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Preparation and barrier property of poly(vinyl alcohol)/SiO$_2$ hybrid coating films

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Abstract−Using sol-gel method, poly(vinyl alcohol)/SiO$_2$ hybrid coating materials with an improved gas barrier property could be produced. Phase compatibility between organic PVA segments and inorganic silicate network in the hybrid was evaluated by analyzing FT-IR spectra and investigating the crystallization behavior in terms of X-ray diffraction patterns for the hybrid gels. For the preparation of coating film with barrier property, the biaxially oriented polypropylene (BOPP) substrate was coated with the hybrid sols by a spin coating method. Morphological analysis for the fractured surface of the hybrid gel and the surface of the coated film was performed not only to examine the microstructure of the hybrid, but also to propose evidence for the oxygen permeation behavior through the coated film. It was revealed that an optimum amount of inorganic silicate precursor, TEOS, should be used to obtain high barrier PVA/SiO$_2$ hybrid coating materials with enhanced micro-phase morphology and optical transparency. This homogeneous morphology densified with nano-structured silicate, obtained at optimal conditions, was found to result in a significant increase in the oxygen barrier property of film coated with PVA/SiO$_2$ hybrid by about 50 times relative to the pure BOPP substrate. In addition, the effect of pretreatments of the BOPP substrate surface on the barrier property was also examined.

Key words: Sol-gel, Barrier Property, PVA/SiO$_2$ Hybrid, Coating Film

INTRODUCTION

The sol-gel process has been recognized as a fascinating methodology because it offers the possibility of combination of organic component with inorganic ceramic materials at molecular scale to produce organic-inorganic hybrid nano materials with high performance [1-4]. In particular, the organic-inorganic hybrid materials, which are obtained via sol-gel method, have been mainly used as coating materials on the polymeric substrate in a wide variety of industrial areas. These coating materials provide various surface characteristics such as abrasion resistance, antistatic, antiadhesive, antifogging properties, and so on through chemical functionalization [5-7]. In addition, the barrier properties of the hybrid-coated films can be improved remarkably due to the incorporated inorganic component. Therefore, the researches of hybrid coating materials with high barrier property have been performed through sol-gel method using silicon alkoxide as an inorganic precursor, and organic polymer or organically modified trialkoxysilanes as the organic components [8-10]. The organic polymers such as poly(vinyl alcohol), poly(vinylpyrrolidone), and poly(vinyl acetate) have been incorporated into the inorganic silicate network not only to prevent the crack formation of the coating layer during gelling process, but also to endow the function of organic polymer itself [11,12].

The interfacial interaction between organic and inorganic phases has been known as one of the significant factors affecting the final hybrid products. It is expected that when strong interfacial adhesion between two phases is formed, the hybrid materials exhibit stable homogeneous microstructure without macro-phase separation and improved material properties. Hence, in order to enhance interfacial adhesion in hybrid materials, silane coupling agents, which can result in physical or chemical covalent bonding between organic and inorganic phases, have been employed during the sol-gel process [13-17]. Interfacial adhesion may be also enhanced without silane coupling agents by forming physical bonding such as hydrogen bonding between functional groups of organic segments and silanol groups of the silicate network. In this respect, poly(vinylalcohol) (PVA) resin having a large number of hydroxyl groups in its segments appears to be an attractive organic component to produce high performance hybrid materials.

In this study, the organic-inorganic hybrid materials for the application of gas barrier coating layers was prepared by using PVA as the organic component and tetraethoxyothosilicate (TEOS) as inorganic precursor. The oxygen barrier properties of the BOPP films, that were spin coated with hybrid sols, were investigated with the inorganic composition. In addition, the effect of pretreatments of the polymer substrate surface on the barrier property was examined. The phase interaction and micro-phase morphology of the hybrid gels were analyzed by Fourier transform infrared (FT-IR) spectrometer, X-ray diffractometer, and field emission scanning electron microscopy (FE-SEM). The optical transparency and surface topology of the hybrid coated BOPP films were also observed with ultraviolet-visible (UV-VIS) spectroscope and atomic force microscopy (AFM).

EXPERIMENTAL

Tetraethoxysilane (TEOS) purchased from Acros Organics Company was used as an inorganic silicate precursor. PVA (86 mol% hydrolyzed; average molecular weight 24,000-27,000; grade name PA-05), obtained from Dong Yang Chemical Company, was used as an organic polymer. A mixture of TEOS, distilled water, and ethyl

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alcohol was stirred for 1 h at room temperature to obtain partially hydrolyzed TEOS sols under acid catalyst of hydrochloric acid. The initial pH of TEOS solution was fixed at 1. The molar ratio of TESO : water : EtOH was kept at 1 : 2 : 2. 2.0 grams of PVA powder resin was thoroughly dissolved in a 20 ml distilled water. This PVA solution was mixed with partially hydrolyzed silica sol containing TEOS content of 0.01, 0.02, 0.04, 0.07, 0.1 mol, and then the mixture was stirred for 2 h at room temperature to produce PVA/SiO_2 hybrid coating solutions with various compositions.

The biaxially oriented polypropylene (BOPP) films with thickness of 40 μm were coated by the obtained hybrid coating sols using a spin coater, which was operated under the conditions of rotation speed 6,000 R.P.M. and coating time 30 sec. Before spin-coating with hybrid solution, the surface of the BOPP substrate was pretreated by corona and water-borne polyurethane primer treatment to enhance phase adhesion between hybrid coating layer and base film. The hybrid coated films were dried at 60 °C for 24 h in a drying oven. In addition to preparation of coated films, the hybrid gels were also obtained by casting the hybrid sols onto Petri-dishes covered with polyimide film and drying for 15 days at room temperature. The filter was covered on the gelling samples to prevent contamination from impurities in the air. All of the dried samples were kept in a dessicator to prevent the moisture influence prior to performing the characterization. The experimental procedure for the preparation of PVA/SiO_2 hybrid coated films and hybrid gels is described in Fig. 1.

The oxygen permeability of the coated film was measured by hand-made permeation apparatus, which was designed and made according to the standard method of ASTM D3985. The detailed descriptions of the apparatus and experimental measurements were presented elsewhere [18,19]. Fourier transform infrared spectroscopy (FT-IR; JASCO-430) and wide angle x-ray diffraction (WAXD; Bruker) were used to identify the interfacial interaction between organic polymers and silicate network. The morphologies of the fractured surfaces of the hybrid gels were observed by using a field emission scanning electron microscope (FE-SEM; JSM-6700A). Light transmittance for the evaluation of optical transparency was measured with an ultraviolet visual spectrometer (UV-Vis; 2120 UV plus) in the wavelength range of 200-800 nm. The surface topologies of the hybrid materials were examined by atomic force microscope (AFM; Nanoscope 3100) in the contact mode. A root-mean-square (RMS) roughness was calculated from the roughness profile determined by AFM.

RESULTS AND DISCUSSION

For the preparation of the hybrid thin films with improved oxygen barrier property and optical transparency, one of the significant variables is to control phase compatibility between organic and inorganic phases. Microstructure affecting the performance of depends greatly on the interaction between two phases. The enhanced interfacial adhesion in the organic-inorganic materials is expected to induce the stable and homogeneous microstructure without phase separation, ultimately resulting in high performance hybrid nano materials. As mentioned before, it can be expected that PVA resin used as organic component in this study has the ability to form strong hydrogen bonding with silanol groups of the silicate network due to a large number of hydroxyl groups contained in its segments. Hence, in order to examine the physical interaction between two phases in the hybrid gels, an FT-IR analysis for the PVA/SiO_2 hybrid gels with various TEOS contents was performed. The measured FT-IR spectra are shown in Fig. 2. As shown in the figure, the characteristic broad peak of hydroxyl group (Si-OH) of pure silica gel appeared at 3,453 cm^{-1}. This peak was found to be shifted gradually to the region of low wavenumber as the TEOS content in the hybrid gel increased. This chemical shift may be attributable to the formation of hydrogen bonding between hydroxyl groups of silicate network and them in the segments of PVA resin added into hydrolyzed TEOS sols. Therefore, it is confirmed that the increase of TEOS content at constant amount of PVA (in this study, 2 g) can cause the increase of degree of physical interaction, resulting in hybrid gels with enhanced phase compatibility.

X-ray diffraction patterns of the PVA/SiO_2 hybrid gels shown in Fig. 3 exhibited obvious evidence for the effects of the interfacial interaction between PVA polymer and silicate network on the crystallization behavior of PVA. A characteristic peak appeared at $2\theta=$

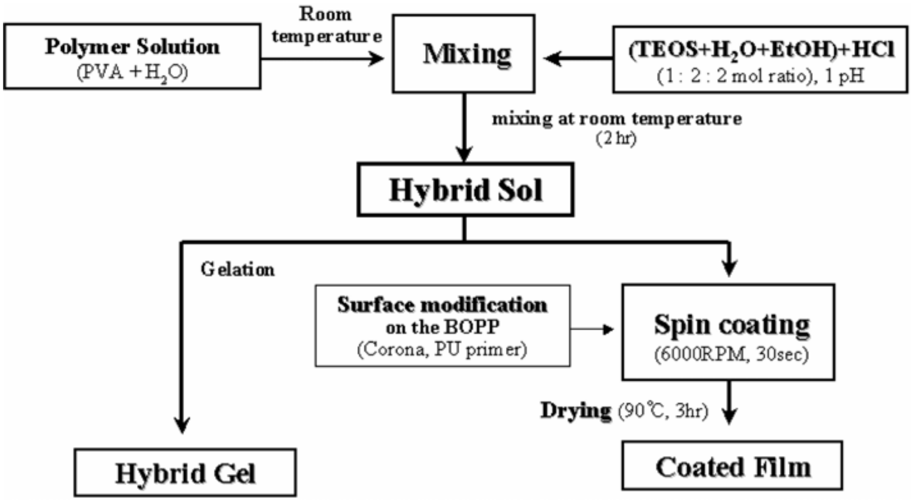


Fig. 1. Experimental procedure for the preparation of PVA/SiO_2 hybrid gel and coated film.

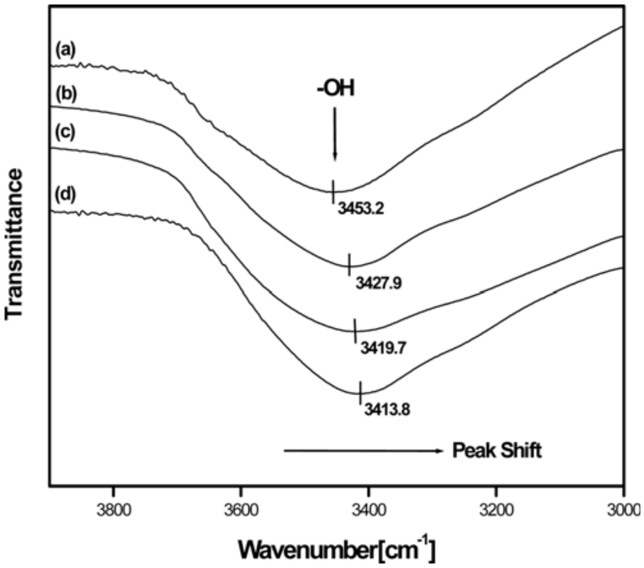


Fig. 2. FT-IR spectra of the hybrid gels with various TEOS contents; (a) pure silica gel, (b) 0.01 mol, (c) 0.04 mol, and (d) 0.10 mol.

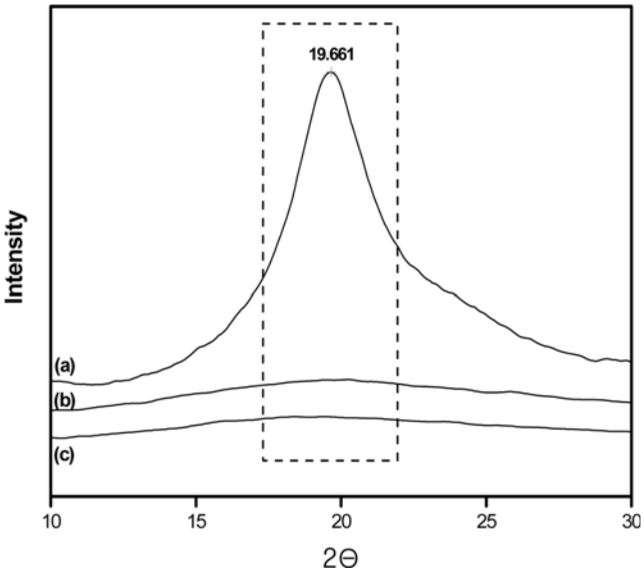


Fig. 3. X-ray diffraction patterns of PVA/SiO$_2$ hybrid gel for the various TEOS contents; (a) pure PVA, (b) 0.02 mol, and (c) 0.04 mol.

19.7° for pure PVA. However, this peak disappeared when the TEOS more than 0.02 mol was added into pure PVA solution to produce hybrid materials, meaning that the crystal growth of PVA was thoroughly prevented due to physical restriction provided by inorganic silicate phase dispersed in the PVA matrix. This physical restriction retarding the crystallization of semi-crystalline polymer can be caused by high degree of interfacial interaction between two phases. Consequently, it was also confirmed that strong hydrogen bond was formed between PVA segments and silicate network.

In addition, the microphase compatibility has a great influence on the morphology of the hybrid materials, which is expected to have an association with barrier, optical, mechanical, and thermal properties. In order to examine the distribution of silica particles produced via sol-gel reaction and microstructure of the PVA/SiO$_2$ hybrid, the morphology of the fractured surfaces was observed by FE-SEM. Fig. 4 shows the morphologies of the pure silica gel and PVA/SiO$_2$ hybrids produced with addition of 0.04 mol and 0.10 mol of TEOS content, respectively. As shown in the micrograph, a dense microstructure, in which an individual silica particle could not be

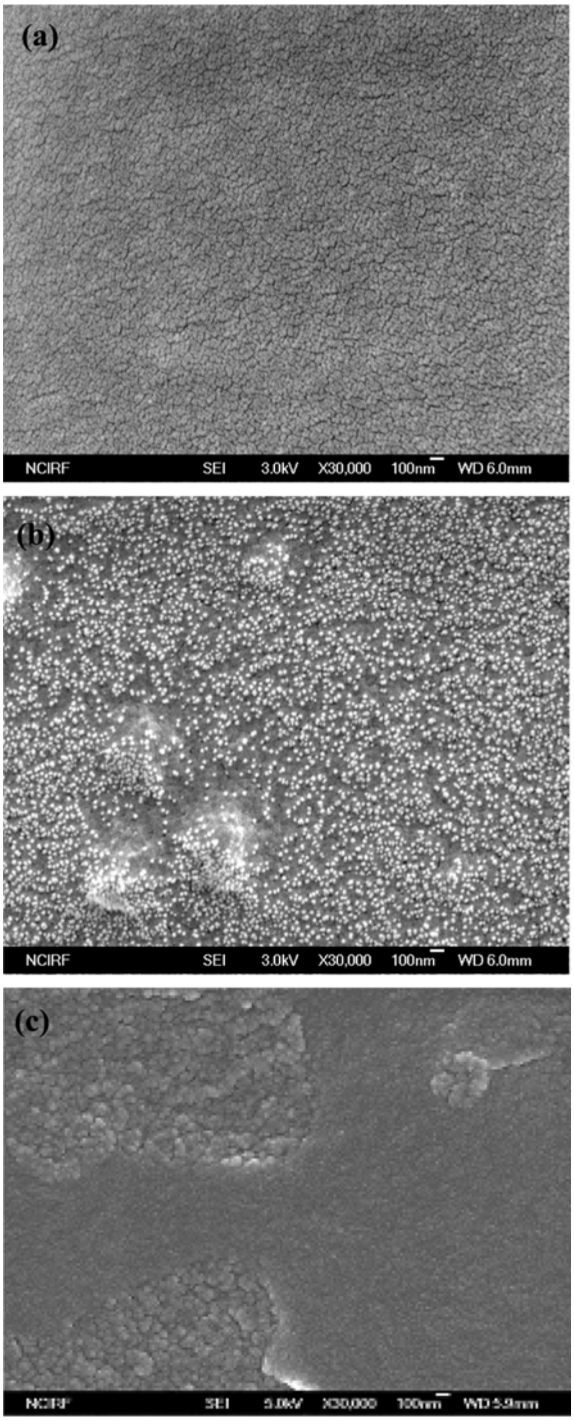


Fig. 4. Phase morphology of PVA/SiO$_2$ hybrid gel with various TEOS contents; (a) pure silica gel, (b) 0.04 mol, and (c) 0.10 mol.

distinguished, was observed for pure silica gel. In the case of hybrid gel prepared with 0.04 mol of TEOS, on the other hand, distinguished silica particles with average size less than 50 nm were uniformly dispersed in the PVA polymer matrix. It can be deduced that the formation of strong interfacial interaction between two phases prevented the microphase separation, resulting in hybrid with homogeneous morphology. However, when an excess amount of TEOS precursor (0.1 mol) was added, the microphase separation was observed on the surface of hybrid gel in spite of the formation of strong interaction between two phases. This may be attributed to the formation of silica clusters with large domain size over 100 nm, resulting from physical coalescence among silica particles or chemical condensation between residual silanols on the silica surface. In phase separation phenomena, the effect of inorganic cluster, that can be easily formed under higher contents of inorganic particles, seems to be dominant over that of degree of physical interaction between two phases. It was revealed from this result that without addition of silane coupling agent, PVA/SiO_2 hybrid system with stable homogeneous microphase morphology could be obtained by controlling the composition of inorganic silicate phase.

Fig. 5 shows the optical transmittance of the hybrid coating films with different TEOS molar content. Light transmittance increased with increasing of TEOS content up to 0.04 mol in all visible light range of 400-800 nm. In particular, at 0.04 mol TEOS content, a coating film with enhanced optical transparency could be obtained. This result may be explained by the fact that the addition of TEOS precursor up to some level of content results in more homogeneous and finer microstructure in the hybrids due to increased interfacial attraction between two phases. However, in the case of hybrid coating films with addition of 0.07 mol and 0.10 mol TEOS, the optical transparency was reduced, compared with the coating film with the addition of 0.04 mol TEOS. It can be believed that at above 0.04 mol TEOS content, the decrease in light transmittance with the increase of TEOS content may result from formation of silica clusters during gelation of the hybrids, followed from occurrence of micro-phase separation between organic and inorganic phase, which can be seen in the SEM micrograph of Fig. 4. Furthermore, when a large amount of inorganic silica is involved in the hybrid, micro-cracks can be easily formed on the surface of coating film due to reduced flexibility, so these defects increase light scattering on the film surface. This can be evidenced by surface morphology, which was observed by SEM, for coating films with various TEOS contents as shown in Fig. 6. It should be noted that there existed no microcrack on the surface of the hybrid coating film obtained from the addition of 0.04 mol TEOS content; on the other hand, at above 0.04 mol TEOS content, the degree of microcrack formation increased with increase of TEOS content. From these results, the optimal content of inorganic silica precursor, TEOS, was found to be 0.04 mol to produce PVA/SiO_2 hybrids with enhanced microstructure and optical transparency.

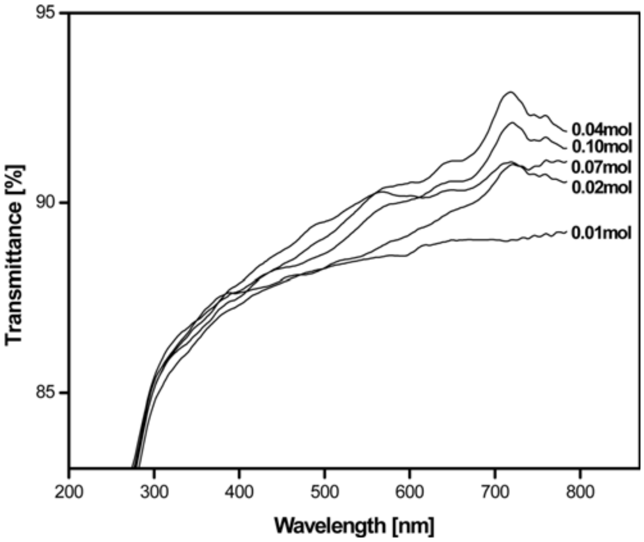


Fig. 5. Light transmittance of PVA/SiO_2 hybrid coating film prepared with various TEOS contents.

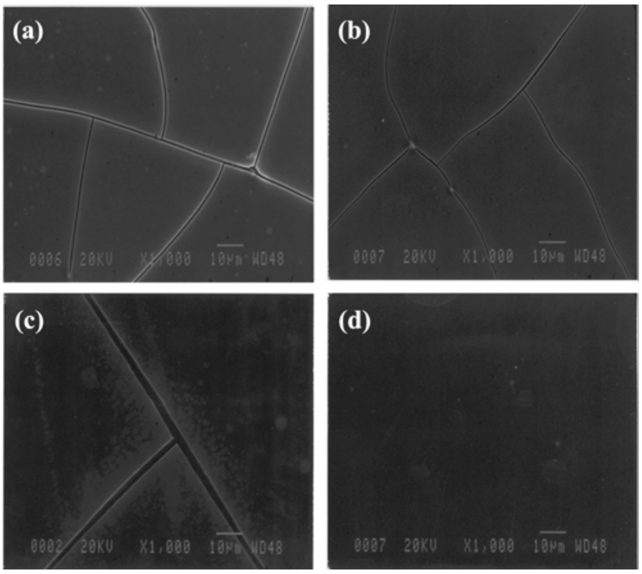
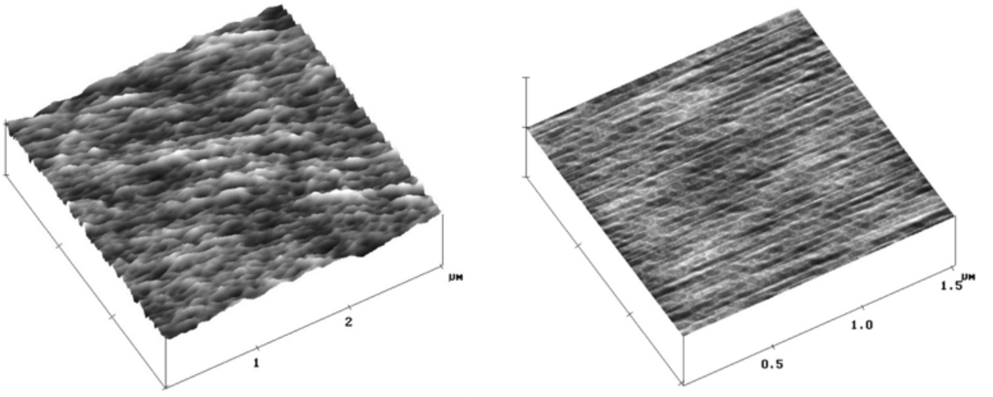


Fig. 6. Surface morphology hybrid coating film with various TEOS contents; (a) pure silica, (b) 0.1 mol, (c) 0.07 mol, and (d) 0.04 mol.

In general, optical transparency of the film depends on its surface morphology because the extent of light scattering on the film surface can be varied by the surface roughness. Fig. 7 shows the AFM images of the surface for the pure BOPP substrate and film coated by PVA/SiO_2 hybrid (TEOS content: 0.04 mol). The BOPP substrate exhibited an RMS (root mean square) value of 3.412 nm, representing the roughness for the film surface. On the other hand, the hybrid-coated film has very smooth surface with RMS value of 0.136 nm. This enhanced surface morphology of the coated film may be attributable to the efficient packing into micro-pores or channels present on the surface of pure BOPP substrate by the hybrid sols containing silica particles with nano size.

The PVA/SiO_2 hybrid sols prepared through sol-gel method were used to produce single-layer coated BOPP film with gas barrier characteristic. The effect of the composition of hybrid sols and surface pretreatment of base BOPP film on the oxygen permeation through the coated films was investigated. In Fig. 8, the measured oxygen permeabilities of the hybrid coated film as a function of TEOS contents are presented. The permeability unit ($cc\cdot mm/m^2\cdot 24\ h\cdot atm$) means the oxygen gas volume (cc) permeated through the coated



(a) BOPP substrate (RMS=3.412nm) (b) hybrid coating film (RMS=0.136nm)

Fig. 7. AFM images of the surface of (a) BOPP substrate and (b) hybrid coated film.

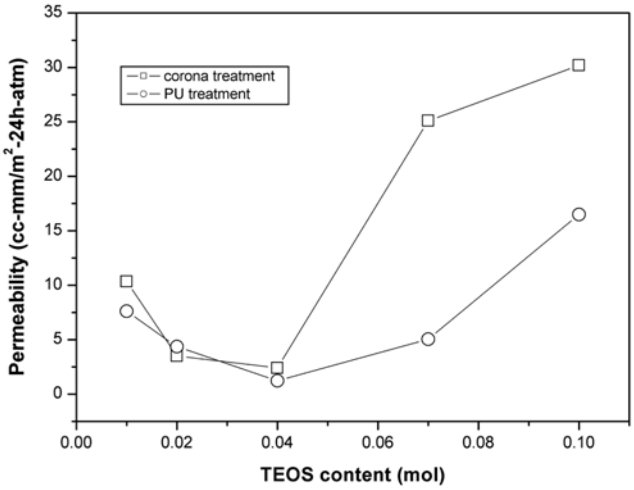


Fig. 8. Oxygen permeabilities of PVA/SiO_2 hybrid coating films as a function of TEOS contents.

film with effective area of m^2 and thickness of mm for 24 h under the pressure difference of 1 atm. The BOPP substrate, of which the surface was pretreated by two kinds of methods such as corona and polyurethane primer, was used as a base film. As shown in the figure, in the range of TEOS content from 0.01 to 0.04 mol, the oxygen permeability is moderately reduced with increasing of TEOS content, which is due to the increase of the amount in inorganic silica particle with high barrier property, formed in the hybrids through sol-gel reaction. Especially, at 0.04 mole of TEOS content, hybrid-coated film with high barrier property could be obtained, exhibiting low values of oxygen permeability (1.23 & 2.40 cc·mm/m^2·24 h·atm), corresponding to the surface pretreatment method. This improved barrier property may be due to stable homogeneous microstructure without microphase separation in the hybrids including 70.5 wt% of inorganic silica content, which was confirmed from SEM observation. Whereas, poor barrier properties were obtained at high levels of TEOS content. As observed in previous SEM microphotographs, the incorporation of inorganic silica component at high level of content (TEOS 0.10 mol) resulted in microphase separation within the hybrids and microcrack formation on the surface of the coated film due to reduced flexibility, and hence high permeability was measured because the oxygen molecules could easily permeate through these micropores formed on the surface. In addition, the reduction in interfacial adhesion between coating layer and substrate, which may be resulting from the occurrence of phase inversion that the inorganic silica component becomes the continuous phase in the hybrids, can be considered as a major factor in the decrease of barrier property. Meanwhile, the effect of pretreatment method applied upon the surface of BOPP substrate on the barrier property was examined. At below 0.04 mol of TEOS content, the difference among two methods in barrier effect was not obvious. On the other hand, in the case of addition of TEOS precursor above 0.04 mol of content, the permeability of the film coated on the BOPP substrate pretreated with polyurethane primer was found to be even lower than that of coating film with corona pretreated substrate. This result indicates that polyurethane pretreatment layer positioned as a middle layer in three layer coating film including substrate could efficiently restrain the micro-crack formation on the film surface by acting as a impact-absorbing buffer layer against capillary stress generated during drying process.

In our previous work, we reported that biaxially stretched PP/EVOH blend film, which was produced at optimal conditions using laminar morphology technology, exhibited an oxygen permeability value of 9.3 cc·mm/m^2·24 h·atm [18]. In the present study, however, by using sol-gel coating technology, a remarkable improvement in barrier property could be accomplished about 30-50 times relative to the pure BOPP film (permeability: 68.0 cc·mm/m^2·24 h·atm) alone. This is a significant improvement in barrier property as compared with our previous result on the blend system with laminar morphology.

CONCLUSIONS

In this study, PVA/SiO_2 hybrid nano coating materials with gas barrier characteristic were prepared by using the sol-gel method. By analyzing FT-IR spectra and investigating the crystallization behavior based on X-ray diffraction patterns for the hybrid gels, it was confirmed that there existed strong physical interaction in terms of hydrogen bonding between silicate network and PVA segments. In addition, PVA/SiO_2 hybrid materials with a stable homogeneous nano-structured morphology could be produced by only controlling the composition of the hybrids without employing the silane coupling agent. Micro-phase separation was observed in the hybrid gel prepared with an addition of excess amount of TEOS. It was also revealed that there existed an optimum content of inorganic silicate precursor (in this study, 0.04 mol) to obtain high barrier PVA/SiO_2 hybrid coating materials with enhanced microstructure and optical transparency. The oxygen permeation of film coated with nano-structured hybrid materials, which was obtained under optimal conditions by incorporating inorganic silicate particle with PVA polymer matrix, could be considerably suppressed by a factor of about 98% compared with pure BOPP film. The effect of the surface pretreatment on the permeation behavior through the coated film was found to be dependent on the amount of inorganic silicate component added into hybrids.

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REFERENCES

1. J. D. Wright and N. A. Sommerdijk, *Sol-gel materials chemistry and applications*, Gordon and Breach Sci. Publishers, Amsterdam (2001).
2. K. H. Haas, S. Schwab and K. Rose, *Thin Solid Films*, **351**, 198 (1999).
3. S. Yano, K. Iwata and K. Kurita, *Mater. Sci. Eng.*, **C6**, 75 (1998).
4. S. R. Davis, A. R. Brough and A. Atkinson, *J. Non-Cryst. Solids*, **315**, 197 (2003).
5. K. H. Haas, S. A. Schwab, K. Rose and G. Schottner, *Surface and Coatings Technol.*, **111**, 72 (1999).
6. H. Schmidt, G. Jonschker, S. Goedicke and M. Mennig, *J. Sol-Gel Sci. Technol.*, **19**, 39 (2000).
7. R. A. Caruso and M. Antonietti, *Chem. Mater.*, **13**, 3272 (2001).
8. K. Azuta, K. Tadanaga and T. Minami, *Journal of the Ceramic Society of Japan*, **107**(3), 293 (1999).
9. S. Y. Lee, J. D. Lee and S. M. Yang, *J. Mater. Sci.*, **34**, 1233 (1999).
10. S. A. Schwab, M. Hoffmann and A. Burger, *J. Sol-Gel Sci. Technol.*, **19**, 125 (2000).
11. W. Y. Sung and S. W. Kim, *Theories & Application of Chem. Eng.*, **9**, 2734 (2003).
12. J. Jang, J. Bae and D. Kang, *Polym. Int.*, **50**, 1247 (2001).
13. M. Ochi, R. Takahashi and A. Terauchi, *Polymer*, **42**, 5151 (2001).
14. H. H. Qin, J. H. dong, K. Y. Qiu and Y. Wei, *J. Polym. Sci.: Part A: Polymer Chemistry*, **38**, 321 (2000).
15. J. H. Park and S. W. Kim, *Theories & Application of Chem. Eng.*, **10**, 2112 (2004).
16. W. Z. Zhou, J. H. Dong, K. Yuan Qiu and Y. Wei, *J. Appl. Polym. Sci.*, **73**, 419 (1999).
17. C. Chiang and C. M. Ma, *Eur. Polym. J.*, **38**, 2219 (2002).
18. J. H. Yeo, C. H. Lee and S. W. Kim, *Adv. in Polym. Tech.*, **20**, 191 (2001).
19. D. Kim and S. W. Kim, *Korean J. Chem. Eng.*, **20**, 776 (2003).