Preparation of silica/poly(vinyl alcohol) organic–inorganic hybrid gas barrier films via sol–gel method by microwave irradiation

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Silica/poly(vinyl alcohol) organic–inorganic hybrid gas barrier layers on PP were prepared by the sol–gel method by microwave irradiation. The effects of microwave irradiation on the oxygen barrier property and surface hardness of the films were investigated. From IR measurement, no difference was observed in the spectra of the film prepared by microwave irradiation and by conventional heating. The oxygen barrier property of the film prepared by microwave irradiation was better than that of the film prepared by conventional heating. The results indicated that microwave irradiation was effective for synthesizing the organic–inorganic hybrid gas barrier layers in a short time. The hybrid barrier film obtained by microwave irradiation exhibits oxygen barrier properties.

Key-words : Organic–inorganic hybrid, Gas barrier film, Sol–gel method, Microwave irradiation

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The gas barrier property of plastic films is an important factor that decides their application as packaging materials. Poly(vinylidene chloride) (PVDC) films and plastic films coated with PVDC show high oxygen and water vapour barrier properties. Therefore, PVDC has been utilized in packaging materials. Recently, the possibility of PVDC being an environmental pollutant releasing dioxins due to the presence of 73 mass% of chlorine atoms has become a topic of concern for several individuals. From this view point, PVDC should be replaced by other non-chlorine-containing materials. Glass and ceramics are potential candidates for gas barrier materials instead of PVDC. The deposition of SiO_x and Al_2O_3 films on polymer films using vapour deposition and chemical vapour deposition methods has been used for gas barrier applications in food and pharmaceutical technologies.[1)] Clay/polymer composites[2),3)] and organic–inorganic hybrids[4),5)] were also used for such applications. We have also succeeded in depositing silica/poly(vinyl alcohol) (PVA) organic–inorganic hybrid gas barrier films on poly(ethylene terephthalate) by the sol–gel method.[5)] The prepared films exhibited gas barrier ability; however, the long heating time of this technique restricted its practical applicability.

Recently, microwave irradiation has attracted considerable attention as a heating method in the laboratory for the synthesis of organic,[6)] polymer,[7)] and inorganic materials.[8)] Unlike the conventional heating method, microwave irradiation offers a clean, energy-effective, fast, and convenient heating process, which results in a higher yield and shorter reaction time.

In the present paper, we wish to report the preparation of silica/PVA organic–inorganic hybrid gas barrier layers on polypropylene (PP) films via the sol–gel method by microwave irradiation. We investigated the effect of microwave irradiation on the oxygen barrier property and surface hardness of the films.

Silica/PVA organic–inorganic hybrid gas barrier films were prepared using the sol–gel method. The composition of the sol was tetraethoxysilane (TEOS, $Si(OC_2H_5)_4$):methyltriethoxysilane (MTEOS, $CH_3Si(OC_2H_5)_3$):H_2O:HNO_3 = 0.75:0.25:28:0.01 in terms of the molar ratios. PVA was added to the precursor solution in a concentration of 10 mass% the alkoxides TEOS and MTEOS. Commercially available reagent grade chemicals were used. The mixture was stirred overnight to obtain a homogeneous sol. PP films with a thickness of 70 μm were used as the supports. The support was spun at a rate of 3000 rpm for 30 s, and 0.5 cc of the sol was dropped on the support. Following the spin-coating procedure, two sets of films have been treated for promotion of a solvent evaporation, hydrolysis and condensation as follows: one set was exposed to microwave irradiation (2.45 GHz) at 500 W for 10 min (sample ID: SiO_2–PVA–MW), and the second set was heated at 373 K for 12 h in air at heating and cooling rates of 0.5 K/min (sample ID: SiO_2–PVA–HT). Both films were transparent and the thicknesses of coating layers were about 2 μm, which were measured by a contact-type film thickness meter (Hakattaro G, Seiko EM Co., Ltd.). Oxygen permeation through the films at 313 K was measured by a variable pressure method[9)] using a gas permeation measurement apparatus (K–315N–01, Tsukubarikaseiki Co., Ltd.). The pencil hardness test (load: 50 g) was conducted to determine the hardness of the films.

The structures of the organic–inorganic gas barrier films were determined using a Fourier-transform infrared spectrometer (FTIR) (FT/IR–4100, JASCO Co.). The IR spectra of SiO_2–PVA–MW and SiO_2–PVA–HT are presented in **Fig. 1**. Both the films show a typical band at ~960 cm^{-1} associated with the stretching mode of Si–OH along with the characteristic bands related to the Si–O–Si bond (~1200, 1050, 800 cm^{-1}), which confirm the presence of the Si–O–Si network in the films.[10),11)] The absorption band near 2900 cm^{-1} is assigned to the C–H stretching vibration of PVA. The strong and broad band at ~3700–3000 cm^{-1} is assigned to the hydroxyl groups of Si–OH and PVA.[11)] Other characteristic bands originating from PVA and CH_3–Si were also observed. The IR spectrum of the sol is also indicated in Fig. 1. The strong absorption bands at ~3400 and ~1700 cm^{-1} corresponding to water (solvent) were observed. These absorption bands decreased after microwave irradiation and conventional heating treatment. And the broad strong band around 1100 cm^{-1} originating from alkoxides (TEOS and MTEOS) was also observed. This band changed to the Si–O–Si bond after applying

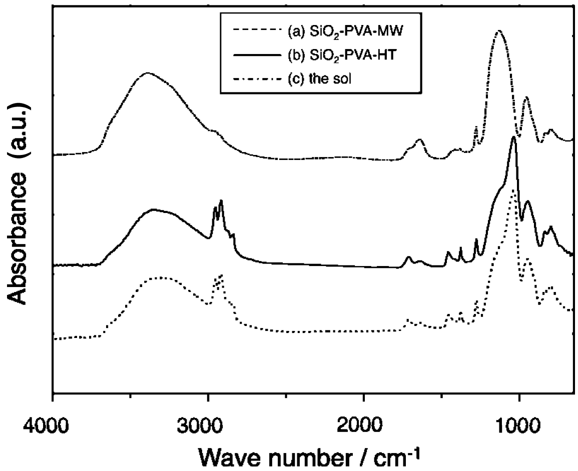

Fig. 1. IR spectra of (a) SiO_2–PVA–MW, (b) SiO_2–PVA–HT and (c) the sol.

microwave irradiation and conventional heating. From these absorption bands changes, microwave irradiation thought to promote a solvent evaporation, hydrolysis and condensation in the same manner as conventional heating. Furthermore, no difference was observed in the spectra of SiO_2–PVA–MW (microwave irradiation) and SiO_2–PVA–HT (conventional heating). This result indicates that microwave irradiation is more efficient in shortening the reaction time than the conventional heating technique.

Optical micrographs of the surface morphologies for the films are shown in **Fig. 2**. The SiO_2–PVA–MW film had no cracks and exhibited a smooth surface (Fig. 2 (a)). Although the SiO_2–PVA–HT film also had a smooth surface, some cracks were observed (Fig. 2 (b)). This difference between the two films was caused by the characteristics of the heating technique. Microwave heating is more homogeneous than conventional heating wherein the heat must diffuse from the surface to the interior of the materials. Therefore, no cracking of the film has been observed in the case of heating by microwave irradiation; this could be due to homogeneous heating and slow evaporation of water, which is the solvent used in the present case.

Table 1 shows the properties of the prepared organic–inorganic gas barrier films and the PP film. The oxygen permeances of SiO_2–PVA–HT and SiO_2–PVA–MW were 4.7×10^{-12} and 2.8×10^{-12} mol·m^{-2}·s^{-1}·Pa^{-1}, respectively, while that of the PP film was 1.7×10^{-11} mol·m^{-2}·s^{-1}·Pa^{-1}. These values reveal that the coating of SiO_2–PVA is effective in suppressing the oxygen permeation. The low permeance can be explained by the formation of a dense structure and lesser number of defects. In Table 1, it can be seen that microwave irradiation results in lower oxygen permeance than the conventional heat treatment. This result can be attributed to a decrease in the cracks on the coating layer, as shown in Fig. 2, which prevents the oxygen molecules from permeating through the coating layer. The oxygen permeability coefficients, calculated from the permeance and the thickness, of SiO_2–PVA–HT and SiO_2–PVA–MW were 9.4×10^{-18} and 5.6×10^{-18} mol·m·m^{-2}·s^{-1}·Pa^{-1}, respectively. These values were same order of that of PVDC (1.7×10^{-18} mol·m·m^{-2}·s^{-1}·Pa^{-1} at 298 K).[12] Thus the hybrid coating layer could be applicable for oxygen barrier. The pencil hardnesses of SiO_2–PVA–HT and SiO_2–PVA–MW were F and HB, respectively. SiO_2–PVA–HT is slightly harder than SiO_2–PVA–MW because the conventional heating technique heats up the surfaces more effectively.

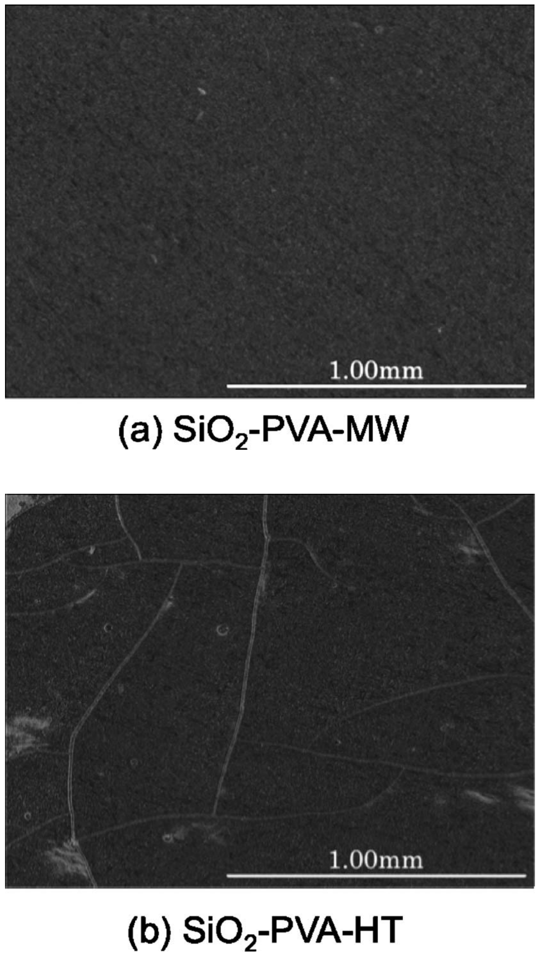

Fig. 2. Optical micrographs showing the surface morphology of (a) SiO_2–PVA–MW and (b) SiO_2–PVA–HT.

Table 1. Oxygen Permeance and Pencil Hardness of PP and the Prepared Films

Sample	Oxygen permeance (mol·m^{-2}·s^{-1}·Pa^{-1})	Pencil hardness
PP	1.7×10^{-11}	6B
SiO_2–PVA–HT	4.7×10^{-12}	F
SiO_2–PVA–MW	2.8×10^{-12}	HB

In conclusion, silica/poly(vinyl alcohol) organic–inorganic hybrid gas barrier layers on PP were prepared by the sol–gel method by microwave irradiation. The results indicated that microwave irradiation was effective for synthesizing the organic–inorganic hybrid gas barrier layers in a short time. The hybrid barrier film obtained by microwave irradiation exhibits oxygen barrier properties.

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