RESEARCH ARTICLE

Gas and flavor barrier thin film coating to plastic closures

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Abstract

The gas and flavor barrier enhancement of plastic closures for food and beverage applications was attempted through thin film coating. Diamond-like carbon (DLC) thin films were formed onto the inner surface of closures, using a specific plasma-assisted chemical vapor deposition (PECVD) technique. In order to overcome the difficulty in forming a high gas barrier thin film coating onto the surface of the sealing parts of plastic closures, wet treatment using 3-aminopropyltrimethoxysilane (3APTMS) was applied in prior to DLC coating. As a result, the oxygen gas barrier of the sealing parts was significantly increased. Flavor barrier enhancement was also confirmed based on the sorption of d-limonene inside the coated sealing parts.

Keywords: gas barrier, flavor barrier, permeation, sorption, DLC, 3-aminopropyltrimethoxysilane, d-limonene, closure, polyethylene, PET

1. Introduction

Polymer materials are widely used in the packages for the food and beverage industry. While polymer materials have unique useful properties, the deficiency of gas barrier property limits the shelf-life of sensitive products in polymer packages.

Rigid containers are often used for food and beverage packages often based on their high speed production and ease of handling for machinery and human users. While the most appropriate polymer materials are different depending on their applications, the general useful properties such as transparency and shapability have made poly(ethylene terephthalate) (PET) the most widely used material for rigid plastic containers in the beverage industry. As a result, PET bottles are the most intensive package formats for gas barrier enhancement study [1, 2].

Recently, two industrial trends encourage the study on the gas barrier enhancement of products in PET bottles. One is the global increasing attention to environmental burden such as material saving. In this aspect, the design of light-weighted PET bottles leads to a situation where a thinner bottle wall allows more gas permeation, as gas transmission rate through polymer materials is known as proportional to material thickness [3]. As a result, light-weighting causes higher demand for gas barrier enhancement. Another is the extension of product categories which use PET bottles. As the usefulness of PET bottles is recognized widely, challenge has been made to new categories where sensitive products such as beer, wine, and juice require enhanced flavor retention properties to PET bottles.

A suitable example can be seen in beer products in PET bottles. Beer is known as extremely sensitive beverage to oxidation, and oxygen permeation through polymer packages accelerates the oxidative deterioration in terms of taste quality to a degree where the gas barrier property of normal PET bottles is not sufficient [4]. Beer is also a type of carbonated beverage, where carbon dioxide permeation decreases carbon dioxide content and affects the overall flavor. Barrier property against flavor components, so-called anti-sorption property, is also required in terms of permeation through and dissolution into polymer packages. Sorption is highly related to flavor scalping [5], and affects the overall taste through the loss of subtle balance among various organic compounds including the ingredient of hops in beer.

Recent progress in the study on the gas barrier enhancement of PET bottles has proved various technical approaches are practical [1, 6, 7]. Especially, thin film coatings over the inner surface of PET bottles have shown that they effectively inhibit both gas permeation through and sorption into PET bottles. Nowadays, for this purpose, carbon or silicate oxide thin films are mainly used due to their availability in PECVD techniques and safety issues [7, 8, 9]. However, as the performance of PET bottles is enhanced, the performance of plastic closures used in combination with PET bottles has become more important to determine the overall performance of the package.

The sealing parts of these plastic closures are usually made of polyethylene (PE) due to its suitable rigidity and shapability, and therefore the enhancement of the gas barrier and anti-sorption properties of PE is the key for extended shelf-life and quality extension of sensitive products in a PET bottle format.

In attention to anti-sorption property as well as gas barrier property, the authors attempted to form practical thin film coating to the inner surface of PE sealing parts. It should be stressed that the gas barrier enhancement of polyethylene 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 diamond-like carbon (DLC) coating was effective in enhanced adhesion and gas barrier enhancement [10]. Because one of these organic silane compounds, 3-amino-propyltrimethoxysilane (3APTMS), is known as a relatively safe compound, the authors 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.

2. Materials and methods

2.1. Preparation of primary package components

2.1.1. Preparation of PET bottles

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

2.1.2. Plastic closures

A variation of commercial two-piece plastic closures developed for PET bottles for beer products were used for this study as shown in Figure 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 Figure 2. The inner area of the inner ring of the sealing part had 27.4 mm in diameter and 1.1 mm in thickness..

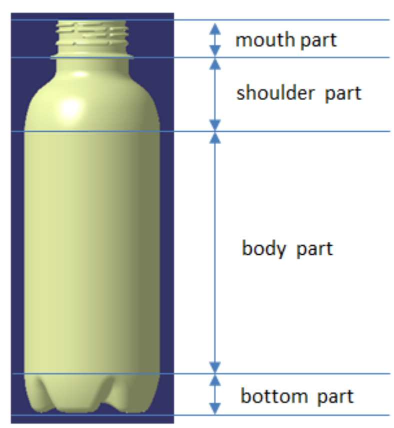


Figure 1. Appearance and parts of PET bottles used.

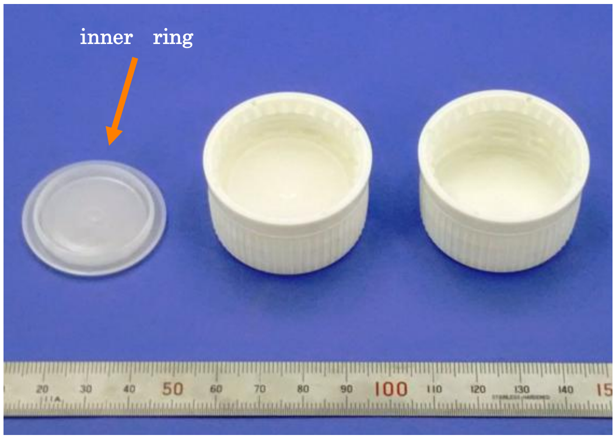


Figure 2. Appearance of a two-piece closure used. A sealing part, assembled sealing and shell parts, and a shell part are shown from left to right.

2.2. DLC and its pretreatment coating to packages

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 were performed as described in our previous study [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., Chiba, Japan, specifically designed for PET bottle coating. Figure 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 PECVD technique. The vacuum chamber was closed and vacuumed to 5 Pa. Acetylene gas was supplied into the bottle at a rate of 80 standard cubic centimeters per minute. 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.

2.2.2. DLC coating to 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 Figure 3 (b).

For the pretreatment of 3APTMS undercoating, 70 µm of 3APTMS, supplied by Shinetsu Silicon Chemicals Co., Ltd., Tokyo, Japan, was dropped to the center of the inner ring of a sealing part and distributed over the surface based on a spincoat technique using 3000 rpm in a draft chamber under 23^{o}C. The resultant 3APTMS undercoating was dried in a room temperature around 23^{o}C or immediately applied to DLC coating without any specific drying process.

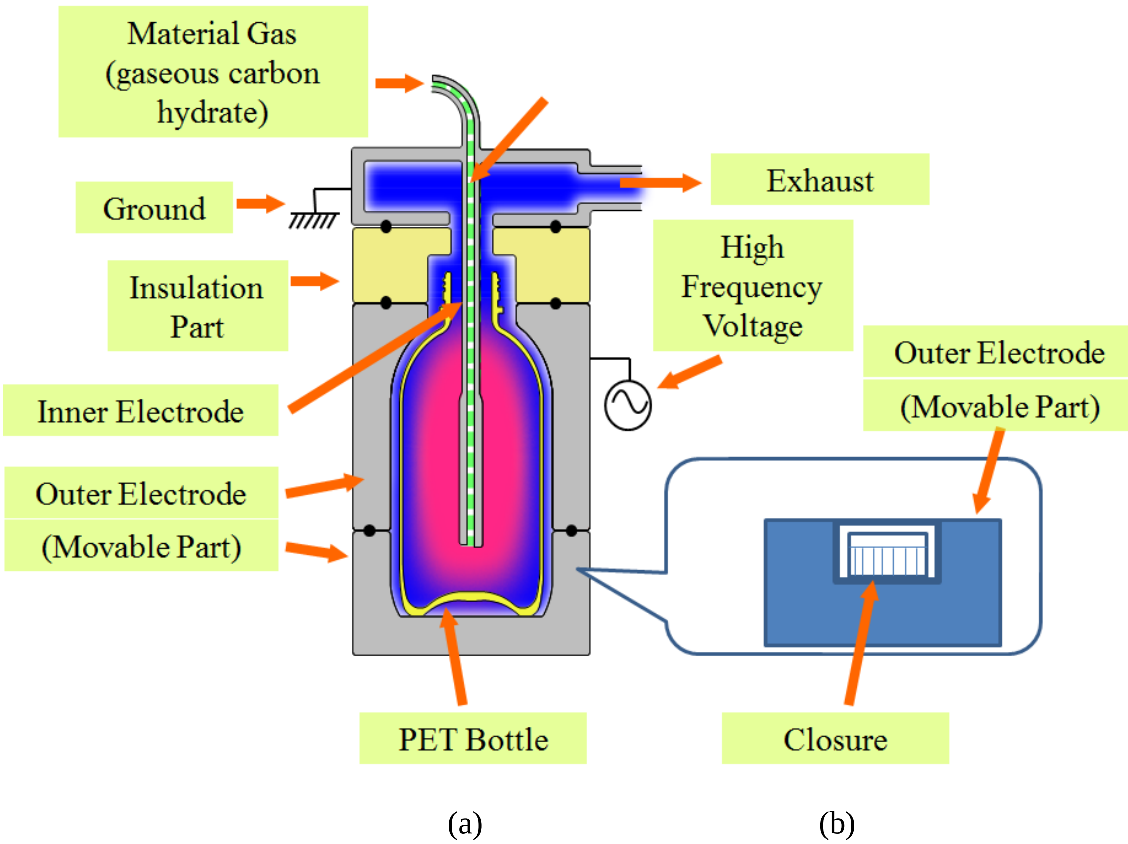


Figure 3. Schematic illustration of DLC coating devices for (a) PET bottles and (b) plastic closures. The exchange of outer electrodes enables coating to different bottles and closures in a single device. The above figures illustrate a closure can be coated with a specific movable part of the outer electrode. 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.

2.3. Measurement of oxygen barrier properties of PET bottles

2.3.1. Oxygen barrier property of PET bottles

Oxygen transmission rate (OTR) was measured with Oxtran 2/21. Mocon Co., Ltd., MN, USA, for 72 hours under the conditions of 23 ^{O}C and RH 90 %, based on ASTM F-1307 method [13]. It should be commented 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 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. As a result, 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.

The average of OTR obtained from three samples was adopted.

2.3.2. Oxygen barrier property of 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.

2.4. Measurement of deposition rate on closures

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, 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.

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., Tokyo, Japan.

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 over 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 used tend to be spontaneously cracked in the thickness of 100 nm and more. As a result, the deposition of 80 nm thickness was aimed in this experiment.

To complement the above Raman

spectroscopy, 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, based on the AlKα radiation (1486.6 eV) was used for the spectral regions of Si2p, O1s, and C1s (N1s was omitted in consideration of the results of our previous study [12]). For samples of this analysis, thin films of ca. 20 nm in thickness were formed on the sealing parts of plastic closures.

2.7. Sorption test

2.7.1. Sample preparation

1.00 ml of commercial orange juice was dropped to the inside of the inner ring of a sealing part, and stored at 35^{o}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 used. After the storage, each sample was gently rinsed with distilled water, and dried at room temperature.

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, Kyoto, Japan, was used. Each sample containing fragments of an individual sealing part in a glass vial was hermetically transferred to the detector controlled at 250^{o}C, using helium for a constant carrier gas flow. Before measuring 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 used was measured in the same manner.

The average of detection obtained from three samples was adopted.

3. Results

3.1. DLC coating to closures and resultant OTR

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.

Figure 4 shows the visual appearance of each sample. It should mentioned even with spin coating, slight flow lines from the center to the peripheral directions were visually observed after the coating of 3APTMS, resulting in the slightly white appearance of PE / 3APTMS / DLC compared to PE / DLC. The thickness of the 3APTMS and DLC layers was measured as 1.3 µm, and 21.6 nm, respectively.

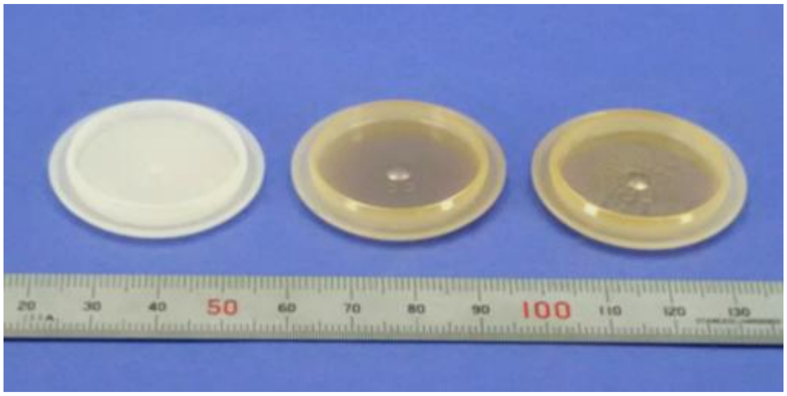


Figure 4. Visual appearance of coated and uncoated sealing parts of plastic closures. Samples of PE, PE / DLC, and PE / 3APTMS / DLC were shown from left to right.

Figure 5 shows the OTR of uncoated and coated closures. DLC coating significantly enhanced oxygen barrier property only in case with 3APTMS undercoating. Without the undercoating or with undercoating itself, OTR was slightly decreased. It should be noted that the any visible defects including cracks were not observed on the surface of DLC coating in the sample of PE / DLC.

Based on the OTR of uncoated and DLC coated PET bottles used was 0.0375 and 0.0030 cc (standard temperature and pressure) / bottle / day, respectively, the total OTR of the package composed of a bottle and a closure was calculated. As shown in Figure 6, a remarkable oxygen barrier enhancement compared to the uncoated bottle and closure was mainly derived from the coated bottle. On the other hand, in comparison to the coated bottle and uncoated closure, a remarkable oxygen barrier enhancement was mainly derived from the coated closure, because the majority of oxygen permeation occurred through the closure part in the combination of the coated bottle and the uncoated closure used.

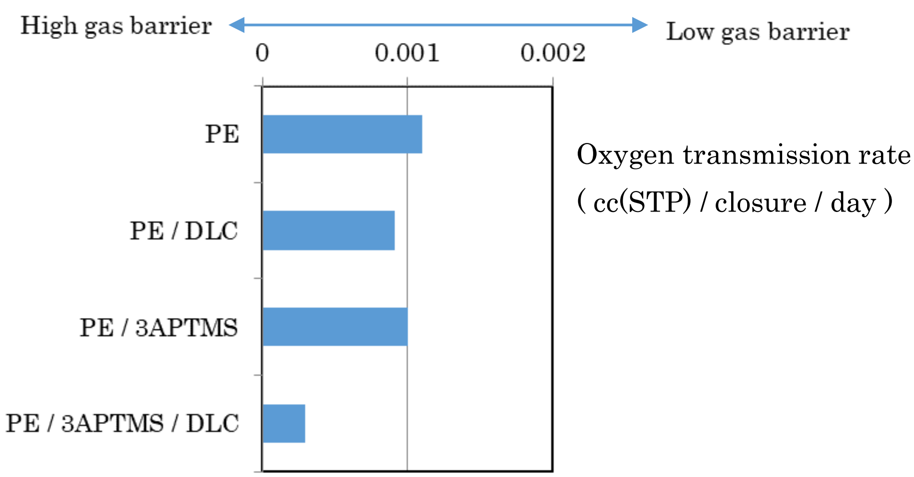


Figure 5. Oxygen transmission rate of uncoated and coated closures

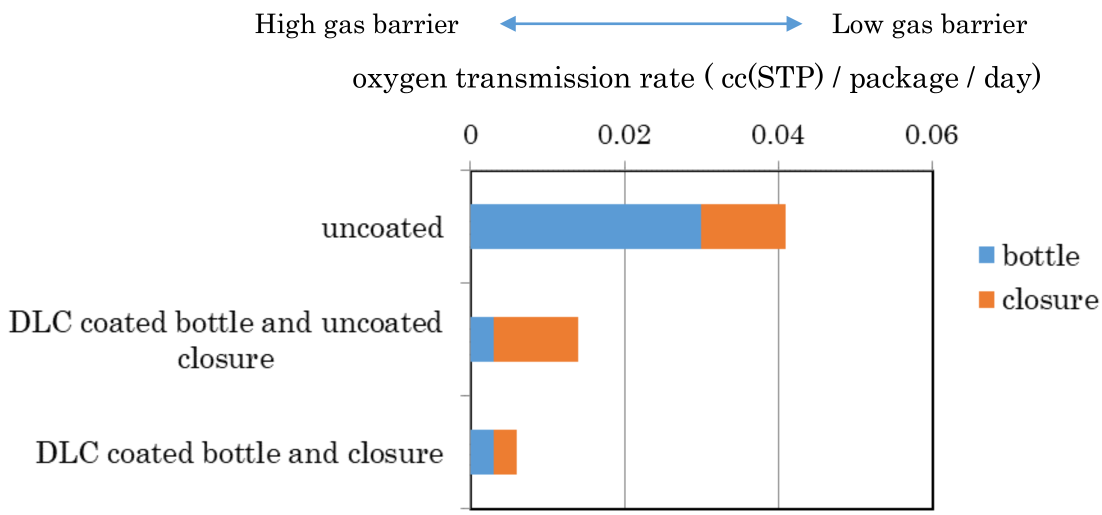


Figure 6. Calculated total oxygen transmission rate of the whole packages. Compared to a set of uncoated bottle and closure, the OTR of a set of DLC coated bottle and uncoated closure was decreased to about 34 %. Also, the OTR of a set of DLC coated bottle and closure was decreased to about 15%.

3.2. Surface roughness

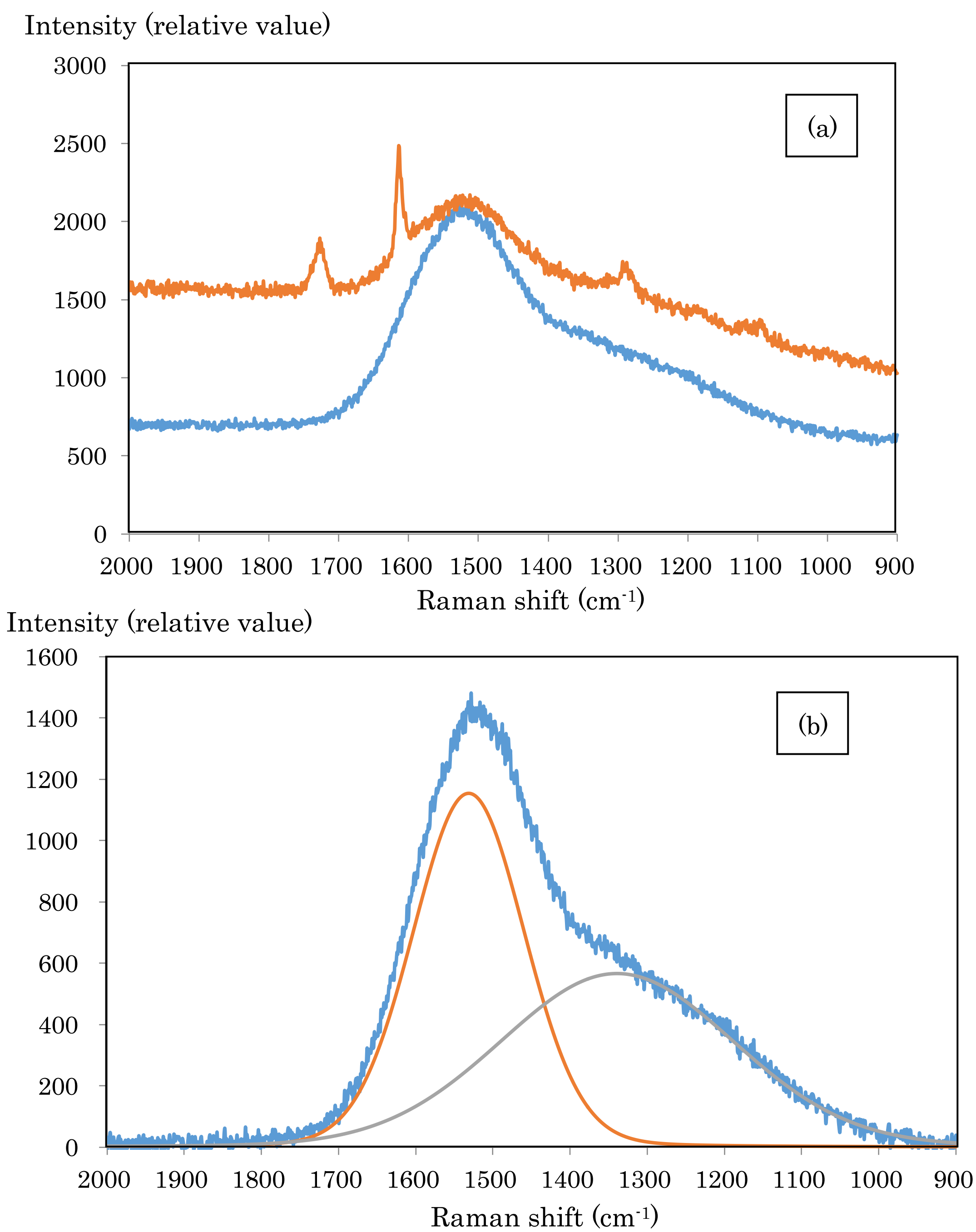
Four types of closures, (1) PE, (2) PE / DLC, (3) PE / 3APTMS, and (4) PE / 3APTMS / DLC, were prepared in order to compare their surface roughness. The result was summarized in Table 1. It was observed that DLC coating directly applied to PE surface was deposited basically along the surface morphology of the substrate used. Interestingly, 3APTMS undercoating had a significant effect to increase surface roughness, and did not show any leveling effect. It should be noted that, despite of the rough undercoating, the oxygen barrier was enhanced with DLC coating on the 3APTMS layer, as mentioned above. For reference, the roughness of the inner surface of PET bottles was around 0.6 nm in Ra.

Table 1. Surface roughness of uncoated and coated sealing parts of closures. Ra was shown in average ± standard deviation in nm.

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

3.3. Chemical analyses

Raman spectrometry was conducted with a 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 Figure 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 Figure 7 (b) and (c), and the ratio of these peaks indicates equivalent DLC coating was formed as shown in Table 2.



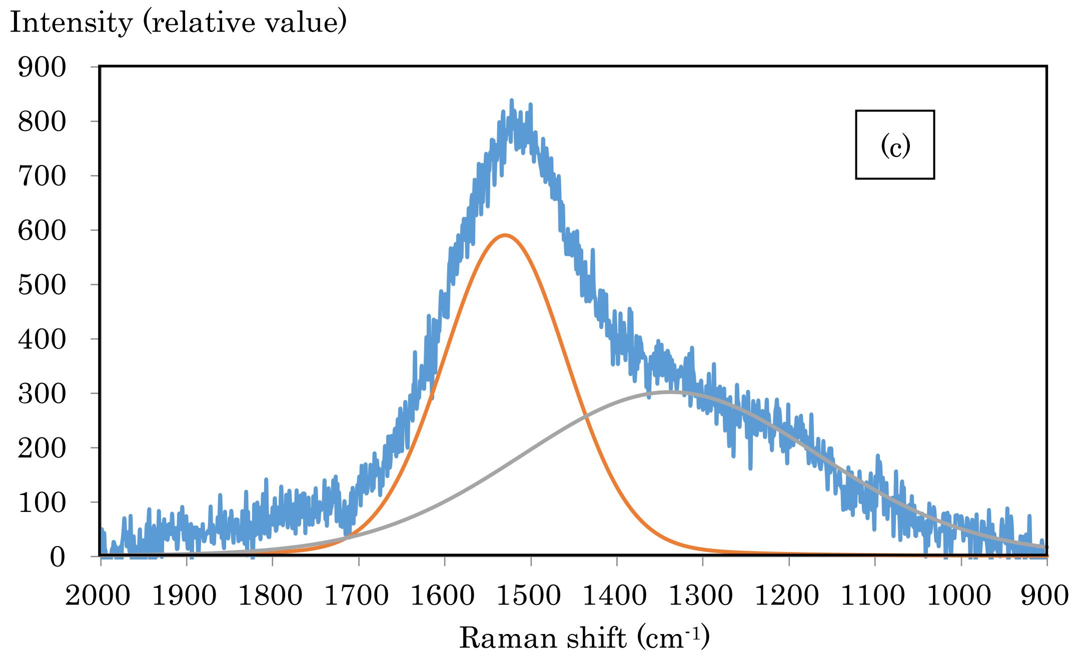


Figure 7. Raman spectra of DLC coatings (a) formed on PET (red line) and PE / 3APTMS (blue line), (b) formed on PET (blue line) fit to G and D bands (red and gray lines, respectively), and (c) formed on PE / 3APTMS (blue line) fit to G and D bands (red and gray lines, respectively)

Table 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	

In order to confirm whether or not 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. Figure 8 clearly shows that one layer composed of carbon only was formed on another layer containing carbon, silicon and oxygen. 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 XPS analysis conditions used, and also matched with the deposition rate of DLC coating mentioned above.

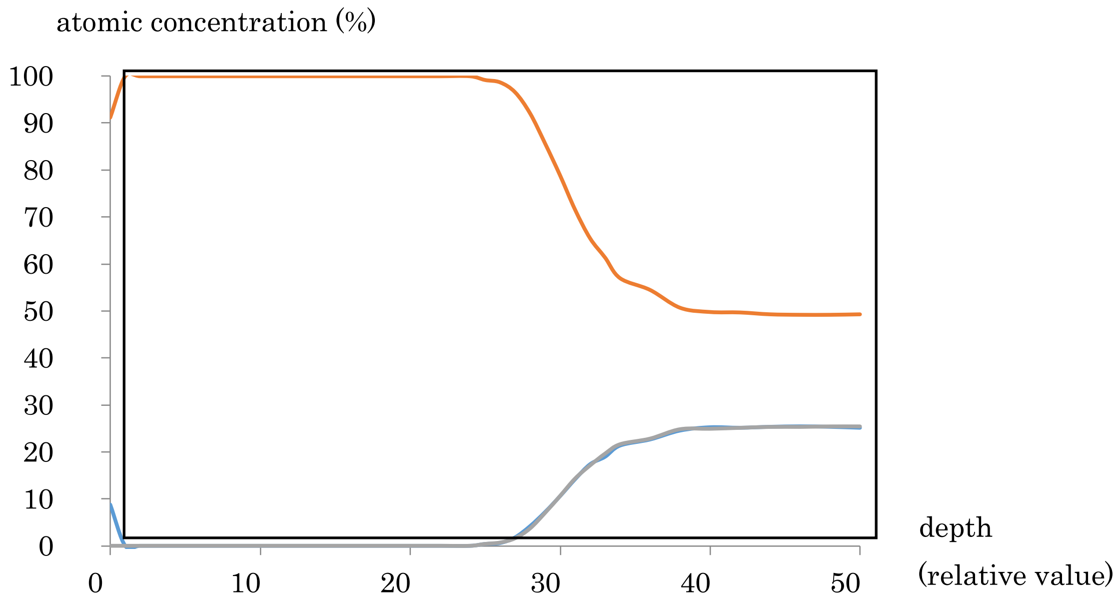


Figure 8. Depth atomic profile of PE / 3APTMS / DLC. From left to right, the uppermost surface of DLC coating (to be in contact with the content of the package) to the interface with 3APTMS was shown. Blue, red, and gray lines represent oxygen, carbon, and silicon, respectively. It should be noted that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

3.4. Sorption test

Table 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 detected was observed with PE / 3APTMS / DLC samples, compared to uncoated PE samples. Interestingly, another coated samples of PE / DLC also showed a significant decrease of d-limonene detection, in spite of its quite limited oxygen gas barrier enhancement as mentioned above. 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.

It should be mentioned that the concentration of d-limonene in the orange juice used was measured to be 29.2 µg / ml.

Table 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

4. Discussion

4.1. Performance of coated plastic closures

In this study, DLC coating was applied to closure parts made of polyethylene, with the aid of undercoating using 3APTMS. As a result, the OTR of closure was decreased by about two thirds, even though the value of OTR included the passage of oxygen molecules through interface between sealing parts and mouth parts as well as permeation of polyethylene matrix.

With this oxygen barrier enhancement of closures, the overall OTR of the package composed of the DLC coated plastic closure and DLC coated bottle was decreased by about one half, compared to the case with the uncoated closure and DLC coated bottle. 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.

Furthermore, 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 hop 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.

4.2. Chemical structure of coated plastic closures

Based on the Raman and XPS analyses performed, it can be concluded that homogeneous DLC thin films were formed either on PET or 3APTMS substrates. Interestingly, in spite of the fact that

3APTMS layers provided wet substrates to DLC coating, the dense structure of DLC thin films was formed in similar to the cases with other solid polymer substrates [15]. On the other hand, the quite limited oxygen barrier enhancement in case with PE / DLC indicated the importance of interface conditions between polymers and DLC thin films for restricting permeation.

The importance of interface conditions was also seen in case with PE / 3APTMS / DLC. 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 [14] reported that plasma treatment using such as oxygen or nitrogen modified the surface of 3APTMS layers into high gas barrier structures. This plasma assisted chemical modification was reported to highly increase silicon and oxygen contents in the uppermost surface layer. Even though the XPS analysis performed in this study showed the surface region examined was mainly composed of carbon at any depth, without any significant silicon or oxygen rich layer, similar gas barrier enhancement appeared to occur. The reason of the missing silicon or oxygen rich layer probably lies in the PECVD technique used. A possible explanation is that a quite thinner layer of 3APTMS was modified due to a shorter exposure to plasma and/or the deposition of dense DLC thin films. TEM observation or positron annihilation techniques might be able to provide a clue to more detailed information on the mechanism of how rough 3APTMS layers can facilitate gas barrier enhancement with DLC thin films.

4.3. Significance of coated plastic closures

In similar to the gas barrier enhancement technologies of PET bottles, plural technologies for plastic closures have been proposed such as coatings, multi-layers, and oxygen scavengers.

Among them, the coated closures proposed in this study suggest a clear advantage in anti-sorption performance because both multi-layer and scavenger approaches cannot modify polyethylene surface nor inhibit the sorption of flavor components.

In beverage industry, for this kind of plastic closures both with gas and flavor barrier enhanced performance, relatively costly means are used such as perforated PE searing parts laminated with thin PET sheets. Because the coated closures proposed in this study can be produced relatively in a simple and established method as well as with a small amount of materials, economical benefits can be expected.

4.4. Possible further quality and economical improvements

This study can be extended to functional coating onto 2- to 3-dimensional objects because the results of this study suggest approaches to coatings with little defects over typical rough objects.

While several technical approaches are proposed to form a smooth surface of molded materials such as hot and cool molding [16], 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.

As a result, a more universal approach to form undercoating to 2- to 3-dimensional objects would be a useful technique for functional coating. 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 [14] has an advantage in requiring virtually a single material and a simple process in machinery. 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.

5. Conclusions

A DLC coating technique used for PET bottles were applied to plastic closures. When the coating was applied directly onto the surface of PE sealing parts of the closures, oxygen gas barrier property was not significantly enhanced, while anti-sorption property was significantly enhanced. 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 organosilan, 3APTMS. The formation of equivalent DLC thin films was confirmed between the surface of 3APTMS and PET layers.

Acknowledgement

The authors would like to express our gratitude to Nihon Yamamura Glass Co., Ltd., for the prototyping and supply of plastic closures. We are also thankful to all the staff related to this study in Keio University, and Kirin Co., Ltd., Japan.

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