and N1s were measured using QuanteraSXM, Physical Electronics, Inc., USA, based on the AlKα radiation (1486.6 eV).

5.2.7 Measurement of water vapor barrier property of PET bottles

The water vapor transmission rate of a PET bottle was determined based on the average rate of the decrease in the weight (mass fraction) of bottles filled with 500 mL distilled water, stored under the conditions of 23^{o}C and 50% relative humidity. The weight of each filled sample was regularly measured using an electronic balance. The resultant weight loss rate includes water vapor permeation both through bottle and closure parts.

5.3 Results and discussion

5.3.1 Oxygen barrier property of coated PET bottles

The result of OTR measurement was shown in Fig. 5-4. The OTR of coated bottles were decreased when the flow rate of material gas was increased from 30 sccm to 50 sccm, and then gradually increased when the flow rate was increased from 50 sccm to 90 sccm. It is considered that appropriate balance between the supply amount of material gas and the pressure inside the bottle (the length of mean free path) is important for high gas barrier enhancement. As a result, the highest oxygen gas barrier was achieved at the flow rate of 50 sccm. Because the OTR of the resultant bottle and an uncoated bottle was 0.0025 and 0.0350 cubic centimeter at standard temperature and pressure (cc (STP)) / day / bottle, BIF value was calculated as 15.2. This oxygen gas barrier enhancement of more than 10 in BIF indicates a highly practical oxygen barrier enhancement for food and beverage applications. Fig. 5-5 shows coating thickness obtained with different gas flow rates. The coating thickness was increased as the flow rate of material gas increased. It is considered that thicker coatings obtained with the flow rates of 70 and 90 sccm were not dense, compared to that obtained with the flow rate of 50 sccm. Based on the result in Fig. 5-5, with the flow rate of 50 sccm, the deposition rate of the thin film in the center part of the bottle was ca. 6.4 nm/sec. In the following experiments, the gas flow rate of 50 sccm was used for thin film coating.

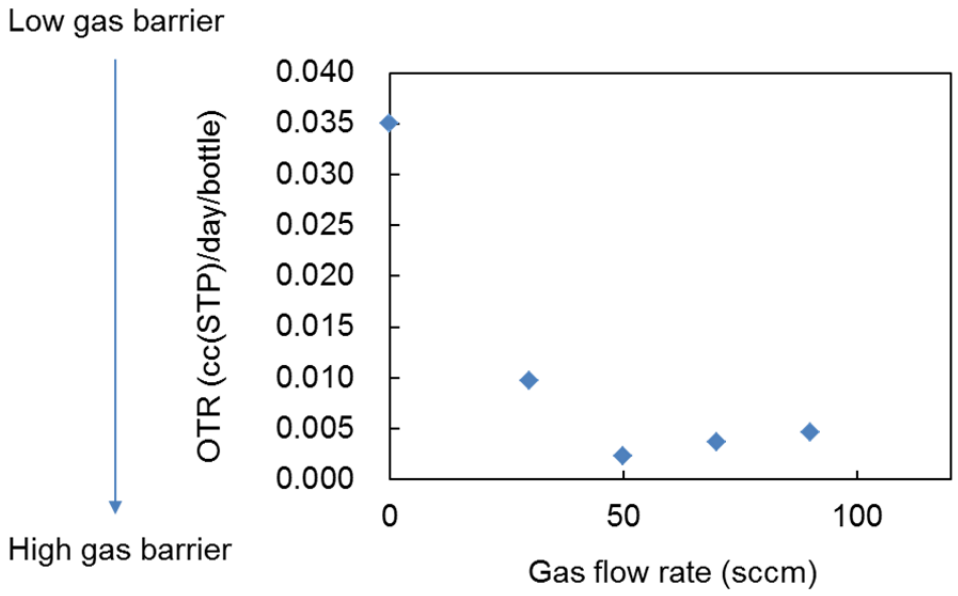


Fig. 5-4. Dependence of the oxygen barrier of coated bottles on gas flow rate. OTR refers to oxygen transmission rate. Gas flow rate of vinylsilane was arranged between 30 and 90 sccm, and the resultant OTR of coated bottles was measured. The value of OTR at the gas flow rate of 0 sccm shows the OTR of uncoated bottles.

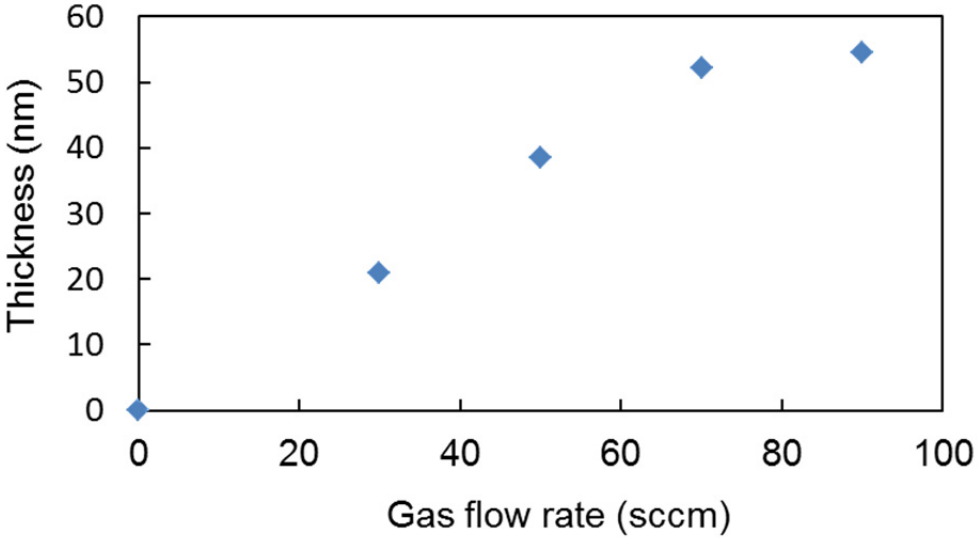


Fig. 5-5. Dependence of coating thickness on gas flow rate. The thickness of thin films formed at coating time of 6.0 sec was measured.

5.3.2 Observation of thin film coating

To confirm the influence of coating time on oxygen barrier property, thin film was formed under conditions of the gas flow rate of 50 sccm and coating time of 2.0 sec. The OTR and consequent BIF of the bottle was OTR of 0.0032 cc (STP) / day / bottle, and 11.0, respectively. Fig. 5-6 shows the microscope images of uncoated and coated surface of PET bottles. As sown in this figure, the tint of coating was remarkably reduced, and the appearance of the coated bottles was virtually colorless.

The surface of the thin coated film prepared under the same conditions as the sample (c) of Fig. 5-6 was observed with scanning electron microscopy (SEM), in order to characterize the surface morphology of the obtained coating. Fig. 5-7 (a) and (b) shows the SEM images of uncoated and coated surface of PET bottles, and the coated surface observed was smooth, equivalent to the uncoated surface.

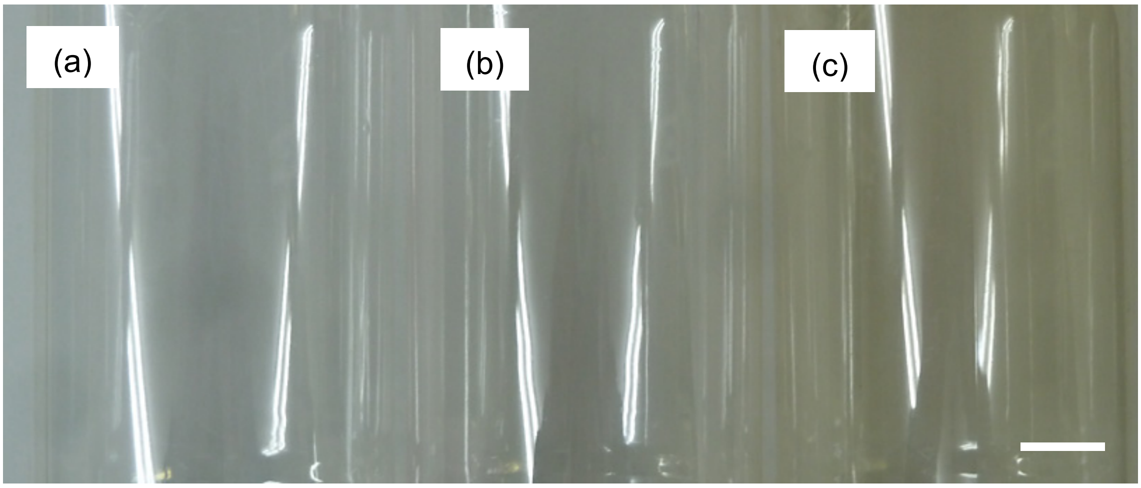


Fig. 5-6. The tint derived from thin film coating. Pictures show the body part of (a) uncoated, (b) coated for 2.0 sec, and (c) coated for 6.0 sec PET bottles. The bar represents 10 mm.

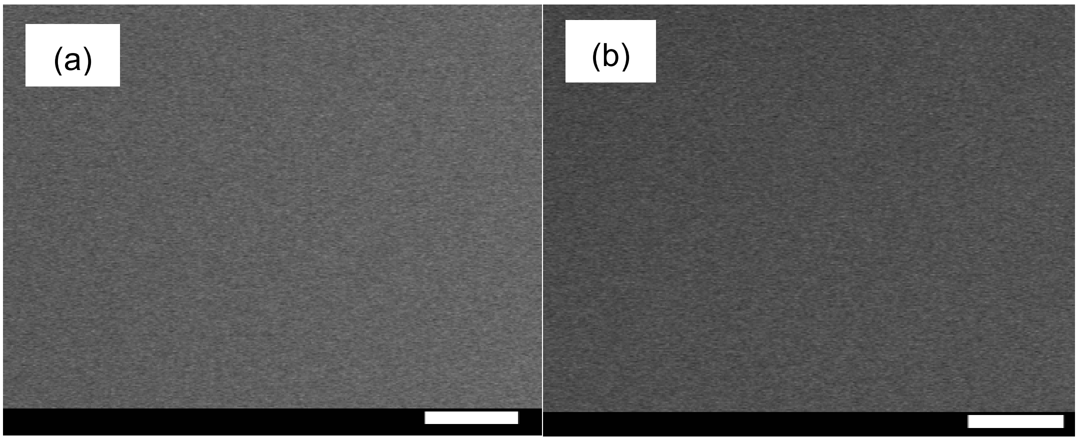


Fig. 5-7. The surface images of (a) uncoated and (b) coated PET bottles. The bar represents 1 μm.

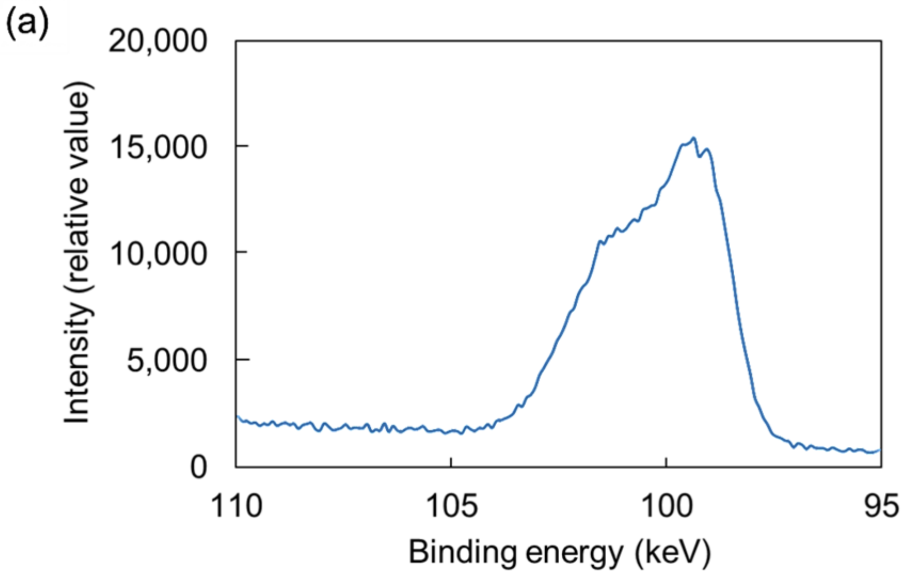
It should be mentioned that when we removed the coating with caustic agents from the substrate as described in author's previous study $^{17)}$, we confirmed the fragments separated from the bottles had a slight tint, and the remnant PET substrate was colorless. This indicated that the slight tint of coated bottles was caused the coating itself.

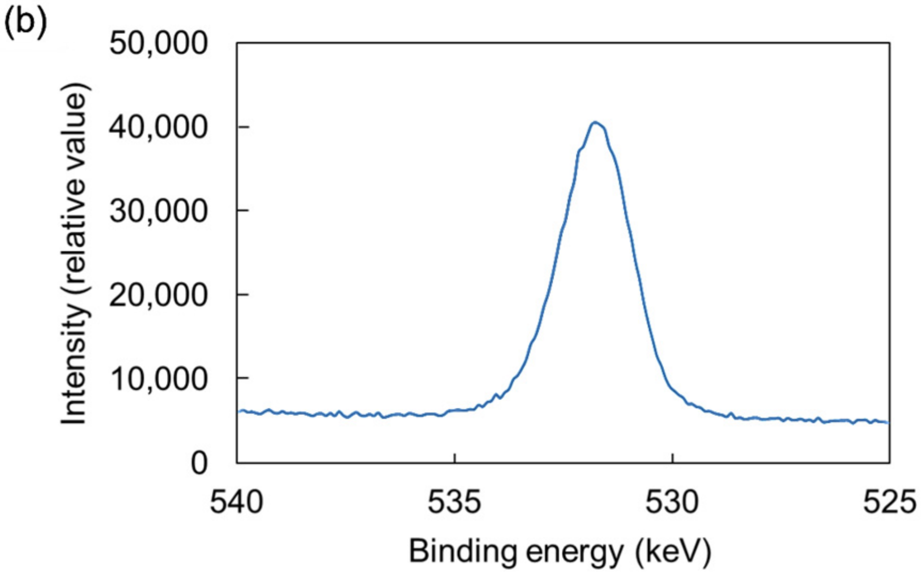
5.3.3 Chemical identity of thin films

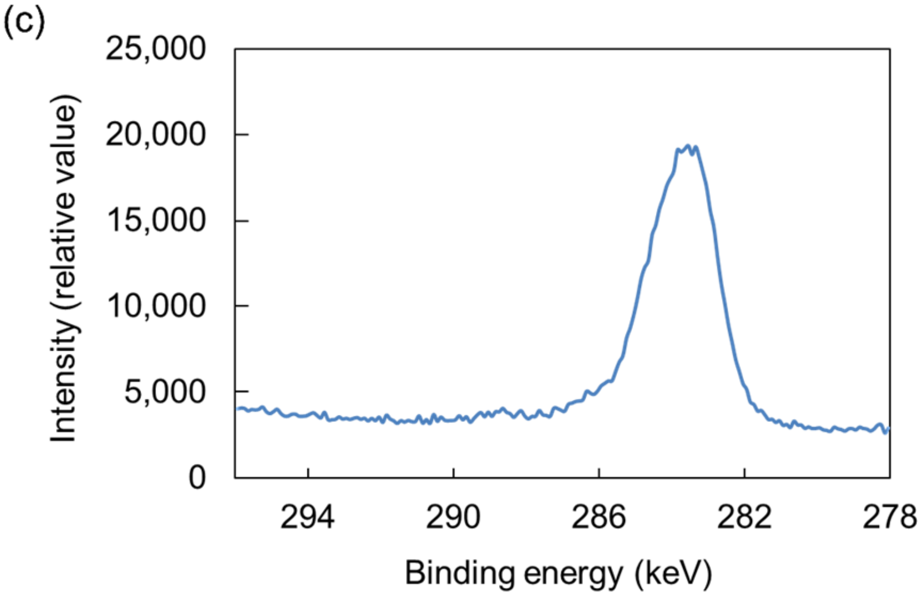
XPS analysis was conducted in order to confirm the chemical composition and structure of the formed thin film. Table 5-1 shows the result of chemical composition obtained with XPS analysis. The film contained silicon, carbon, oxygen, and hydrogen, and could be expressed as a type of SiOC film. Nitrogen component was not detected. Fig. 5-8 shows XPS spectra of the film. Interestingly, the obtained spectra indicated that the SiOC film contained Si-Si bonds (99.0 keV) at least in its outer surface.

Table 5-1. Composition of thin film obtained based on XPS analysis.

	Atomic percentage
Silicon	33.0
Oxygen	29.5
Carbon	37.5
Nitrogen	not detected


(a)
Intensity (relative value)
20,000
15,000
10,000
5,000
0
110
105
100
95
Binding energy (keV)


(b)
Intensity (relative value)
50,000
40,000
30,000
20,000
10,000
0
540
535
530
525
Binding energy (keV)



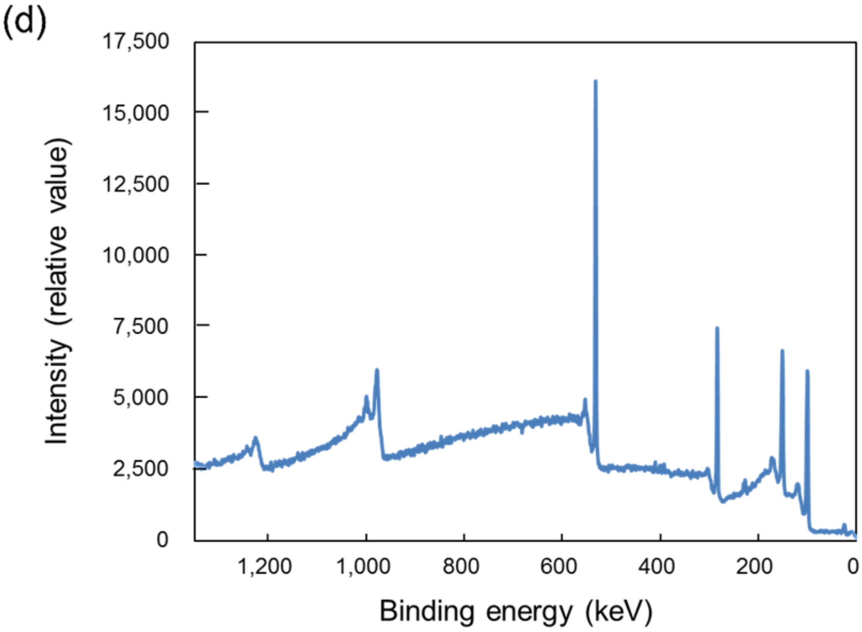


Fig. 5-8. XPS spectra on (a) Si2p, (b) O1s, and (c) C1s and (d) the wide scan of the surface of thin film obtained.

It is considered that oxygen atoms contained in the SiOC thin film were derived from water vapor released from PET substrate rather than oxygen molecules remained in the vacuum chamber through the vacuuming process, because the tint of the SiOC thin film was not affected when the pressure of the vacuum chamber before coating was decreased to 0.5 Pa.

The presence of Si-Si bonds in the SiOC thin film revealed in XPS analysis suggests hydrogen atoms associated with the silicon atom in vinylsilane molecules were, partially or totally, disassociated in contact with hot tantalum wire and produced active fragments such as radicals.

5.3.4 Water vapor barrier property of coated PET bottles

To confirm the stability of the gas barrier property of the thin film described above, a storage test was performed based on water vapor permeation. In this test, PET bottles were filled with distilled water and sealed with typical commercial plastic closures.

Fig. 5-9 shows the change of the weight (mass fraction) of filled bottle along time lapse. The weight was gradually decreased due to water vapor permeation. For a specific weight loss percentage, coated samples took about three times longer, compared to uncoated samples. This indicates that a highly practical water vapor barrier enhancement was achieved with the coated bottles. It should be mentioned that the steady rate of the weight loss of the coated bottles due to water vapor permeation during the storage period strongly suggests the stability of the thin film coated on the surface of PET bottles in water close to neutral in terms of pH, and that the storage period over 1 year indicates a highly practical stability in contact with food and beverage applications. As a result, it is expected that these bottles do not have the restriction of applications seen in SiO_x coated bottles, which tend to show the decrease of gas barrier properties in contact with neutral water solutions such as still water and tea products.

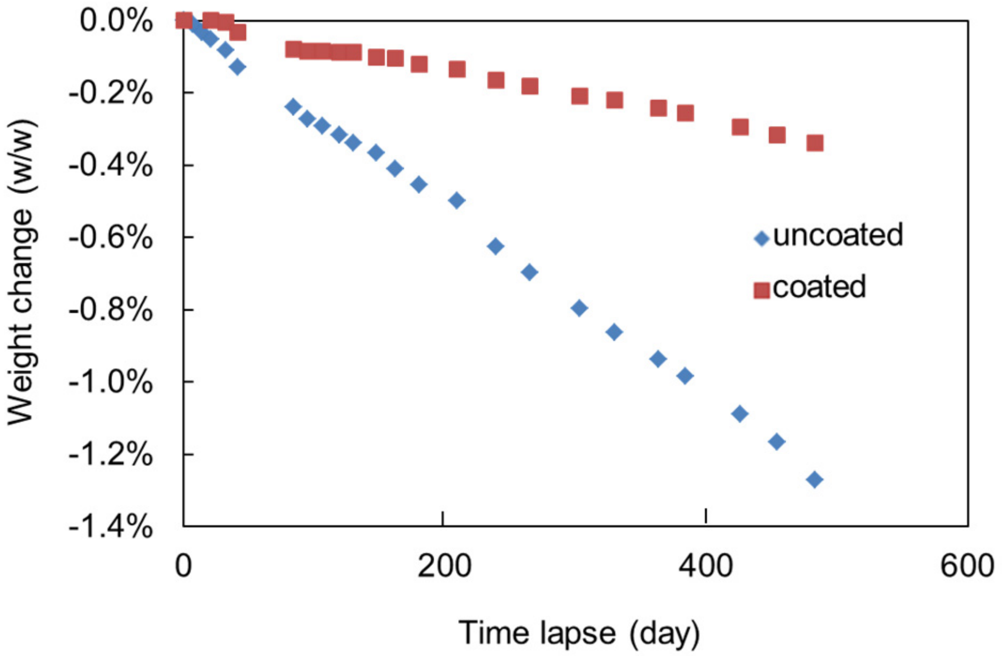


Fig. 5-9. Water vapor loss from sealed PET bottles. 500 g of distilled water was filled in coated and uncoated PET bottles, and the decrease in the weight derived from water vapor permeation was measured regularly. The weight loss of -1.0% refers to 5.0 g decrease from the initial weight.

5.4 Conclusions

A unique hot wire CVD technique using tantalum wire and vinylsilane gas was developed which is applicable to the surface coating of PET bottles. With this technique, the obtained thin film coating was virtually colorless, and enhanced the gas barrier properties of PET bottles. The oxygen barrier improvement factor of coated bottles could be increased above 10, and their increased water vapor barrier property was stable in contact with water over one year. As a result, the SiOC coating obtained in this study is likely to share the advantages of carbon (high gas barrier against oxygen, carbon dioxide, and water vapor even in contact with neutral water solutions) and SiO_x

(colorless) coatings. The result of the conducted XPS analysis indicated that the obtained thin film was composed in 32.9% silicon, 29.4% oxygen, and 37.4% in atomic percentage, and characteristically contained Si-Si bonds in its surface. As a result, the formed thin film was confirmed as a type of SiOC thin film.

It can be expected the obtained coating is highly practical in the applications of food and beverage PET containers, because of high gas barrier, virtually colorless, and physico-chemically stable properties mentioned above.

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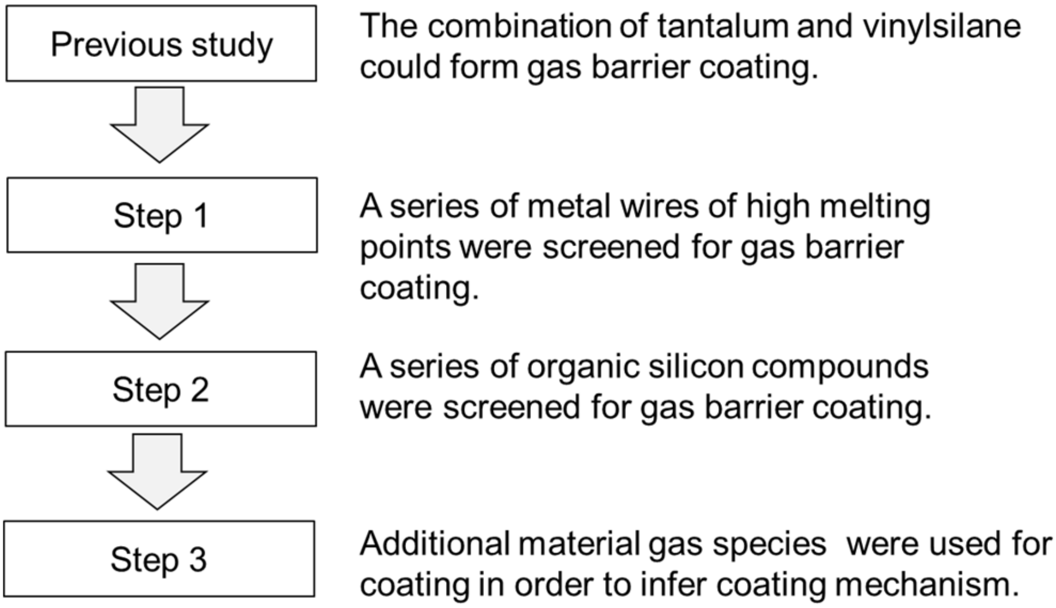
Chapter 6

Research for Hot Wire and Material Gas Species for a Novel Hot Wire CVD (Cat-CVD) Technique Applicable to Gas Barrier SiOC Thin Film Coatings onto PET Bottles

6.1 Introduction

In the original hot wire technique described in the previous chapter 5, a unique combination of tantalum and vinylsilane was used, and demonstrated to form a thin film composed of silicon, carbon, and oxygen (SiOC thin film). While some study reported SiOC films may be formed as porous [1)], the obtained SiOC thin film had a smooth morphology on the inner surface of PET bottles, and functioned as gas barrier coating [2)]. It should be noted that, in the field of gas barrier thin film formation, an intensive study was made with tungsten hot wire. For example, some proposals for gas barrier thin films include the use of the combination of tungsten and a mixture of silane and ammonium [3)], and tungsten and hexametyldisilazane [4)], respectively. These instances are considered to utilize catalytic behaviors of metal wires, and specifically referred to as catalytic CVD or Cat-CVD [5)].

In this chapter, in attempt to find out the practical application and basic mechanism of this original coating, a series of screening experiments were made with different wire and material gas species. As summarized in Fig. 6-1, in the first step, thin film forming onto the inside of PET bottles was attempted using various wire species in contact with vinylsilane gas, based on author's previous study [2)]. In the second step, using the selected wire species which provided the highest oxygen gas barrier property in the first step, material gas species available for gas barrier coating were screened, based on the rapid measurement of oxygen transmission rate (OTR). In the last step, additional material gas species were synthesized with a certain similarity in their chemical structures to the screened compounds in the previous step, and then used for extra measurements and analyses in order to infer the mechanism of gas barrier thin film formation.



The combination of tantalum and vinylsilane could form gas barrier coating.

A series of metal wires of high melting points were screened for gas barrier coating.

A series of organic silicon compounds were screened for gas barrier coating.

Additional material gas species were used for coating in order to infer coating mechanism.

Fig. 6-1. Experimental scheme of this chapter.

6.2 Experiments

6.2.1 Materials

Tantalum wire was supplied by Pransee Japan Co., Ltd., Japan, and other kinds of wire used in this paper were supplied by Furuya Metal Co., Ltd., Japan, and other commercial suppliers. Vinylsilane ($H_3Si\text{-}CH{=}CH_2$) and other kinds of materials were prepared by Japan Advanced Chemicals Co., Ltd., Japan.

6.2.2 Preparation of PET bottles

As described in the previous chapters, for manufacturing PET bottles (500 mL in volume, ca. 210 mm in height, ca. 66 mm in diameter, and 0.035 mm in thickness) of typical shape and weight (29 g) for carbonated soft drinks, a preform injection machine, KS100T Kata System Co., Ltd., Japan, and a blow molding machine, LB01E, KHS, Germany, were used.

6.2.3 Thin film formation onto a PET bottle

An originally designed device, as described in the previous chapter of this paper (Fig. 6-2), for coating the inner surface of plastic containers was used for forming thin film onto PET bottles [4)]. In a coating chamber for a single container, a pair of metal wires of 0.5 mm in diameter, and 42 cm and 44 cm in length, was crossly set in a non-contact manner to insulated supports around a gas inlet pipe made of ceramic (alumina) of 6.0 mm in the outer diameter and of 4.0 mm in the inner diameter so that the most parts of the inner wall of PET bottle set to this chamber are placed ca. 20 mm apart from the nearest wire portion. The bottle substrate, the wires, and the gas inlet pipe were set inside the vacuum chamber connected to vacuum pumps, EH500IND and E2M80, Edwards Co., Ltd., USA. In this device, wires of different materials can be set for electrical heating with a DC power supply, and also material gas of different chemicals can be supplied through a mass flow controller installed in the middle of the gas inlet pipe and a gas cylinder. The temperature of heated wires was controlled through applied voltage to the wires, and measured with a handy radiation thermometer, through a window made of Pyrex® glass which forms a part of the chamber.

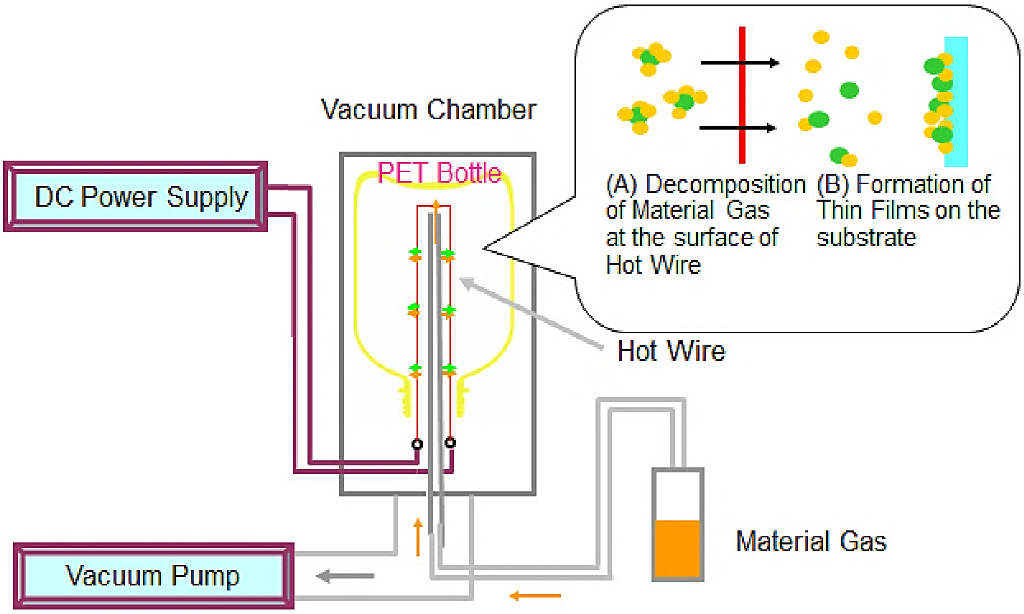


Fig. 6-2. Schematic illustration of a hot wire CVD chamber designed for PET bottle coating. Hot wires through electrical heating with DC power decompose material gas inside the bottle and thin films are formed over the inner surface of PET bottles.

6.2.4 Measurement of deposition rate

The deposition rate of thin films formed in the manner mentioned above was measured as described in author's previous study [4)]. Partially masked silicon wafers placed on the inner surface of the center of the body part of PET bottles, and the difference in height between the unmasked and the masked parts is detected using a contact-type thickness meter, α-step, KLA-Tencor Corporation.

6.2.5 Chemical characterization of thin films

The chemical bonds of the surface of thin films were analyzed using an X-ray photoelectron spectroscopy (XPS) technique. In the XPS analysis, QuanteraSXM, Physical Electronics, Inc., MN, USA, based on the AlKα radiation (1486.6 eV) was used for the spectral regions of Si2p, O1s, and C1s. For samples of this analysis, thin films of ca. 50 nm in thickness were formed on silicon wafers.

6.2.6 Measurement of gas barrier property of PET bottles

For the screening of wire and material gas species available for gas barrier coating in the steps 1 and 2 mentioned in Fig. 6-1, the degree of oxygen barrier property of PET bottles was measured with APET-200, Youtec Co., Ltd., Japan. The principle used in the device for the detection of gas concentration in carrier gas is described in ISO 15106-6 [16)]. While this methodology covers the measurement of the transmission rate of film or sheet samples, this device used was designed and modified for a rapid measurement of plastic containers, as shown in Fig. 6-3.

The measurement of OTR with APET-200 was, therefore, performed based on ASTM F-1307 method [7)], which covers the measurement of the transmission rate of container samples. For rapid measurement, sample bottles were heated up to 50°C for 2 hours and then cooled down to 23°C. For the detection of oxygen concentration in argon carrier gas, an atmospheric pressure ionization mass spectrometer API-10A, Nippon API, Co., Ltd., Japan, was used. This device can measure 4 bottles at once through switching carrier gas flow. Coated bottle samples were always measured with uncoated samples in order to obtain barrier improvement factors (BIF) based on the following equation, from the viewpoint of shelf-life extension.

$$\text{BIF} = \text{OTR of an uncoated bottle} / \text{OTR of a coated bottle}.$$

In this paper, this BIF calculation was used in the screening of the steps 1 and 2 mentioned in Fig. 6-2, and high gas barrier coating refers to 3 or higher BIF values.

For bottles with high gas barrier coating obtained in the step 3 mentioned in Fig. 6-2, accurate OTR was measured with Oxtran 2/21, Mocon Co., Ltd., Japan, for 72 hours under the conditions of 23°C and 90% relative humidity, based on ASTM F-1307 method.

It should be noted that ASTM F-1307 is a type of a constant pressure and volume method for containers. In this method, the mouth part of a sample bottle is hermetically sealed to a metal pipe system. One end of the system is connected to carrier gas source, for example nitrogen, and the other is connected to the oxygen detector of the device. Because pure carrier gas constantly passes through the inside of the bottle, the sample volume (including the surface area and the wall thickness) and the oxygen pressure difference between the inside and outside of the sample are controlled to be constant. The resultant OTR, therefore, reflects oxygen permeation through the bottle only.

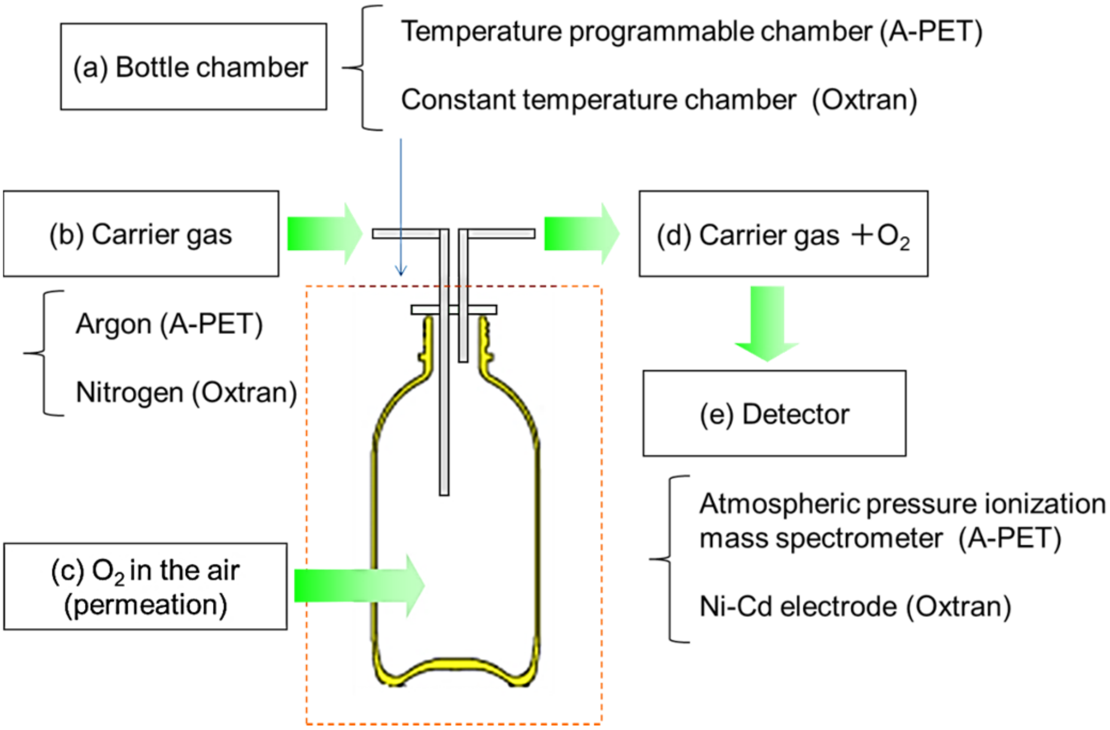


Fig. 6-3. Schematic illustration of the devices (A-PET / Oxtran) used for the measurement of the oxygen transmission rate of PET bottles. The inside of PET bottles set in (a) storage chambers under constant temperature (programmable temperature control / constant temperature control) is subjected to (b) constant carrier gas flow (argon / nitrogen). As a result, the concentration of (c) permeant oxygen contained in (d) the exhausted carrier gas flow can be precisely detected with (e) oxygen detectors (atmospheric pressure ionization mass spectrometer / Ni-Cd electrodes).

6.2.7 Storage test of PET bottles filled with carbonated water

In attempt to confirm the performance of coated PET bottles for carbonated drinks, carbonated water was filled with 500 mL PET bottles of 23 g. These bottles were chosen from commercial PET bottles which were shaped in a typical two stage method as described above, and had an anti-pressure base shape for use in carbonated soft drinks.

All samples were filled with carbonated water, and capped with typical commercial plastic closures designed for the typical bottle mouth finish of PCO 1810 specification. Carbonated water was prepared through a mixture of sodium bicarbonate and citric acid so that the initial carbon dioxide content was 0.33 MPa. Because inner pressure derived from the carbon dioxide content creeps (irreversibly expands) the bottles, filled bottles were stored under 38^{o}C for 5 days, assuming a warming process in filling facilities for avoiding dew condensation before packing filled bottles into paper boxes. Some of the resultant bottles were measured in terms of the carbon dioxide content of filled water and the whole volume expansion. The rest of the resultant bottles were stored under 35^{o}C for 60 days, assuming remarkably high distribution temperature, for observing the decrease of carbon dioxide content derived from carbon dioxide permeation.

The carbon dioxide content of filled water was measured using a gas volume analyzer, GVA-700, Kyoto Electronics Manufacturing Co., Ltd, Japan. This method usually involves an accuracy of pressure values within 0.01 MPa when samples prepared in the same conditions are measured.

The whole volume of bottles was calculated based on the weight and temperature of pure water which could be filled in each sample.

6.2.8 Color characterization of thin film coating

Samples for color characterization were cut from the center of the body part of the same coated and uncoated PET bottles used in the storage test, and placed in a spectrometer, U-3900, Hitachi High-Technologies Corporation, Japan. For characterizing the tint of coated PET bottles, the transmission of each wavelength of visible light ranging from 380 nm to 780 nm was compared between coated and uncoated samples.

6.2.9 TEM observation

Samples for transmission electron microscope (TEM) observation were cut from the center part of the body of a coated PET bottle. The resultant samples were then embedded in epoxy resin matrix of Epok 812 supplied by Oken Shoji Co., Ltd., Japan, under 40^{o}C for 72 hours. Longitudinal sections of ca. 50 nm thickness were sliced from the embedded polymer blocks using an ultramicrotome, MT-XL, RMC Boeckeler Instruments, Inc., USA, and observed with a Tecnai Spirit TEM, FEI Company, USA, in a condition of 120 eV.

6.3 Results and discussion

6.3.1 Screening of metal species in hot wire CVD with vinylsilane (Step 1)

In addition to tantalum, following eight metal species with high melting points were chosen for this experiment: tungsten, niobium, vanadium, molybdenum, hafnium, iridium, rhenium, and platinum (40%) - rhodium (60%) alloy. With a combination of vinylsilane, three metal species of tantalum, tungsten, and molybdenum were selected as candidate wire materials, based on their significant oxygen barrier enhancement effects with thin film formation onto PET bottles.

Wires of each metal species and a PET bottle were set to the coating device used in hot wire CVD to PET bottles as described above. After the coating chamber was vacuumed to 5.0 Pa, the supply of vinylsilane to the inside of the bottle was started, and adjusted to 50 cubic centimeter at standard pressure and temperature per minute (sccm) with a mass flow controller. The wires were then heated inside the PET bottle for 6.0 seconds. As a result, coating was started at 7.2 Pa. As higher temperature is considered to be effective to gas barrier enhancement through hot wire CVD, the temperature of heated wires was adjusted to ca. 2000^{o}C using a radiation thermometer in consideration of heat load to PET bottles. In case the used metal species were not resistant to 2000^{o}C, these metal species were heated to lower temperature. The resultant bottle was removed from the chamber after the pressure release of the chamber, and deposition rate and oxygen barrier measurements were performed.

Table 6-1 summarizes the used wire species and the results of oxygen barrier measurement. In addition to tantalum, tungsten, and molybdenum can be categorized as effective for high gas barrier coating because, using these species, thin film coatings with significant oxygen barrier enhancement effects were formed, based on the criteria of the oxygen barrier enhancement of 3 and more BIF values. While thin film coatings were formed using hafnium and niobium, the oxygen barrier of the resultant bottles was not significantly enhanced. The use of other metal species did not appear to form coatings based on the results of visual observation and deposition rate measurement.

Because molybdenum provided the highest gas barrier enhancement, this metal species was selected to use in the following experimental steps.

Table 6-1. List of wire species used for screening test.

No.	Name of wire species	Name of material gas	Melting points	Temperature of wires	BIF (relative value)
1	Tungsten	Vinylsilane	3380^{o}C	2000^{o}C	7.7
2	Niobium		2477^{o}C	1800^{o}C	1.6
3	Vanadium		1910^{o}C	1600^{o}C	<1.1
4	Molybdenum		2623^{o}C	2000^{o}C	20.2
5	Hafnium		2233^{o}C	2000^{o}C	<1.1
6	Iridium		2443^{o}C	2000^{o}C	<1.1
7	Rhenium		3186^{o}C	2000^{o}C	<1.1
8	Platinum (40%) - Rhodium (60%)		ca. 1650^{o}C	1600^{o}C	<1.1
Reference	Tantalum		2980^{o}C	2000^{o}C	11.9

Note: BIF is calculated based on “OTR of an uncoated bottle / OTR of a coated bottle” as described in materials and methods.

6.3.2 Screening of material gas species in hot wire CVD with molybdenum (Step 2)

The material gas species prepared for the screening experiment for high gas barrier coating are summarized in Table 6-2.

PET bottles were coated using molybdenum wires in the same manner in the previous experimental steps 1 as mentioned in Fig. 6-1. After the chamber was vacuumed to 5.0 Pa, the supply of material gas to the inside of the bottle was started, and adjusted either with a mass flow controller or with the temperature of a material container depending on that material species were gaseous, or liquid in room temperature, respectively. When the container of a material was placed at room temperature, and any thin film formation did not appear to occur, then, the container was warmed in order to use relatively higher pressure. As a reference, the chamber pressure used was recorded for each material species.

Table 6-3 summarizes the result of these measurements. Two material species, that is, vinylsilane and disilacetylene, can be categorized as effective for high gas barrier coating because they provided significantly higher BIF values than the criteria of oxygen gas barrier enhancement (BIF values of 3 and more).

Table 6-2. List of material gas species and their abbreviation.

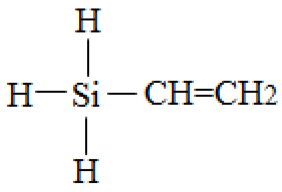
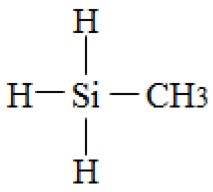
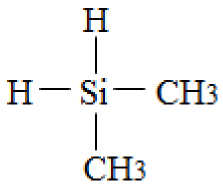
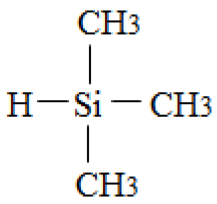
No.	Name of compounds	Abbreviation	Chemical structure	Status at room temperature
1	Vinylsilane	VS	 $\mathrm{H-\overset{\overset{H}{\vert}}{\underset{\underset{H}{\vert}}{Si}}-CH{=}CH_2}$	Gas
2	Monomethylsilane	MMS	 $\mathrm{H-\overset{\overset{H}{\vert}}{\underset{\underset{H}{\vert}}{Si}}-CH_3}$	Gas
3	Dimethylsilane	DMS	 $\mathrm{H-\overset{\overset{H}{\vert}}{\underset{\underset{CH_3}{\vert}}{Si}}-CH_3}$	Gas
4	Trimethylsilane	TMS	 $\mathrm{H-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{Si}}-CH_3}$	Gas

Table 6-2. List of material gas species and abbreviation (continue 1).

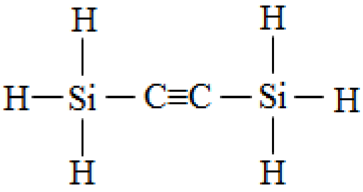
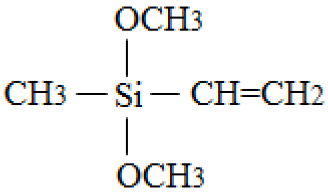
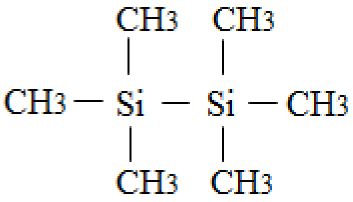
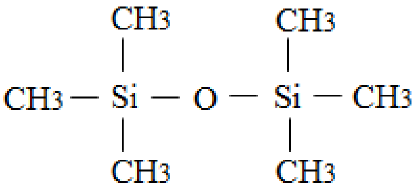
No.	Name of compounds	Abbreviation	Chemical structure	Status at room temperature
5	Disilylacetylene	DSA	 $H_3Si-C\equiv C-SiH_3$	Liquid
6	Dimethoxymethyl vinylsilane	DMVS	 $CH_3-Si(OCH_3)_2-CH=CH_2$	Liquid
7	Hexamethyldisilane	HMDS	 $(CH_3)_3Si-Si(CH_3)_3$	Liquid
8	Hexamethyldisiloxane	HMDSO	 $(CH_3)_3Si-O-Si(CH_3)_3$	Liquid

Table 6-2. List of material gas species and abbreviation (continue 2).

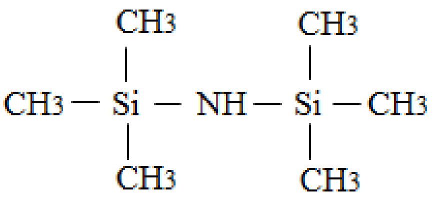
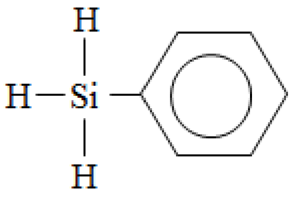
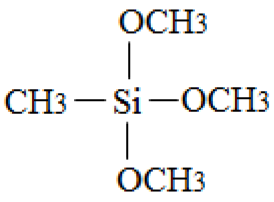
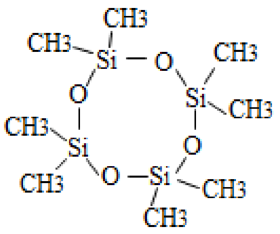
No.	Name of compounds	Abbreviation	Chemical structure	Status in room temperature
9	Hexamethyldisilazane	HMDSN	 $CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-NH-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$	Liquid
10	Phenylsilane	PS		Liquid
11	Methyltrimethoxy sillane	MTMOS	 $CH_3-\underset{OCH_3}{\overset{OCH_3}{Si}}-OCH_3$	Liquid
12	Octamethylcyclotetrasi loxane	OMCTS		Liquid

Table 6-3. List of material species used for screening test.

No.	Material gas	BIF (relative value)	Deposition rate (nm/sec)	Pressure after gas supply (Pa)	Remarks
1	VS	11.9	6.4	6.0	BIF≧3
2	MS	<1.1	<1.0	6.0	
3	DMS	<1.1	3.0	6.0	
4	TMS	<1.1	6.3	7.2	
5	DSA	34.1	6.8	6.1	BIF≧3, vaporized at 23°C
6	DMVS	<1.1	1.4	5.9	vaporized at 23°C
7	HMDS	<1.1	<1.0	6.0	vaporized at 23°C
8	HMDSO	<1.1	6.0	6.2	vaporized at 23°C
9	HMDSN	<1.1	5.7	5.7	vaporized at 23°C
10	PS	<1.1	<1.0	5.8	vaporized at 23°C
11	HTMOS	<1.1	5.9	5.8	vaporized at 23°C
12	OMCTS	<1.1	13.6	5.8	vaporized at 60°C

Note: BIF is calculated based on “OTR of an uncoated bottle / OTR of a coated bottle” as described in materials and methods.

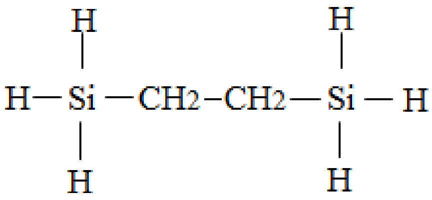
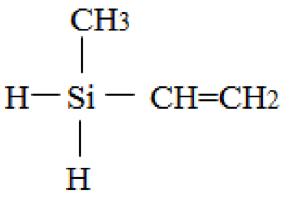
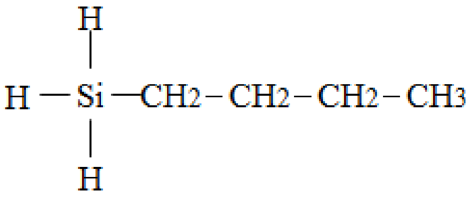
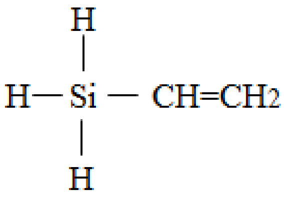
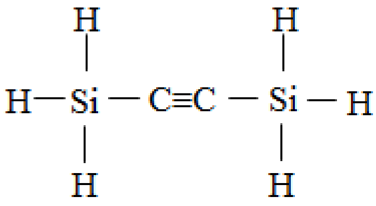
6.3.3 Generalization of the effective chemical structure of material gas species (Step 3)

Based on the result of Table 6-3, it was inferred that the chemical structure of material species is highly influential on the formation of gas barrier thin films. While both vinylsilane and disilylacetylene were shown as effective materials for gas barrier coating, some similar species such as methylsilane, which also have one or two silyl groups in their molecules, could not form gas barrier coating. In consideration of organic structure bonded to a silyl group, three chemical compounds, that is, 1, 4-disilabutane, methylvinylsilane, and n-butylsilane were additionally prepared.

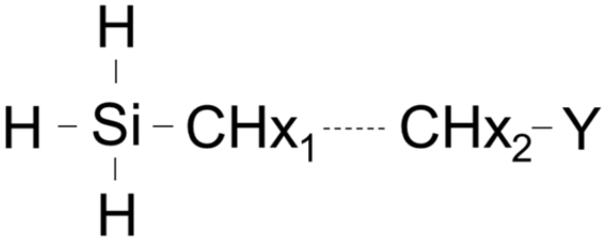
These compounds, which have slightly different chemical structures from vinylsilane and disilylacetylene, were used for the hot wire CVD process described above.

Table 6-4 summarizes the oxygen transmission rate of coated PET bottles using these five chemical compounds as material gas species and uncoated bottles.

Table 6-4. Chemical structures of material gas species used in step 3.

No.	Name of compounds	Chemical structure	Remarks in chemical structure	OTR (cc(STP)/bottle/day)
A	1,4-Disilabutane (DSB)	 $H_3Si-CH_2-CH_2-SiH_3$	- Two silyl functions - Single bonded carbons	0.0016 (high gas barrier enhancement)
B	Methylvinylsilane (MVS)	 $H_2Si(CH_3)-CH=CH_2$	- No silyl groups - Double bonded carbons	0.0292 (low gas barrier enhancement)
C	n-Butylsilane	 $H_3Si-CH_2-CH_2-CH_2-CH_3$	- One silyl group - Single bonded carbons	0.0298 (low gas barrier enhancement)
Ref. 1	Vinylsilane	 $H_3Si-CH=CH_2$	- One silyl group - Double bonded carbons	0.0025 (high gas barrier enhancement)
Ref. 2	Disilylacetylene	 $H_3Si-C\equiv C-SiH_3$	- Two silyl groups - Triple bonded carbons	0.0018 (high gas barrier enhancement)
Ref. 3	Control (uncoated)	-	-	0.0350

Based on the results of coating experiments mentioned above, the chemical structure of material gas species which enabled high gas barrier coating can be generalized as shown in Fig. 6-4. The chemical structure of these species has in common one or two silyl groups which bond to one of two carbons like either H_3-Si-C-C-, H_3-Si-C=C- or H_3-Si-C≡C-. Based on the comparison of the results with vinylsilane and methylvinylsilane, it is suggested that the substitution of a hydrogen of a silyl group with a methyl group inhibit the formation of a high gas barrier thin film, while a relatively high deposition rate (5.5 nm/sec) was obtained with methylvinylsilane. It is also suggested that, based on the comparison of the results with vinylsilane, 1,4-disilabutane, disilylacetylene, methylsilane, and n-butylsilane, two (and maybe three) carbon atoms associated to a silyl group are essential to the formation of a high gas barrier thin film. This suggests compact radicals are considered to be effective for the formation of the dense structures of gas barrier thin films. A precedent study by Toukabri and Shi 8) leads to an inference that the cleavage of hydrogen from Si-H bond and the resultant occurrence of Si radical associated with a single Si-C bond is important for the formation of high gas barrier thin films. Also, the reason of the higher oxygen barrier enhancement with the use of either 1,4-disilabutane or disilylacetylene, compared to the use of vinylsilane, may lie in that two silyl groups per molecule facilitate the formation of the dense thin film structure, for example, through an active chemical reaction of the silyl groups with the formed radicals.



$$H-\underset{\displaystyle H}{\overset{\displaystyle H}{Si}}-CHx_1\cdots\cdots CHx_2-Y$$

Fig. 6-4. Schematic illustration of the generalized chemical structure of material gas which enabled high gas barrier SiOC coatings in this study. The dotted line represents either a single, double, or triple bond between carbons. X refers to the number of hydrogen (from 0 to 2) depending on carbon bonds and the type of function Y. Y refers to either SiH_3 or H.

6.3.4 Chemical identity of gas barrier thin films

Even in cases where thin films were formed at a relatively high deposition rate, some combination of wire and material gas species did not significantly enhance the gas barrier property of PET bottles.

XPS analysis was conducted with the formed thin film samples in order to find difference on the chemical structure of the films with or without gas barrier enhancement effect.

Samples obtained from seven material gas species, that is, vinylsilane, disilylacetylene, 1,4-disilabutane, methylsilane, dimethylsilane, trimethylsilane, and dimethylvinylsilane were prepared for this XPS analysis study. Figs. 6-5 (a) - (c) and Table 6-5 show each sample has peaks in the spectra of Si2p, O1s, and C1s, respectively. As shown in Fig. 6-5 (a), the obtained Si2p spectra indicated that the thin films with high gas barrier contained significant Si-Si bonds (99.0 keV) at least in their outer surface, while the thin films without high gas barrier did not show any significant or weaker peak signal to these bonds. Therefore, it is indicated that these thin films were composed of silicon, oxygen, and carbon, and can be expressed as SiOC in short.

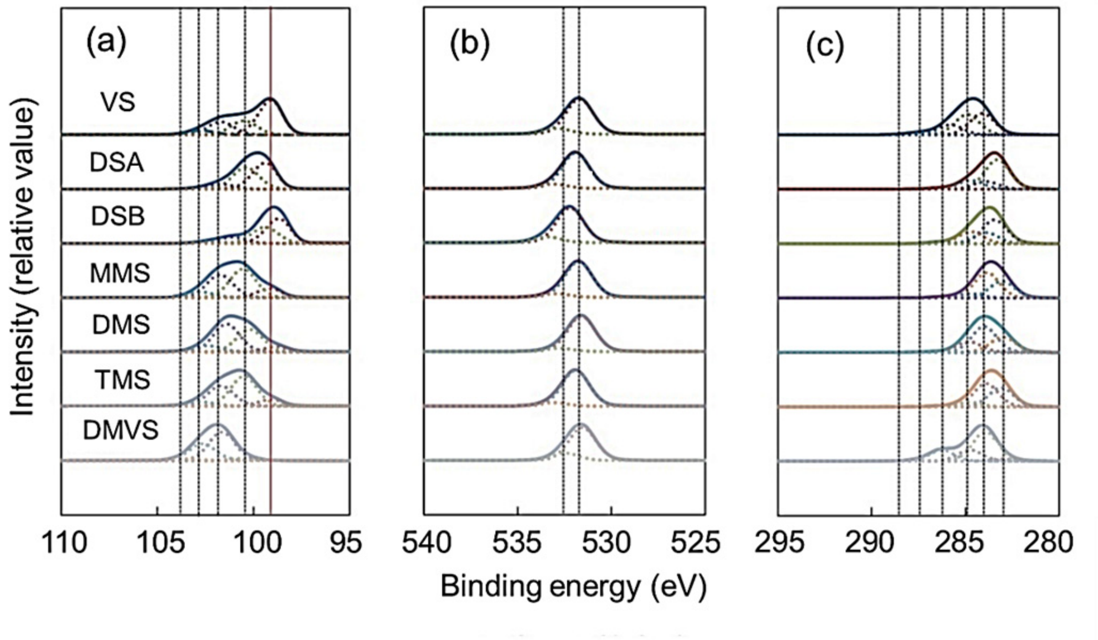


Fig. 6-5. XPS spectra on (a) Si2p, (b) O1s, and (c) C1s of the surface of thin films obtained from different organic silicon compounds. The results with VS, DSA, DSB, MMS, DMS, TMS, and DMVS are shown from top to bottom. For abbreviations, see Tables 6-2 and 6-4. For the peaks of dotted lines, see lists in Table 6-5.

Table 6-5. Peak areas of XPS analysis

	Peak area (%)				
Material gas species	Silicone				
	Si-Si	SiC SiO_1C_3 Si_2O etc.	SiO_2C_2 SiO etc	SiO_3C_1 Si_2O_3 etc	SiO_2 etc
	99.0 eV	100.5 eV	101.7 eV	102.7 eV	103.6 eV
VS	50.3	22.5	20.5	6.6	0.0
DSA	46.8	41.8	9.8	1.6	0.0
DSB	48.5	34.4	12.9	4.2	0.0
MMS	12.9	43.5	35.0	8.6	0.0
DMS	7.6	36.7	45.3	10.3	0.1
TMS	10.1	48.8	33.5	7.6	0.0
DMVS	0.0	5.1	57.2	33.9	3.9

Material gas species	Oxygen	
	SiOC C=O etc	SiO_2 C-O-C etc
	531.7 eV	532.9 eV
VS	86.4	13.6
DSA	89.3	10.7
DSB	85.5	14.5
MMS	91.2	8.8
DMS	91.3	8.7
TMS	91.2	8.8
DMVS	81.8	18.2

Material gas species	Carbon					
	SiC SiO_1C_3 etc	SiO_2C_2 etc	SiO_3C_1 C-C C-H etc	C-O etc	C=O etc	O=C-O etc
	283.1	283.9	284. 8	286.3 eV	287.5	288.7 eV

	eV	eV	eV		eV	
VS	39.5	37.0	18.4	4.4	0.7	0.0
DSA	62.8	16.4	18.3	2.5	0.0	0.0
DSB	49.3	22.8	24.6	3.2	0.0	0.0
MMS	35.2	53.0	9.1	2.3	0.0	0.4
DMS	29.0	49.0	20.0	1.4	0.6	0.0
TMS	40.3	48.2	10.0	1.5	0.0	0.0
DMVS	4.2	53.3	20.3	20.1	2.2	0.0

In brief, the specific combinations of wire and material gas species were required for the barrier enhancement of PET bottles in the coating system described above, and the resultant barrier SiOC coating had unique Si-Si bonds. These facts indicate specific wire species under certain temperature could promote the formation of gas barrier SiOC thin films. Based on the requirement of specific wire species for the formation of gas barrier thin films in addition to the common unique chemical bonds in these films, the authors concluded that this process is a type of catalytic CVD process 3).

6.3.5 Storage test

With the combination of molybdenum and vinylsilane, the hot wire CVD process described above was applied to 500 mL PET bottles of 23 g in weight. Based on the conducted XPS analysis, coating used was composed of silicon, oxygen, and carbon at a ratio of 36.5, 27.5, and 36.0 in atomic percentage, respectively. Fig. 6-6 shows the microscope image and the transmission spectra of the visible light of the uncoated and coated PET samples. While the coating was practically colorless, the use of molybdenum provided visually slightly golden tint, similar to the use of tantalum 4). Fig. 6-7 shows the TEM image of the cross section of coated PET bottles. As shown in the figure, the existence of a thin film could be observed as a roughly 20-30 nm thick layer which was evenly distributed on the PET substrate.

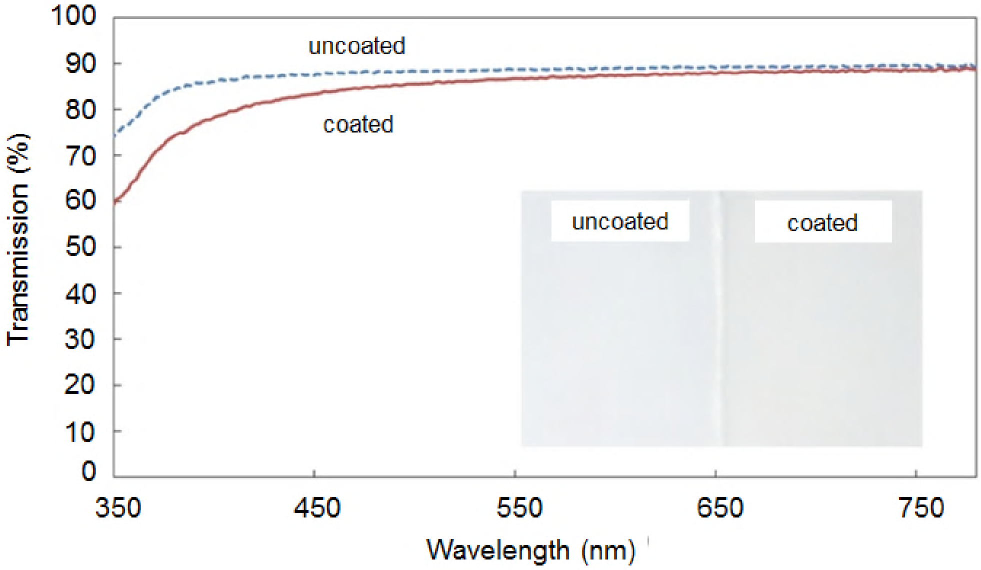


Fig. 6-6. Visual appearance of uncoated and coated PET bottles. For coating, vinylsilane and molybdenum was used. The transmission of visible light of uncoated and coated samples was shown dotted blue and solid red lines, respectively. Also, the optical microscope images of uncoated and coated samples were shown in left and right in the embedded picture, respectively.

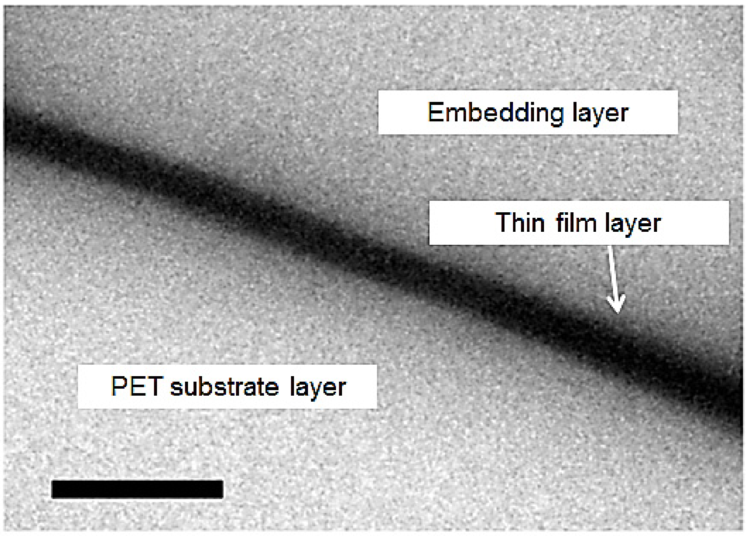


Fig. 6-7. TEM image of a coated PET bottle. A cross section of the thin film layer was shown between PET substrate and embedding layers. Bar represents 100 nm.

These coated bottles were then filled with carbonated water for storage test in order to confirm the practical performance for carbonated drinks.

Some of the bottles were destroyed for measuring the change in the whole volume of bottles after 5 days under 38°C. The results were shown in Fig. 6-8. Interestingly, the volume expansion of coated bottles was slightly small, compared to that of uncoated bottles. It is considered that the dense structure of the thin film could restrict the creep of PET wall.

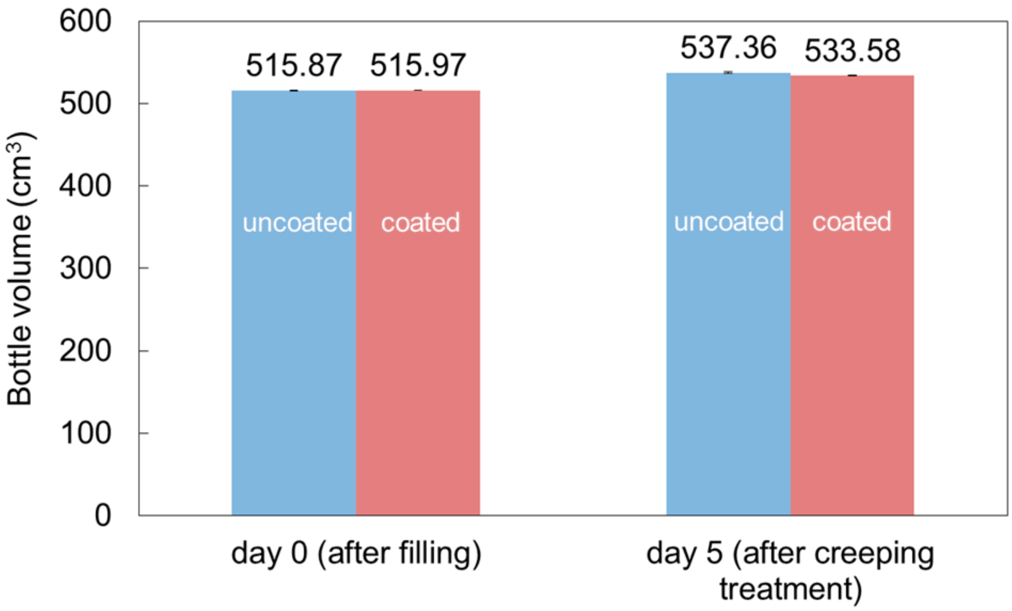


Fig. 6-8. Bottle volume before and after creeping treatment. PET bottles were coated using vinylsilane and molybdenum. Left and right bars of each pair represent the volume of uncoated and coated PET bottles, respectively. The difference between left and right pairs showed the increase of bottle volume due to the creeping treatment of storage at 38°C for 5 days. Bars represent the standard deviation of each sample set.

The rest of PET bottles was stored under 35°C for 60 days, and regularly measured the decrease of carbon dioxide content in the filled water. As shown in Fig. 6-9, coated bottles with plastic closures slowly released carbon dioxide content by the factor of about 2.3, compared to uncoated bottles with the same plastic closures. The steady decrease of carbon dioxide content observed in this storage test supports the coating formed was stable in carbonated water and other drinks.

It should be also noted that neither visible color change nor decrease in carbon dioxide barrier was observed. This is probably because a relatively high content of carbon in the coating inhibited the oxidation of the coating due to oxygen in air or water.

In brief, gas barrier enhancement shown in this storage test was quite likely to be practical for the extension of shelf-life extension and the light-weighting of bottles.

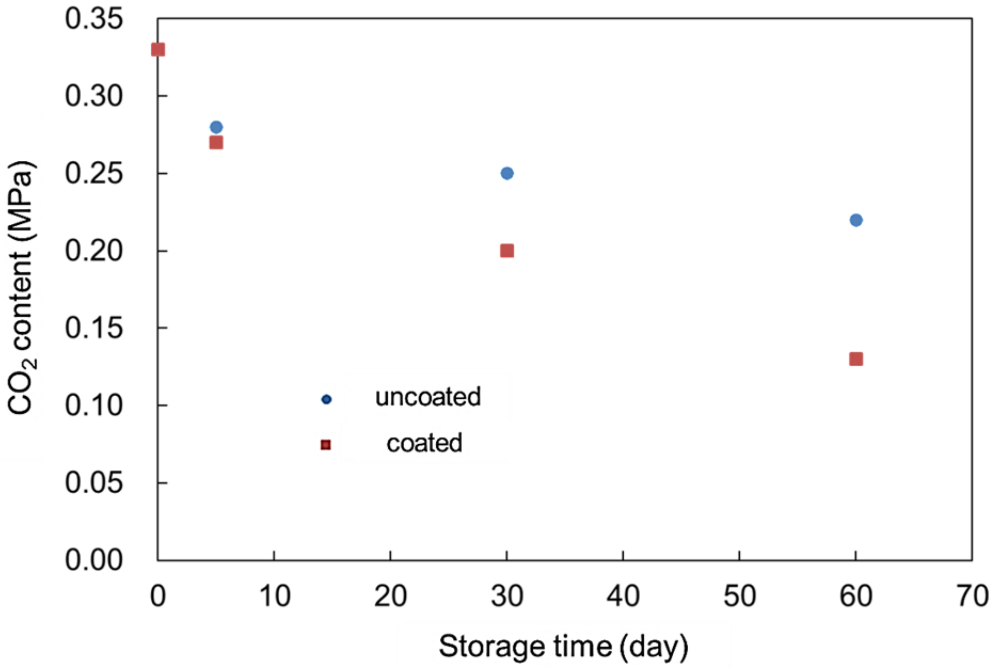


Fig. 6-9. Retention of carbon dioxide content of carbonated water filled in uncoated and coated PET bottles. Molybdenum and vinylsilane were used for coating. Square and circular plots represent the carbon dioxide content of uncoated and coated PET bottles. Note that each sample was stored at 38°C for the first 5 days for creeping treatment and then at 35°C for the rest of storage period.

6.3.6 Practical coating to plastic containers in food and beverage field

The systematic approach described above clearly showed the specific chemical structure of material gas was required for the formation of high gas barrier SiOC thin films using hot molybdenum and a series of organic silicon gas.

Based on the discussion above, the chapters 5 and 6 of this paper propose a unique

Cat-CVD process which can form gas barrier SiOC coatings to three dimensional plastic substrates. Due to a low heat load to the substrate, this coating can be applied to plastic containers like PET bottles. Furthermore, based on the experience in thin films produced through plasma-assisted CVD, gas barrier SiOC coating is readily applicable to PET containers for beverage and food from both viewpoints of safety issue and visual appearance (virtually colorless transparent coating can maintain the transparent appearance of PET containers). These characteristics, in addition to relative advantages of Cat-CVD process compared to other CVD processes such as economical coating device, and ease to enlarge coating area, favor the use of the proposing process in beverage and food fields among different industrial fields.

While a series of wire and material gas are useful to form the gas barrier SiOC thin film described above, the combination of tantalum or molybdenum with vinylsilane is likely to be most practical. For a hot wire CVD system for beverage plastic containers like PET bottles, both tantalum and molybdenum are a useful material for hot wires because they have the heat resistance of above 2200°C in the device described above and are known as a generally safe material for human dietary 9). While tantalum seems more resistant with oxidation, molybdenum is likely to be more economical. The question which is more appropriate for this CVD system remains yet to be answered.

From a viewpoint of material gas species, organic silicon gas was chosen in the aim to achieve colorless and physico-chemically stable coating which can be used in contact with various beverage and food. Based on the properties of a material gas and its subsequent thin film, it is considered that vinylsilane is the most appropriate material gas for the beverage industry because it can provide relatively high gas barrier coating and can be synthesized in the most economical manner. It should be mentioned that vinylsilane is at a gaseous status under room temperature and atmospheric pressure, and also of no explosive nature in contact with oxygen, not like (mono-)silane. Both properties can be utilized for the relatively easy handing of material gas in terms of safety and economics.

Based on the specific use of hot wire and material gas, gas barrier coatings in this study can provide an appropriate system to understand the catalytic production of active atoms and molecules for deposition onto polymer substrate, as seen in the study on free-radical reaction chemistry 10).

6.4 Conclusions

Based on the result of the study described in the previous chapter 5 of this paper, where a novel high gas barrier coating on PET bottles was formed through an original hot wire CVD process using tantalum and vinylsilane, a series of screening experiments were made with different wire and material gas species for appropriate gas barrier SiOC coating onto PET bottles, and attempted to clarify the basic mechanism of the gas barrier SiOC coating. As a result, it was found the specific combination of wire and material gas species produced the high gas barrier coatings with rich Si-Si bonds in their SiOC structure. For wire species, tungsten and molybdenum in addition to tantalum were effective for gas barrier coatings. Also, for material gas species, 1,4-disilabutane, or disilylacetylene in addition to vinylsilane were effective, and the author could generalize these effective chemical structures, where one or two silyl groups bond to one of two carbons like either H_3-Si-C-C-, H_3-Si-C=C- or H_3-Si-C≡C-. These specific combinations, especially the requirement of specific hot wire species, led to a conclusion that this coating system is a type of catalytic CVD process.

Also, the result of the conducted storage test showed that PET bottles coated with the Cat-CVD technique could maintain a high gas barrier performance in direct contact with carbonated water. When PET bottles were coated using molybdenum and vinylsilane, the carbon dioxide gas barrier property of the set of a coated bottle and an uncoated closure was increase by about 2.3 in BIF through the test period. Also, the coated bottles showed slightly restricted bottle creep (substrate stretch), compared to uncoated bottle. It is expected that the unique simple device for the coating system compared to the current plasma assisted CVD processes can be developed into an economical technique, for instances, for high gas barrier PET bottles for sensitive beverages and foods.

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Chapter 7

General Conclusion

7.1 Review of each chapter

This paper describes studies for the advancement of functional thin film techniques applied to three dimensional polymer packages.

The chapter 1 describes the background of studies in this paper, including the general function of packages, the examples of the function of thin film coatings used in polymer packages, and the recent trends of packages in beverage and food industry. As one of the recent trends, demand for the gas and flavor barrier enhancement of three dimensional polymer packages has increased in the beverage and food industry as well as other industries, in an increasing attention to the environmental, economical, and social sustainability of packaging. In other expression, the sustainability is the goal of the advancement of the thin film techniques in the studies of this paper.

The chapter 2 proposes approaches to the issues of gas barrier enhancement technologies used in beverage polymer containers, along with the description of the detailed background of the technologies. Thin film coating approaches are considered as most effective among several gas-barrier-enhancement technologies because of the degree and coverage of gas barrier enhancement, and recyclability. Because the majority of packaged beverage products are filled in containers made of poly(ethylene terephthalate) (PET), the studies in this paper were mainly focused on the applications to beverage products filled in PET bottles. In order to achieve the sustainable goal, original approaches using diamond-like carbon (DLC) and other coatings were proposed in this chapter, including (1) the improvement of current techniques, (2) challenge to the use of different polymer substrates in addition to PET, and (3) challenge to a novel coating method.

The purpose of the approach (1) lies in the improvement of the visual appearance and gas barrier properties of DLC coated PET bottles. Regarding the visual appearance, the tint of thin films is an issue for the wide spread of the use of DLC coating. The reduction of the tint of DLC thin films can, therefore, increase the psychologically acceptable products of coated bottles. Also, regarding the gas barrier property, the financial expenditure of specific coating machines is an issue for the wide spread of the current plasma-assisted chemical vapor deposition (PACVD) techniques including DLC coating. The increase of the degree of gas barrier enhancement, therefore, makes possible a shorter coating time and a higher cost performance of the coating machines.

The purpose of the approach (2) lies in the extension of applicable polymer substrates in addition to PET substrates. Because most of the current products using thin film coated polymer containers are PET bottles and little is known about the use of containers made of other polymers, various polymer substrates were coated with DLC thin films with the same conditions. The barrier improvement factor (BIF) of oxygen barrier enhancement was quite different, ranging from ca. 1 (almost no barrier enhancement) to ca. 12 (a high gas barrier enhancement for beverage applications), depending on the used substrates. In order to infer the reason of this difference, positron annihilation analysis was conducted. Because almost the same S parameter around 0.495 was detected in the analysis among the DLC layers coated on the various polymer substrates, it was considered that the structure of DLC thin films was equivalent on these substrates and the variance of the BIF values was caused by difference in the interface between DLC and substrate layers. This inference led to the employ of organosilane undercoating described in the chapter 4.

The purpose of the approach (3) lies in the development of a novel coating technique to provide the decrease of machine expenditure and the improvement of coating performance, compared to the current PACVD techniques. As mentioned above in the approach (1) of this chapter, the decrease of machine expenditure is an issue of the current thin film coating techniques. For the improvement of coating performance, in addition to the useful properties of DLC such as high gas barrier property and physico-chemical stability in contact with filled liquids, the coating is demanded to have more useful properties such as colorless appearance.

The chapter 3 relates to the approach (1) mentioned above in this chapter. The optimization of the power frequencies of a capacitively-coupled PACVD machine was conducted to enhance the gas barrier property of DLC layers on the inner surface of PET containers.

Power frequencies ranging from 2.50 MHz to 13.56 MHz were used to coat PET bottles. Compared to the use of conventional 13.56 MHz (OTR: 0.023 cc (STP)/day/bottle), the use of 6.00 MHz provided the minimum OTR of 0.015 cc (STP)/day/bottle.

The results of the obtained positron annihilation property, chemical composition, and chemical structure indicated that virtually homogeneous DLC coatings were formed with the examined frequencies, except the power frequency of 7.00 MHz.

Tint caused by DLC coatings and the adhesion property of DLC coatings in contact with caustic solution were also examined. The use of power frequency of 6.00 MHz provided the minimum difference in tint between the shoulder and body parts of coated PET bottles. The use of higher and lower frequencies had tendencies of thicker shoulder and body, respectively. Also, the duration of adhesion had a decreasing tendency as the used frequency decreased. With these results, the modification of power frequency was considered to cause a shift of spatial distribution of plasma concentration inside the PET container.

Form the industrial viewpoint, the power frequency of 6.00 MHz provided the most optimized properties for DLC coated PET containers in terms of gas barrier, tint and adhesion stability. These properties can be utilized for the improvements of product quality and cost performance. Furthermore, this method is easy to install in the conventional machines because no modification of machine configuration is required. Based on the result of the optimization of power frequency, 3 L PET kegs for beer have already been commercialized (Fig. 7-1). Long neck PET bottles for wine are another candidate for commercialization using this method (Fig. 7-2). In these containers, evenly distributed coating was confirmed to achieve with the use of power frequency of 6.00 MHz, compared to the use of conventional 13.56 MHz.

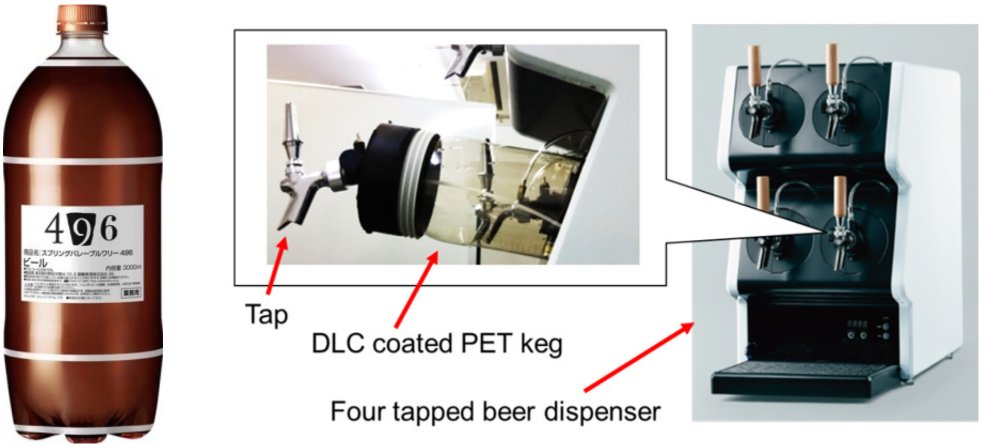

Fig. 7-1. An example of recently commercialized DLC coated products for beer. The left part of this figure shows a keg of three litter volume, made of PET. The slight tint of a keg in the middle part shows that this keg is coated with a DLC thin film. The middle and right part shows that these kegs are used in the beer dispensers.

Fig. 7-2. An example of pre-commercialized DLC coated products for wine. The left was coated using conventional 13.56 MHz. The right bottle was coated using 6.00 MHz, and evenly distributed coating was achieved especially in mouth and neck parts, compared to the left bottle.

The chapter 4 relates to the approach (2) mentioned above in this chapter. DLC coating was applied to plastic closures used for PET bottles. When the coating was applied directly onto the surface of PE sealing parts of the closures, the OTR of closures of these samples was 0.009 cc (STP) / closure / day, and almost same as that of uncoated samples (0.011 cc (STP) / closure / day). On the other hand, the anti-sorption property of d-limonene, a representative substance in the study of sorption to polymer materials, was significantly enhanced (the detected concentration from sealing parts was decreased from 2.1×10^3 to 2.8×10^2 ng / sealing part). Also, a significant enhancement of oxygen gas barrier property as well as anti-sorption property was achieved with the aid of undercoating using a type of organosilane, 3APTMS (the OTR of these samples was 0.03 cc (STP) / closure / day). The large and polarized molecules of d-limonene, compared to oxygen molecules, were considered to cause the difference of the behavior between gas permeation and sorption. The conducted Raman spectrometry and XPS analyses indicated that equivalent DLC thin films were formed on the surface of 3APTMS and PET layers. The results of the measurement of OTR and the thin film analyses supported the result of positron annihilation analysis described in the chapter 2, and the significant role of interface between thin films and substrates for oxygen barrier enhancement.

It is suggested that surface modification with wet treatment, for example, using organosilane, can be an effective technique for gas barrier thin film formation to three dimensional polymer substrates. It can be also speculated that effective wet agents can be found not only in silane coupling agents but also in ultra violet curable agents, and that the topcoating to thin films can enhance the function of thin film coating as well as undercoating [3-5)].

Both with gas and flavor barrier enhancement function of DLC coated plastic closures with 3APTMS, it was expected that corresponding quality improvement and shelf-life extension to products filled in gas barrier enhanced PET bottles such as beer.

A possible extension of the study in this chapter is to design a coating device that can process wet treatment and thin film coating in the same chamber. This kind of integrated process is expected to easily and rapidly handle various types of polymer substrates including three dimensional polymer packages.

The chapter 5 relates to the approach (3) mentioned above in this chapter. A unique hot wire CVD technique using tantalum wire and vinylsilane gas was developed which is applicable to the surface coating of PET bottles. With this technique, the obtained thin film coating was virtually colorless, enhanced the oxygen barrier properties of PET to the oxygen barrier improvement factor of more than 10, and stable in contact with water over 1 year in terms of water vapor barrier enhancement. The result of the conducted XPS analysis indicated that the obtained thin film was composed in 33.0% silicon, 29.5% oxygen, and 37.5% in atomic percentage, and characteristically contained Si-Si bonds in its surface. As a result, the formed thin film was confirmed as a type of SiOC thin film. Because the obtained coating is likely to share the advantages of carbon (high gas barrier against oxygen, carbon dioxide, and water vapor even in contact with neutral water solutions) and SiO_x (colorless) coatings, the practical use of this coating can be highly expected for beverage and food PET containers.

The chapter 6 relates to the approach (3) mentioned above in this chapter. Based on the results of the chapter 5, further study was made with extensive wire and material gas species, in order to find out the practical process and mechanism of gas barrier enhancement coating. Interestingly, specific combinations of wire and material gas species were turned out to form gas barrier enhancing SiOC thin films on PET bottles. The conducted XPS analysis indicated that these thin films had unique Si-Si bonds in common. Also, a generalized chemical structure of material gas species which can be used to form the gas barrier SiOC thin films was conceived, where one or two silyl groups bond to one of two carbons like either H_3-Si-C-C-, H_3-Si-C=C- or H_3-Si-C≡C-. These findings indicated that this coating system was a type of catalytic CVD, (Cat-CVD) because only specific hot wire species were effective to form the gas barrier SiOC thin films.

The result of the conducted storage test confirmed that the thin film formed with this technique using molybdenum and vinylsilane showed stability in direct contact with carbonated water. Also, the resultant coated bottles showed slightly restricted bottle creep (bottle expansion due to inside pressure), compared to uncoated bottles.

From the results of the chapters 5 and 6, it is concluded that the combination of tantalum (or molybdenum) and vinylsilane is likely to provide highly practical coatings in terms of gas barrier enhancement, human safety, and economics. The resultant coatings showed high gas property and stability in contact with water solution. It is considered that the commercialization of a coating technique like this is highly demanded in food and beverage industry. Fig. 7-2 shows a schematic image of a mass production machine using the technique described in the chapters 5 and 6.

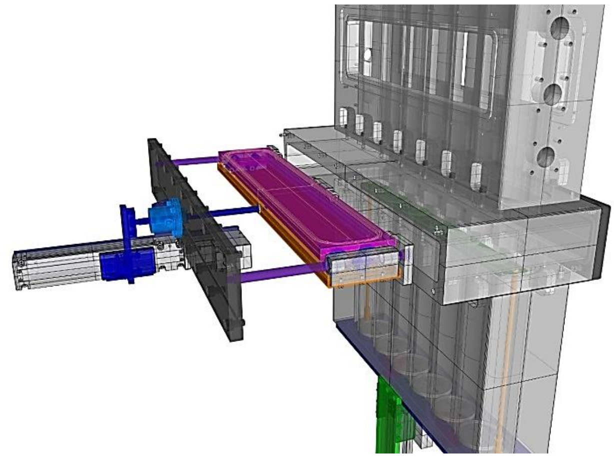

Fig. 7-3. A schematic image of mass production system based on the process described in the chapters 5 and 6, by courtesy of Kirin Techno System Co., Ltd., Japan.

7-2 Comparison of DLC and SiOC coating processes and their future perspective

Table 7-1 summarizes the comparison of thin film coatings studied in this paper, where DLC coating is performed using the current PACVD processes, and SiOC coating is performed using the novel Cat-CVD process described in this paper. Green highlighted boxes showed the main expected advantages of the latter coating in practical use for PET bottles.

It is conceivable that the current DLC coating technology used in this study will have an advantageous position for the gas and flavor barrier enhancement of polymer packages, even after the commercialization of the above-mentioned Cat-CVD process (SiOC coating). For example, a recent trend of increasing polymer kegs mainly for beer can be handled with the DLC coating technique described in this paper, because this technique is applicable to PET containers larger than 3 L as shown in Fig. 7-1. On the hand, Cat-CVD process is likely to involve difficulty such as the low throughput of coating machines in coating to large containers where the increase of distance between hot wires and substrates tend to the decrease of the concentration of active molecules in contact with the unit area of substrates.

Table 7-1. Comparison of DLC and SiOC coatings.

Properties	**DLC**	**SiOC**
Thin film composition except hydrogen	Carbon	Carbon Silicone Oxygen
Material gas	Acetylene	Vinylsilane
Oxygen barrier (BIF)	> 10, compared to uncoated bottles	
Color	Golden to Brown tint	Slightly golden to invisible tint
Adhesion in contact with beverages*	Stable	
Process type	Plasma-assisted CVD	Catalytic CVD
Power supply	Radio frequency supply (with a matching unit)	Direct current supply (without a matching unit)
Principle of deposition	Electromagnetic field inside the bottle	Catalyst and heat on hot wires inside the bottle
Pressure to coat	5 Pa	
Coating time	2.0 sec (– 6.0 sec**)	
configuration of a coating chamber	Less compact (Double walled)	More compact (Single walled***)

*: Beverages refer to water solution of pH 7 and less

**: Coating time of 2.0 sec for SiOC coating resulted in more than 10 of BIF value for oxygen gas barrier enhancement, while most of experiments with SiOC coating was performed with coating time of 6.0 sec.

***: Unnecessity of electromagnetic shield enables an economical process of multiple bottle coating in a single chamber, which is difficult in plasma assisted CVD

In conclusion, expected further studies are on (1) interfacial control to widen the applications of thin film coating to gas-barrier-enhanced polymer packages, and (2) the commercialization of Cat-CVD process for gas-barrier-enhanced polymer packages. These advancements are likely to enable the wider spread of thin film coating to polymer packages including three dimensional containers.

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Published Papers Related to this Thesis

1) M. Nakaya, A. Uedono, A. Hotta, Recent progress in gas barrier thin film coatings on PET bottles in food and beverage applications, *Coatings*, Vol. 5, pp. 987-1001 (2015)

2) M. Nakaya, M. Shimizu, A. Uedono, Impact of the difference in power frequency on diamond-like carbon thin film coating over 3-dimensional objects, *Thin Solid Films*, Vol. 564, pp. 45–50 (2014)

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In total, 56 patent applications represented by the following applications.

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