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Deodorisation effect of diamond-like carbon/titanium dioxide multilayer thin films deposited onto polypropylene

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ABSTRACT

Many types of plastic containers have been used for the storage of food. In the present study, diamond-like carbon (DLC)/titanium oxide (TiO_2) multilayer thin films were deposited on polypropylene (PP) to prevent flavour retention and to remove flavour in plastic containers.

For the flavour removal test, two types of multilayer films were prepared, DLC/TiO_2 films and DLC/TiO_2/DLC films. The residual gas concentration of acetaldehyde, ethylene, and turmeric compounds in bottle including the DLC/TiO_2-coated and the DLC/TiO_2/DLC-coated PP plates were measured after UV radiation, and the amount of adsorbed compounds to the plates was determined. The percentages of residual gas for acetaldehyde, ethylene, and turmeric with the DLC/TiO_2 coated plates were 0.8%, 65.2% and 75.0% after 40 h of UV radiation, respectively. For the DLC/TiO_2/DLC film, the percentages of residual gas for acetaldehyde, ethylene and turmeric decreased to 34.9%, 76.0% and 85.3% after 40 h of UV radiation, respectively. The DLC/TiO_2/DLC film had a photocatalytic effect even though the TiO_2 film was covered with the DLC film.

1. Introduction

The use of plastic materials for food container has some advantages due to the low cost, light weight, and heat stability of plastics. Therefore, plastic food containers have experienced high demand. In particular, the use of polypropylene (PP) is widespread because of its flexibility and low cost [1,2]. One disadvantage of plastic food containers is the sorption of food flavours to the food container because the interior linings are in direct contact with foodstuffs for long periods of time [3–6]. Once a strong food flavour, such as curry or garlic, is adsorbed to the container, it is difficult to remove by washing. Consumers are reluctant to use containers to which flavours have adsorbed for the storage of other foods. Amerongen has proposed that the adsorption of organic compounds to polymers proceeds according to the following steps: adsorption on the surface of the polymer, cohesion, absorption (solubility) into the polymer, and diffusion within the polymer [7].

Diamond-like carbon (DLC), known as amorphous hydrogenated carbon (a-C:H), is a material with excellent mechanical, tribological and biological properties [8–10]. In addition, DLC films have good gas barrier properties and high chemical stability. Recently, DLC has been applied in the field of beverage packaging. Shirakura et al. reported that the DLC-coated polyethylene terephthalate (PET) has excellent gas barrier properties for O_2 and CO_2, thus preventing oxidation of the beverage and outgassing from carbonated drinks [11]. This superior gas barrier property of DLC films can be expected to prevent flavours from adsorbing onto polymers.

Photocatalyst can be used to promote active decomposition of flavours adsorbed to polymers. Titanium dioxide (TiO_2) is widely recognised as an effective photocatalyst for the oxidative degradation of organic pollutants in air and water. TiO_2 eliminates odours, microbes and moulds by catalysing their decomposition into carbon dioxide, water and other small molecules [12–14]. However, the direct application of TiO_2 on polymers leads to photochemical decomposition of the polymer substrate [15]. The insertion of a DLC film between the polymer substrate and the TiO_2 film was hypothesised to prevent photochemical decomposition of the polymer and to prevent flavour adsorption/retention.

In this study, the DLC/TiO_2 multilayer films were prepared on PP using plasma-enhanced chemical vapour deposition (PE-CVD) and a sputtering technique. We hypothesised that the photocatalytic activity of the TiO_2 film and the superior gas barrier properties of the DLC film would synergistically protect food containers from flavour retention. The coated film was analysed by laser Raman spectroscopy. The gas barrier properties of the DLC film were investigated using gas permeation measurements. The prevention of

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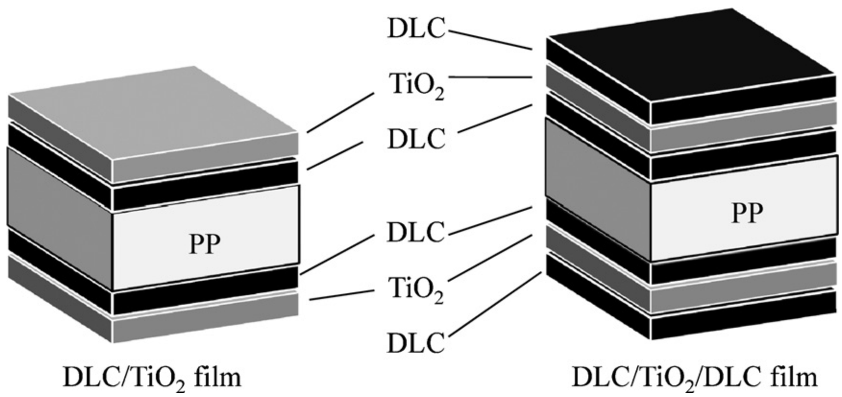

Fig. 1. Schematic drawing of the DLC/TiO_2 and $DLC/TiO_2/DLC$ films.

flavour retention and flavour removal effects of the film were evaluated using gas chromatography.

2. Materials and methods

2.1. Sample preparation

PP plates (Kyoeijushi Co. Ltd., Japan) (72 mm × 16 mm × 1 mm) were used as the substrate. In this experiment, two types of multilayer films were prepared, DLC/TiO_2 and $DLC/TiO_2/DLC$ films (Fig. 1). For the DLC coating, CH_4 (99.999%) was introduced into the vacuum chamber. Both sides of PP plate were coated with CH_4 plasma at 13 Pa and 250 W (power density: 7.4 mW/mm^2) using a PED-301 RF (13.56 MHz) PE-CVD system (Cannon Anelva Corp.). The temperature of the substrate remained below 100 °C during the deposition process. The film thickness was 0.1 μm.

After the DLC coating, a TiO_2 film was applied to the DLC-coated PP plate using an r.f. magnetron sputtering system. The sputter coating was carried out using an L-210HS-F system (Cannon Anelva Corp., Japan). The distance between the target and the substrate was approximately 60 mm, and the diameter of the Ti target (99.9%) was two inches. Both the target and the substrate were water cooled during the sputtering process. The sputtering chamber was evacuated to a pressure below 1×10^{-5} Pa using an oil-diffusion pump equipped with a liquid nitrogen trap. A mixture of argon gas (99.999%) and oxygen (99.99%) was introduced into the chamber using a mass flow controller. The $O_2/(Ar + O_2)$ flow ratio was kept at 0.1. Sputtering was carried out at a pressure of 5.0 Pa and a discharge power of 100 W. The TiO_2 film was deposited on the DLC-coated PP plate to form a 0.5 μm thick film. The total thickness of TiO_2 and DLC films was 0.6 μm.

In the case of preparation of the $DLC/TiO_2/DLC$ films, a third layer of DLC film was applied to the TiO_2 layer using the CVD system. The coating thickness was 0.05 μm.

The DLC, DLC/TiO_2, and $DLC/TiO_2/DLC$ films were characterised using Raman spectroscopy (inVia Reflex; Renishaw). The Raman spectroscopy was performed using the 532 nm line from an Ar laser, and the laser power was kept constant at 1 mW at the sample surface. Spectra were recorded from 1000 to 1800 cm^{-1}.

2.2. Gas permeation measurements

For the evaluation of the gas barrier properties of the DLC-coated PP, a gas permeation test was conducted. PP films with thicknesses of 30 and 50 μm were used. The DLC film was applied to the PP films (Futamura Chemical Co., Ltd.) using the PE-CVD system with a thickness of 0.1 μm. The amount of O_2 gas that permeated through the DLC-coated PP films was measured with gas-permeability measurement apparatus (Gasperm-100; Jusco). A sample of PP film hermetically partitioned the chamber into two sections, as seen in Fig. 2. The upper section was pressurised to P1 (5 atm), while the other was kept at P2 (1 atm). Gas molecules permeated through the PP film into the bottom section of the chamber, and the incremental volume change of the bottom chamber was measured. Each result was obtained from an average of three samples.

2.3. Prevention of flavour retention and flavour removal test

For both of the prevention of flavour retention and flavour removal tests, acetaldehyde, ethylene and turmeric were used as the evaluation gases. Ethylene is a growth hormone released by fruit and vegetables that promotes ripening. Turmeric is a major constituent of curry powder. In the prevention of flavour retention test, DLC-coated PP, TiO_2/DLC-coated PP and the non-coated PP plates (72 mm × 16 mm × 1 mm) were put into glass bottles (40 cm^3), and each gas was injected into the bottles. The bottles were stored in the dark at room temperature (25 °C). After 24 h, the concentration of each gas was measured using a gas chromatograph (GC-4000, GL Sciences, Inc., Japan) equipped with a flame ionisation detector. An 60 m × 0.25 mm i.d. (0.25 μm film thickness) InertCap WAX columns (GL Sciences, Inc., Japan) was used. In the direct injection method, the sampled gas (0.5 ml) was applied by split/splitless injection (250 °C) with the oven temperature held at 150 °C. Nitrogen at a flow rate of 1.0 mL min^{-1} was used as the carrier gas. The chromatogram of each gas was shown in Fig. 3. To measure the concentration of turmeric, the β-turmerone peak was used because turmeric is more than 80% β-turmerone [16]. The final result was obtained from an average of three samples.

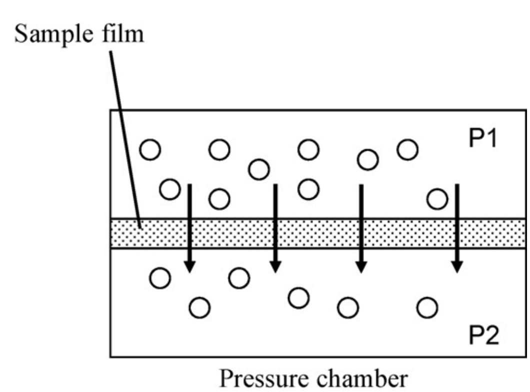

Fig. 2. Schematic drawing of the pressure chamber used in the gas permeation measurements.