Preparation of Oxygen Gas Barrier Polypropylene Films by Deposition of SiOx Films Plasma-Polymerized from Mixture of Tetramethoxysilane and Oxygen

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ABSTRACT: Silicon oxide (SiOx) film deposition on the surface of oriented poly(propylene) (OPP) films was done to form a new oxygen gas barrier material using plasma polymerization of the tetramethoxysilane (TMOS)/O_2 mixture. The SiOx film deposition on OPP films never improved oxygen gas barrier properties. The inefficacy of the SiOx deposition was due to poor adhesion at the interface between the deposited SiOx and OPP films and also to the formation of cracks in the deposited SiOx film. If prior to the SiOx film deposition surface modification of OPP films was done by a combination of the argon plasma treatment and TMOS coupling treatment, this contributed effectively to strong adhesion leading to success in the SiOx deposition on the OPP film surface, and then the oxygen gas barrier ability was improved. The oxygen permeation rate through the SiOx-deposited OPP film was decreased from 2230 to 37–52 cm^3/m^2/day/atm, which was comparable to that of poly(vinylidene chloride), 55 cm^3/m^2/day/atm at a film thickness of 11 μm. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 2389–2397, 2000

Key words: SiOx; PVDC; OPP; films

INTRODUCTION

Poly(vinylidene chloride) (PVDC) films and oriented polypropylene (OPP) films coated with PVDC (which are called K-coated films in the packaging film industry) show excellent oxygen gas and moisture barrier properties. The oxygen gas and moisture permeation coefficients for PVDC are 5.3×10^{-3} cm^3-cm/cm^2/s/cmHg at 30°C and 1.4 $cm^3 \cdot cm/cm^2$/s/cmHg at 90% RH (relative humidity) at 25°C, respectively, which are the lowest coefficients of all polymer films.[1] This advantage of PVDC films is applied practically in packaging materials for foods and green vegetables. Many people have a concern that PVDC films may be an origin of polluting our life-environment by acid rain and dioxins, because PVDC possesses 73 wt % of chlorine atoms. From this viewpoint, PVDC and K-coated films as packaging materials should be replaced by other materials containing no chlorine atoms. Silicon oxide (SiOx) may be a good substitute, as an oxygen gas barrier material, for PVDC. SiOx film is used already as a passivating film for protecting the surface of LSI (Large Scale Integrated Circuit) devices in microelectronics technology. Recently, the expanded application of SiOx film as a gas barrier material to food and pharmaceutical technologies, besides the microelectronics technology, became of interest. SiOx film deposition on polymeric films, such as polyester, polyethylene (PE), and polypropylene using the plasma chemical vapor deposition (CVD) technique, has been used for such applications.[2–5] We also have succeeded in

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SiOx deposition on biaxially-stretched polyester poly(ethylene terephthalate) (PET) film by plasma polymerization of tetramethoxysilane (TMOS).[6,7] The SiOx-deposited PET film shows an extremely low oxygen gas permeation rate of 0.10 cm^3/m^2/day/atm at a SiOx deposition of 100 nm thickness, compared with the original PET film of 44 cm^3/m^2/day/atm.[7] This comparison indicates that the deposited SiOx film acts as an excellent gas barrier material. Expansion of the SiOx deposition technique to OPP film could be expected as a new packaging material containing no chlorine, because OPP film is more popular as a packaging material than PET and PE films.

There are two key issues for flawless SiOx film deposition on OPP film surfaces. One is integrity of the deposited SiOx films. This may be related to the quality of the SiOx films such as chemical composition and structure. The other is adhesion at the interface between the SiOx and OPP films. In the SiOx/OPP film system, the adhesion rather than the integrity may be an important issue; but in the SiOx/PET film system, the adhesion may not be a serious issue. OPP film is different from PET film in physical properties. Glass temperature is −10°C for OPP and 70°C for PET, elastic modulus 0.69 and 2.76 GPa for OPP and PET, respectively, and thermal expansion coefficient is 6.5×10^{-5} K^{-1} for OPP and 1.5×10^{-5} K^{-1} for PET.[8,9] The most notable difference is in glass temperatures. The OPP film ($Tg = -10°C$) is in a rubbery state in the process of the SiOx deposition, and the PET film ($Tg = 70°C$) is in a glassy state. The SiOx deposition on the OPP film surface occurs on a thermally mobile surface. On the other hand, the SiOx deposition on the PET film surface occurs on a stable surface. From these differences of physical properties, it is probable that straight extension of the SiOx deposition technique, used for SiOx-deposited PET films, to OPP film surfaces will lead to some problems related to poor adhesion at the interface between the deposited SiOx and OPP films. To provide good adhesion, the OPP film surface should be modified.

In this study, we have made an extension of the SiOx deposition technique to OPP films. Prior to the SiOx deposition, OPP film surfaces were modified by a combination of argon plasma treatment and silane coupling reaction to provide strong adhesion at the interface between the deposited SiOx and the OPP films. How the modification of OPP film surfaces by a combination of argon plasma treatment and silane coupling reaction contributes to the adhesion at the interface between the deposited SiOx and OPP films will be discussed from the viewpoint of oxygen barrier properties.

EXPERIMENTAL

Materials

OPP film (Trade name U-10P#40, 40 μm thick) was kindly provided by Tosero Co. Ltd. and used as a substrate for SiOx deposition. The OPP film was washed with acetone in an ultrasonic washer prior to the SiOx deposition. TMOS, purchased from Petrarch Systems Co. (the purity was 99%), was used as starting material for the SiOx deposition without purification.

Plasma Polymerization Reactor Used for SiOx Deposition

A commercial vacuum deposition apparatus (Ulvac Co., Japan; model EBH6), which had a bell-jar chamber (400 mm diameter, 590 mm high) and a vacuum system with a combination of a rotary pump (320 L/min) and a diffusion pump (550 L/s), was remodeled into a special reactor for the SiOx film deposition. A diode planar electrode made of stainless steel for glow discharge, inlets of the TMOS vapor and oxygen or argon gas, a rolling machine for reeling the OPP film (variable reeling rates of 33–994 mm/min), a thickness monitor (Ulvac Co., Japan; model CRTM-1000) for monitoring the SiOx deposition rate, and a pressure gauge were installed in the bell-jar chamber. An electrical energy input system for initiating a glow discharge (Samuco Co., Japan; model RFG-200), and a flow rate controlling system for the TMOS vapor, and oxygen and argon gases were attached to the reactor. The diode electrode contained a circular electrode (electrode A) with a dimension of 380 mm diameter and a rectangular electrode (electrode B) with a dimension of 50 mm wide and 100 mm long. The gap between the electrodes was 60 mm. The electrode A was grounded, and the electrode B was connected to an electrical power generator at 13.56 MHz (Samuco Co., Japan; model RFG-200). The OPP film was set up midway between the electrodes, and was reeled by the rolling machine during the SiOx deposition. The gas flow rate controlling sys-

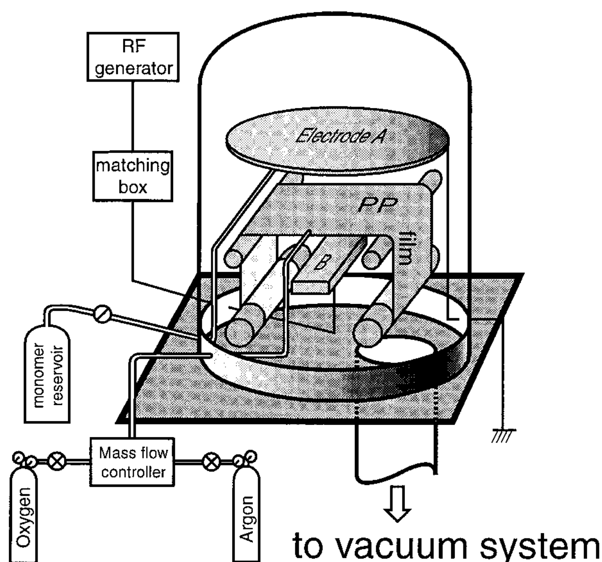

Figure 1 Schematic diagram of plasma reactor.

tem was a metering needle valve (Nupro Co., model BM-4BMG) for the TMOS vapor, and was a mass flow controller (Estec Co., Japan; model SEC-400 MARK3) for oxygen and argon gases. A schematic diagram of the plasma reactor used in this study is shown in Figure 1.

SiOx Deposition from Plasma Polymerization of TMOS/O_2 Mixtures

The OPP film (110 mm wide) was set up midway between the electrodes A and B was set up on reels of the rolling machine. TMOS was poured in a reservoir, and air dissolved in the TMOS was removed by a repeated freezing-fusion procedure. The reservoir was kept in a temperature-controlled oven at 60°C to increase the vapor pressure of TMOS.

Air in the reaction chamber was displaced with argon, and the reaction chamber was evacuated to approximately 0.13 Pa. Afterwards, TMOS vapor, whose flow rate was adjusted to a constant flow rate of 6 cm^3/min by the metering valve, and oxygen gas, which was adjusted to 9 cm^3/min by the mass flow controller, were blown off from the inlets to the reaction chamber. The plasma polymerization of the TMOS/O_2 mixtures was performed at a system pressure of 39.9 Pa at rf powers of 60 W. The deposition rate of SiOx films was determined from a reading of the thickness monitor (Ulvac Co., Japan; model CRTM-1000). After the SiOx deposition, the reaction chamber was evacuated to less than 0.13 Pa for 30 min, and then argon gas was introduced into the reaction chamber up to atmospheric pressure. The OPP film was taken from the reaction chamber, and served as specimens for X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and oxygen permeation rate measurement.

Silane-Coupling Treatment of OPP Film

The OPP film was treated with the Ar plasma at a system pressure of 33.9 Pa at an rf power of 60 W for 3 min using the same plasma polymerization reactor for SiOx deposition, and then exposed to air to form oxygen functional groups on the film surface. The Ar-treated OPP film was immersed in a methanol solution of TMOS (1–10 wt %) at room temperature for 5 min. The pH of the solution was adjusted to 4.5–5.5 with addition of acetic acid. The OPP film was picked up from the solution, and heated at 50°C for 2 hours in a temperature-controlled oven (Yamato Science Co., Japan; model DN43H) to accomplish the silane-coupling reactions with the oxygen functional groups on the film surface. Finally, the silane-coupled OPP film was washed with methanol to remove unreacted TMOS from the film surface using an ultrasonic washer. The OPP film was furnished as an OPP film substrate for the SiOx deposition experiment. In this study the OPP film was treated with a combination of the Ar plasma and silane-coupling reactions to give the silane-coupled OPP film.

XPS Spectra

XPS spectra were obtained on a Shimadzu ESCA K1 using a nonmonochromatic MgKα photon source. The anode voltage was 12 kV, the anode current was 20 mA, and the background pressure in the analytical chamber was 1.5×10^{-6} Pa. The spectra were not smoothed and were decomposed by fitting a Gaussian-Lorentzian mixture function (80 : 20 mixture ratio) to an experimental curve using a nonlinear, least-squares curve-fitting program, ESCAPAC, supplied by Shimadzu. The sensitivity factors (S) for the core levels were $S(C_{1s}) = 1.00$, $S(Si_{2p}) = 0.87$, and $S(O_{1s}) = 2.85$.

Oxygen Permeation Rate through SiOx-Deposited OPP Film

A gas barrier tester (Mocon Co., model OX-TRAN 2/20) was used for measuring the oxygen perme-

ation rate (in cm^3/m^2/day/atm) through SiOx-deposited OPP films (area of 78 mm diameter) at 30°C and at a relative humidity of 70% RH. Three or five specimens were used for the measurement, and the oxygen permeation rate was determined from an average of the measurements within an experimental error of 0.05 cm^3/m^2/day/atm. From the oxygen permeation rate, the oxygen permeability coefficient for the deposited SiOx film in (STP)cm^3-cm/cm^2/s/cmHg was estimated under the assumptions of the two-layer model.

The SiOx-deposited OPP film is a laminated structure consisting of the OPP film layer and SiOx film layer. For the two-layer model, the following eqs. (1) and (2) are given[10]:

$$d = d_1 + d_2 \tag{1}$$

$$\frac{d}{P} = \frac{d_1}{P_1} + \frac{d_2}{P_2} \tag{2}$$

where the subscripts 1 and 2 mean the original OPP film layer and the SiOx film layer deposited on the OPP film surface, respectively. P and d represent the oxygen permeability coefficient and the film thickness, respectively. d_1 and d_2 are 40 μm and 100 nm, respectively. Eq. (2) is modified into eq. (3).

$$\frac{1}{P} = \frac{1}{P_1} + \frac{d_2}{d_1 + d_2}\frac{1}{P_2} \tag{3}$$

The oxygen permeability coefficient, P_2, for the SiOx film in the SiOx-deposited OPP film can be calculated from eq. (3).

RESULTS AND DISCUSSION

SiOx-Deposition on OPP Film Surface and Oxygen Permeation Rate

Our previous study has reported that SiOx films that were deposited from the plasma polymerization of $TMOS/O_2$ mixture on PET films showed great improvement in oxygen barrier properties of the PET film. The oxygen permeation rate was decreased from 44 to 0.10 cm^3/m^2/day/atm by the SiOx deposition at 100 nm thickness. The oxygen permeation coefficient for the deposited SiOx film alone was calculated from data of the oxygen permeation rate for the SiOx-deposited PET film and the PET film using eq. (3). The oxygen permeation coefficient for the SiOx film alone was 1.4×10^{-17} $cm^3 \cdot cm/cm^2$/s/cmHg which was much lower than that for the PET film (2.5×10^{-12} $cm^3 \cdot cm/cm^2$/s/cmHg). This indicates that the SiOx film is a good material for an oxygen gas barrier. From this point of view, we have carried out the SiOx deposition on the OPP film surfaces under the same operational conditions for plasma polymerization as those in the case of the SiOx deposition on the PET film surface, using the same plasma polymerization reactor. The operational conditions were a $TMOS/O_2$ mixture with 60 mol % O_2 as a starting material for the SiOx deposition, a flow rate of the mixture of 15 cm^3/min, a system pressure of 33.9 Pa during the plasma polymerization, and an rf power of 60 W to maintain a glow discharge. The SiOx film at 100 nm thickness was deposited on the OPP film surface, and the oxygen permeation rate through the SiOx-deposited OPP film was elucidated (Table I). There was no significant decrease in oxygen permeation rate even by the SiOx deposition on the OPP film. The oxygen permeation rate for the SiOx-deposited OPP film exceeded a maximum capacity (2000 cm^3/m^2/day/atm) of the permeation rate measurable with a Mocon equipment.

Why was the SiOx deposition on the OPP film surface not able to improve oxygen gas barrier properties, whereas the SiOx deposition was able to ameliorate barrier properties of the PET film? Were there any differences between SiOx films deposited on the OPP and PET film surfaces? The large difference was not due to chemical composition of the deposited SiOx films but to the topological structure of the deposited SiOx films. Table II compares the SiOx films deposited on the OPP and PET film surfaces in atomic composition as a function of oxygen concentration in the $TMOS/O_2$ mixtures that were used as starting materials for the SiOx deposition. The atomic composition for the deposited SiOx films was determined by XPS. As shown in Table II, there is little difference in C/Si and O/Si atom ratios between the SiOx films deposited on the OPP and PET film surfaces by the plasma polymerization of the $TMOS/O_2$ mixture (60 mol % O_2). We conclude that the SiOx films deposited on the OPP and PET film surfaces resemble each other in chemical composition. Figure 2 shows typical SEM pictures of the SiOx films deposited on the OPP and PET film surfaces. The SiOx film deposited on the OPP film surface shows many cracks

Table I Oxygen Permeation through SiOx-Deposited OPP and PET Films

			SiOx-Deposited Polymer Film		SiOx Film
Polymer Films	Silane-Coupling Treatment	SiOx Deposition (100 nm thickness)	Oxygen Permeation Rate (cm^3/m^2/day/atm)	Oxygen Permeation Coefficient (cm^3-cm/cm^2/s/cmHg)	Oxygen Permeation Coefficient (cm^3-cm/cm^2/s/cmHg)
OPP	No	No	> 2000 (2230)[a]	1.2×10^{-10}	—
OPP	No	Yes	> 2000	—	—
OPP	Yes (5%)[b]	Yes	37	2.3×10^{-12}	5.8×10^{-16}
OPP	Yes (7%)[b]	Yes	52	3.2×10^{-12}	8.1×10^{-16}
PET	No	No	44	2.7×10^{-12}	—
PET	No	Yes	0.10	6.1×10^{-15}	1.4×10^{-17}

[a] Estimated from temperature dependence.
[b] TMOS concentration in TMOS coupling treatment.

that run parallel to the neighboring cracks. On the other hand, the SiOx film deposited on the PET film surface shows no cracks. We believe that the lack of a contribution of the SiOx deposition on the OPP film surface to improving the barrier properties may be closely related to the formation of cracks. Furthermore, poor adhesion between the deposited SiOx film and OPP film surfaces also may be an important factor for poor barrier properties. Such assumption gives us a story as to why the SiOx deposition on the OPP film surface was not able to improve oxygen gas barrier properties. When oxygen gases contact with the SiOx-deposited OPP film, immediately the oxygen gases will infiltrate from the cracks on the SiOx film surface into the bottom of the cracks. The oxygen gases at the bottom of the cracks will start to diffuse in every direction at the interface between the deposited SiOx film and OPP film, if the interface is not in a dense state but is sparse. As a result, all of the OPP film surface will be exposed to oxygen gas, and the oxygen will start to permeate all the OPP film surface into the inside of the film. This assumption explains why the deposited SiOx film never contributed to oxygen gas barrier properties of the OPP film. Even if the deposited SiOx film is an excellent material for oxygen gas barrier, the SiOx-deposited OPP film will not show high barrier properties as long as cracks are generated in the SiOx film and the adhesion between the SiOx film and the OPP film is sparse. Therefore, an important factor if the deposited SiOx film is to play a good role in improving gas barrier properties of OPP film is either to generate no cracks in the deposited SiOx film or to have strong adhesion between the SiOx film and the OPP film surface. Strong adhesion means that interface between the SiOx film and the OPP film surface is not only adhered mechanically but also has no cavities where oxygen gas

Table II Atomic Composition of SiOx Films Deposited on OPP and PET Film Surfaces

Plasma Polymerization Conditions		C/Si and O/Si Atom Ratios for SiOx Films			
		Deposited on OPP Film Surface		Deposited on PET Film Surface	
Rf Power (W)	O_2 Concentration in TMOS/O_2 Mixture (mol %)	C/Si Atom Ratio	O/Si Atom Ratio	C/Si Atom Ratio	O/Si Atom Ratio
60	0	1.20	1.8	1.50	1.8
60	20	0.42	1.5	0.39	1.4
60	40	0.39	1.3	0.42	1.4
60	60	0.51	1.4	0.49	1.4

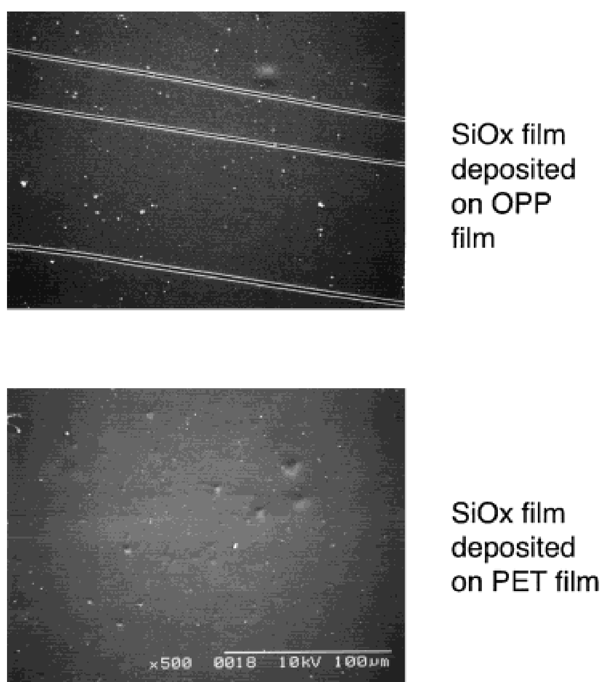

Figure 2 SEM pictures of SiOx films deposited on OPP and PET film surfaces.

travels easily. In the next section, we have investigated how to provide strong adhesion between the SiOx film and the OPP film surface.

Surface Modification of OPP Film by Silane Coupling Reactions and Oxygen Permeation Rate

To provide strong adhesion between the SiOx film and the OPP film surface, we made a trial of surface modification of the OPP film before the SiOx deposition. The modification was the introduction of O—Si—O linkages bonded chemically with OPP polymer chains on the film surface. We believed that the O—Si—O linkage would act as a kind of adhesive between the OPP film surface and deposited SiOx film, and that the interface between the SiOx film and the OPP film could have no cavities. The surface modification was carried out in two steps, the formation hydroxyl groups on OPP film surface by argon plasma treatment and the formation of O—Si—O linkages by coupling reactions between the hydroxyl groups and TMOS. Practically, the OPP film surfaces were exposed to argon plasma at a rf power of 60 W for 3 min. Subsequently, the argon-plasma-treated OPP film was immersed in a methanol solution of TMOS at room temperature for 5 min, and then heated at 50°C for 2 hours to accomplish coupling reactions between TMOS and hydroxyl groups on the OPP film surface. Finally, the TMOS-coupled OPP film surface was washed with methanol to remove unreacted TMOS from the surface using an ultrasonic washer. The OPP film surface, modified by a combination of the argon plasma treatment and the TMOS coupling treatment, was analyzed with XPS.

Table III shows the atomic composition (O/C and Si/C atom ratios) for the OPP film surfaces modified by a combination of the argon plasma treatment and the TMOS coupling treatment. The O/C atom ratio, as shown in Table III, was increased from < 0.03 to 0.13 by the argon plasma treatment, indicating that some oxygen functional groups were formed on the OPP film surface. The XPS (C_{1s}) spectrum showed details of the oxygen functional groups formed on the OPP film surface by the argon plasma treatment (Fig. 3). The C_{1s} spectrum was decomposed into three components (CH_2 groups at 285.0 eV, C—O groups at 286.5 eV, and C═O groups at 288.0 eV)[11] which are illustrated as dotted lines in Figure 3. The relative concentration of the three components was estimated from the relative area of the components (Table III). Table III shows that

Table III Atomic Composition of OPP Film Surfaces Modified by a Combination of Argon-Plasma Treatment and TMOS Coupling Treatment

Argon Plasma Treatment	TMOS Coupling Treatment	Atomic Composition of OPP Film Surface		C_{1s} Components of OPP Film Surface (%)		
		O/C Atom Ratio	Si/C Atom Ratio	CH_2	C—O	C═O
No	No	< 0.03	0.0	96	4	0
Yes	No	0.13	0.0	84	12	4
Yes	Yes	0.08	0.03	91	8	1

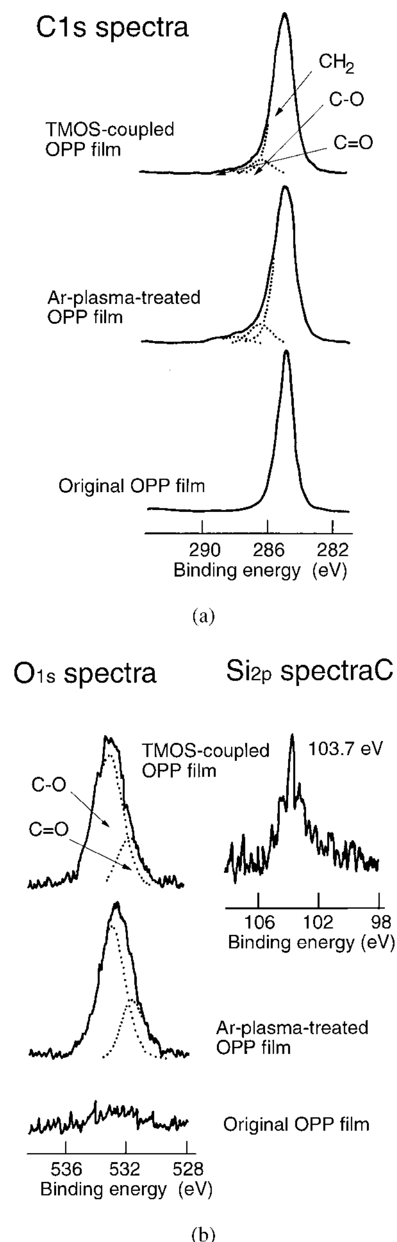

Figure 3 C1s spectra of argon-plasma-treated OPP film and TMOS-coupled OPP film.

C—O and C═O groups were formed as oxygen functional groups by the argon plasma treatment, and that their concentration reached 12 and 4% of the total carbon atoms on the OPP film surface, respectively. It is clear from the XPS spectrum that the argon-plasma-treated OPP film surface possesses hydroxyl groups that could react with TMOS. We believe that the formation of oxygen functional groups such as C—O and C═O groups resulted from following two processes. In the first process, carbon radicals were formed on the OPP film surface by the collision with argon ions and electrons in the argon plasma. The carbon radicals were oxidized into peroxides when the OPP film was taken out from the plasma reactor into air after the argon plasma treatment was finished, and then the peroxides were modified into C—O and C═O groups.

The OPP film surface modified by the TMOS coupling treatment showed a Si_{2p} core level spectrum at 103.7 eV due to Si—O groups.[11] The Si_{2p} spectrum is not shown here because of brevity. The Si/C atom ratio for the TMOS-coupled OPP film surface was 0.03 and the O/C atom ratio decreased from 0.13 to 0.08 (Table III). The C_{1s} spectrum also showed changes by the TMOS coupling treatment (Fig. 3). The C_{1s} spectrum for the TMOS-coupled OPP film surface was decomposed into three components, CH_2 groups at 285.0 eV, C—O groups at 286.4 eV, and C═O groups at 288.2 eV (dotted lines in Fig. 3).[11] The relative concentration of C—O groups was decreased from 12 to 8% by the TMOS coupling treatment (Table III). From these changes in the XPS spectrum, we conclude that coupling reactions between the argon-plasma-treated OPP film surface and TMOS occurred and O—Si—O linkages were formed on the OPP film surface.

On the OPP film surfaces modified by the TMOS coupling treatment, SiOx films were deposited at 100 nm thickness by the plasma polymerization of TMOS. The oxygen permeation rate through the composite films of the TMOS-modified and SiOx-deposited OPP films was evaluated (Table I) as a function of the TMOS concentration in the TMOS coupling treatment. A remarkable decrease in the oxygen permeation rate, as shown in Table I, was accomplished by the TMOS coupling treatment. The oxygen permeation rate was 37 and 52 cm^3/m^2/day/atm when the OPP film surfaces were modified by the TMOS treatment (at TMOS concentrations of 5 and 7 wt %). As described in a previous section, when the OPP film surface was not modified by the TMOS coupling treatment, there was never a decrease in the oxygen permeation rate by the SiOx deposition. The oxygen permeation rate was more than 2000 cm^3/m^2/day/atm. Therefore, it is worth noting that the TMOS coupling treatment is very effective in decreasing oxygen permeation rate by the SiOx deposition.

To analyze why the TMOS coupling treatment was effective in the SiOx deposition on the OPP

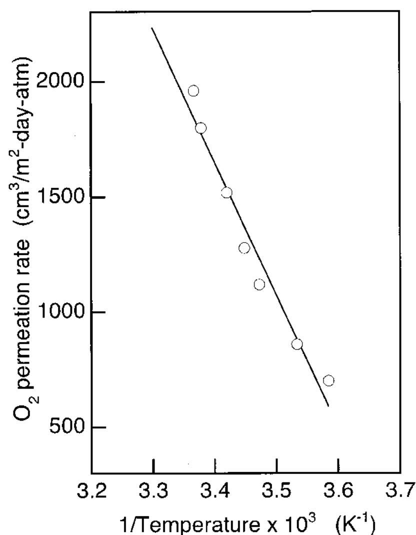

Figure 4 Oxygen permeation rate through OPP film as a function of reciprocal absolute temperature.

film surface, we estimated the oxygen permeation coefficient for the deposited SiOx film itself. The oxygen permeation coefficient for the SiOx film itself in the SiOx/OPP composite film can be estimated by eq. (3) if the oxygen permeation coefficient for the OPP film is known already. The direct measurement of the oxygen permeation rate for the OPP film (40 μm thickness) with a Mocon gas barrier tester, however, was impossible because the permeation rate exceeded the maximum capacity of the tester (2000 cm^3/m^2/day/atm). Instead of the direct measurement, we made estimation of the oxygen permeation rate at 30°C from temperature dependence of the oxygen permeation rate. Figure 4 shows temperature dependence of the oxygen permeation rate through the OPP film in the temperature range of 6 to 24°C. The oxygen permeation rate, as shown in Figure 4, is a linear relationship against the reciprocal of absolute temperature. From extrapolation of the linear relationship, we estimated the oxygen permeation rate through the OPP film at 30°C (1/Temperature = 0.3 K^{-1}) to be 2230 cm^3/m^2/day/atm. Using an oxygen permeation rate of 2230 cm^3/m^2/day/atm, the oxygen permeation coefficient for the OPP film at 30°C was calculated to be 12×10^{-10} cm^3-cm/cm^2/s/cmHg. Furthermore, the oxygen permeation coefficient for the deposited SiOx films also was calculated using eq. (3). Results of the calculation are tabulated in Table I. The oxygen permeation coefficient calculated for the SiOx film itself in the SiOx/OPP composite film is $5.8-8.1 \times 10^{-16}$ cm^3-cm/cm^2/s/cmHg, which is not greatly different from that for the SiOx film deposited on the PET film surface. The oxygen permeation coefficient for the SiOx film deposited on the PET film is 1.4×10^{-17} cm^3-cm/cm^2/s/cmHg. This difference may be due to cracks in the deposited SiOx film. SEM observation showed that there still remained many cracks in the SiOx films deposited on the OPP film surface even when the OPP film was modified by the TMOS coupling treatment before the SiOx deposition.

The oxygen permeation rate (37 and 52 cm^3/m^2/day/atm) for the SiOx-deposited OPP films is comparable to that of PVDC, 55 cm^3/m^2/day/atm at a film thickness of 11 μm,[12] which is widely used as wrapping films for foods and green vegetables. Therefore, the SiOx-deposited OPP film prepared in this study may be a possible substitute for PVDC film in the viewpoint of oxygen gas barrier properties.

CONCLUSION

Results of effects of the surface modification of OPP film, by a combination of argon plasma treatment and silane coupling reactions on SiOx film deposition from plasma polymerization of the TMOS/O_2 mixture, are as follows.

1. The SiOx film deposition on OPP films never improves oxygen gas barrier properties of the OPP films. The inefficacy of the SiOx deposition is due to poor adhesion at the interface between the SiOx and the OPP films and the formation of cracks in the deposited SiOx film.
2. If prior to the SiOx film deposition, the surface of OPP films is modified by a combination of the argon plasma treatment and TMOS coupling treatment, this contributes effectively to improvement of the oxygen gas barrier properties. The oxygen permeation rate through the SiOx-deposited OPP films is decreased from 2230 to 37–52 cm^3/m^2/day/atm, which is comparable to that of PVDC, 55 cm^3/m^2/day/atm at a film thickness of 11 μm.

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