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Enhancement of the gas barrier property of polypropylene by introducing plasma-treated silane coating with SiO_x-modified top-surface

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ABSTRACT

Polypropylene (PP) is a widely used packaging polymer due to its high transparency and high thermal durability. It is, however, also known to possess a relatively low gas barrier property. To solve the gas barrier problem of PP, a surface modification method by a silane coating was introduced: 3-aminopropyltrimethoxysilane (APTMS) was coated onto PP substrate (APTMS/PP) and treated by oxygen plasma. It was found that, after 60 s of the oxygen plasma treatment, the oxygen transmission rate (OTR) of the APTMS/PP was reduced by a factor of 15 as compared with that of pure PP. The free volume size analyzed by the monoenergetic positron beam significantly decreased at the surface of APTMS observed through the plasma-treatment time. The results indicated that the amount of the free volume of APTMS, through which the gas molecules permeated, was significantly decreased, eventually causing a considerable reduction in the OTR of the APTMS/PP. From the X-ray photoelectron spectroscopy (XPS), it was found that the plasma treatment of APTMS notably reduced both the carbon and the nitrogen atom fractions, simultaneously generating additional Si–O bonding to generate SiO_x-like structures at the surface. The formation of the SiO_x-like structure at the top surface of the APTMS/PP was considered as the major reason for the enhancement of the oxygen barrier property. In fact, the drastic decrease in the OTR was actually observed at a certain ratio of C/Si. The time of flight secondary ion mass spectroscopy (ToF-SIMS) also revealed that the side-chain scission from the APTMS molecules could generate amine and amide fragments, which could hinder the polymerization of the SiO_x. Thus the removal of the fragments would promote the efficient formation of SiO_x networks at the top surface of APTMS. Additional plasma treatment could introduce more polymerized SiO_x networks in APTMS, resulting in the smaller size of the free volume and hence the higher gas barrier property of APTMS/PP.

1. Introduction

Polypropylene (PP) is one of the most frequently used materials especially in the packaging industry because of its cost-effectiveness, high mechanical properties, and thermal durability. The improvement of the gas barrier properties of PP, however, has been greatly demanded, since PP has relatively low gas barrier properties compared with other polymer materials [1], allowing more gas molecules to penetrate into PP packaging, leading to the rapid oxygen degradation of the contents [2]. Polyethylene terephthalate (PET) is currently widely utilized to contain most beverage for its cost-effectiveness and high gas barrier properties, whereas PP is a highly prospective material for the bottling owing to its higher thermal durability (~120 °C) than the PET (~70 °C), which would realize the thermal processing and the sterilization of the content. Therefore the improvement of the gas barrier properties of PP will be indispensable.

Improving the gas barrier properties of PP has been actively investigated. Thin film coatings have been extensively applied to add high gas barrier properties to polymer substrates [3–6]. It was, however, difficult to improve the gas barrier properties of PP by simple coating methods because of the high surface roughness, the high chain mobility, and the high thermal expansion coefficient of PP. Thus additional treatments or precise processing conditions were necessary to obtain the high gas barrier of PP films [7–9]. Tashiro et al. introduced 3-aminopropyltrimethoxysilane (APTMS) as an interlayer between a diamond like carbon (DLC) film and a PP substrate to obtain DLC-coated PP (DLC/PP) with high gas barrier properties. APTMS is one of the silane coupling agents with both organic and inorganic groups in its molecule, which has been frequently used for the surface modification [10–18]. They insisted that, by sufficiently filling the gap of the thermal expansion between DLC and PP, the crack density

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of DLC could be effectively reduced, resulting in a great improvement of the gas barrier properties of the DLC/PP [19].

As for other silica-related materials, polydimethylsiloxane (PDMS), a widely used silicone, was also investigated. PDMS could be adequately converted into SiO_x structures after plasma treatment, which could reduce the free volume of the surface, resulting in an enhanced gas barrier property and selectivity of the membrane [20,21]. PDMS, however, is not appropriate for the coating material of polymer substrates due to its high viscosity, whereas APTMS is superior to PDMS in its low viscosity. Moreover, APTMS, when coated, has effective siloxane chains in its structure [19], which could be converted into SiO_x structures after plasma treatment, possibly resulting in the improvement of the gas barrier properties of PP.

In this work, we studied the effects of plasma treatment on APTMS coated on a PP substrate (APTMS/PP) in order to improve the gas barrier properties of PP. There would be two major methods that could improve the gas barrier properties of polymers by coating: one is the formation of the multilayer structure and the other is the densification of the coating layer [22]. Following the latter method, we introduced a dense SiO_x structure by the oxygen plasma process in this work. In fact, oxygen plasma was known as effective plasma species to obtain SiO_x structures on a siloxane membrane [20]. It was found that the experimental conditions of the plasma process indeed gave a profound influence on the resulting film composition [23]. The oxygen transmission rates of the APTMS/PP treated by oxygen plasma were measured. To analyze the structures of the APTMS after the plasma treatment, the depth profiles of the S parameters were studied using a monoenergetic positron beam, which was one of the most effective approaches to estimate the free volume size of the specimens [24–28]. The atomic fractions of the APTMS surface were analyzed by the X-ray photoelectron spectroscopy (XPS). The time of flight secondary ion mass spectroscopy (ToF-SIMS) was also applied to determine the states of the carbon (C) and the nitrogen (N) fractions at the APTMS surface by fragment analyses.

2. Experimental details

2.1. Sample preparations

2.1.1. Substrate

Polypropylene (PP) was used for the substrate, which was molded into a 0.1 mm-thick film by a compact sized heat press equipment (AH-2003, AS ONE Corp.) from PP pellets purchased from Sigma-Aldrich Corporation (isotactic polypropylene #427896). The molecular weight (Mw) and the number average molecular weight (Mn) of the PP pellets were 190,000 and 50,000, respectively. The melting point of PP was detected at 160.5 °C by the differential scanning calorimetry (DSC822e, Mettler Toledo Corporation) and the molding temperature was determined at 180 °C, high enough to melt the PP pellets. The 0.1 mm-thick PP film was cut into a square shape of 40 mm × 40 mm in length and width to prepare the measurement samples for the gas permeation testing, using the circular area of 500 mm^2 for the actual measurements.

2.1.2. Coating material

3-aminopropyltrimethoxysilane (APTMS) was used for the coating material as a precursor, and the molecular structure of the APTMS is presented in Fig. 1. The APTMS (KBM903) was purchased from Shinetsu Silicone Chemicals Corporation. In order to obtain the hydrophilic surface, the PP substrate was pre-treated by plasma for 30 s using the plasma ion bombardment apparatus (the vacuum-device incorporated PIB-10). 100 μL of the APTMS was coated on the substrate at 3000 rpm for 60 s using a spin coater (MS-A100, MIKASA Corp.). After coating, the APTMS precursor changed its structural phases from liquid to solid. This type of change was realized by the formation of Si–O–Si molecular networks through the condensation reactions between Si–OH silanol groups, generated by the hydrolysis of the methoxy groups surrounded by the water molecules in the air. The processing time was set to 24 h at ordinary temperatures (23 °C) according to our previous study [19].

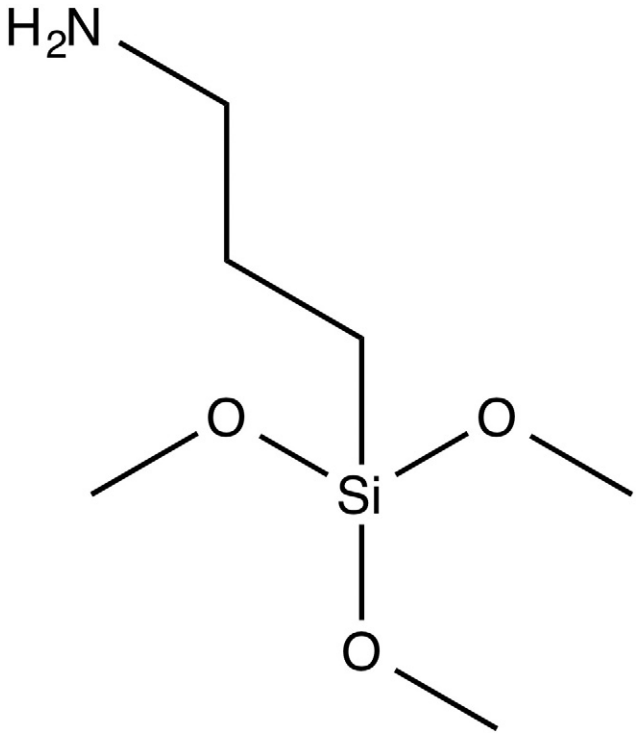

Fig. 1. Chemical structure of the APTMS.

2.1.3. Plasma treatment on APTMS coating

Plasma treatment on APTMS coated on a PP substrate (APTMS/PP) was performed by the radio frequency (RF) plasma equipment (Custom-built, Hirano Koh-on Co., Ltd.). The RF power ranged from 50 W to 200 W and the process gas was oxygen at the flow rate of 120 mL/min. The RF power and the treatment time were changed and optimized to analyze the effects of the plasma treatment on APTMS. In the process of plasma treatment, the vacuum condition was fixed at 13.3 Pa. The substrate temperature during the 60 s of the oxygen plasma treatment at a power of 200 W, which was the most powerful treatment in this study, was measured to be below 50 °C analyzed by a thermo-label.

2.2. Characterization techniques

2.2.1. Thickness of APTMS coating

The thickness of APTMS layer was measured by the scanning electron microscopy (SEM) images by observing the cross sectional views of the APTMS/PP specimens made by freeze fracturing after immersed in liquid nitrogen for 30 min. The fractured film was cut into a strip of 10 mm × 20 mm in length and width for the measurements. The thickness of the APTMS coating was estimated at 1.42 μm, analyzed by SEM micrographs of the freeze-fractured surface of APTMS/PP films presented in Fig. 2.

2.2.2. Gas permeability measurements

A gas permeability tester (OX-TRAN 2/21, MOCON, Inc.) was used to measure the oxygen transmission rate (OTR). OTR was measured in a chamber with the upper section filled with oxygen and the lower section with nitrogen. Some of the oxygen molecules could pass through the specimen, which could be detected at the lowest part of the apparatus by an oxygen detector. OTR could be measured as low as 0.01 cm^3/m^2/day/atm. The sample, in a square shape of 40 mm × 40 mm, covered all