

# Phase Compatibility and Barrier Properties of Ethylene/Vinyl Alcohol Copolymer Based Hybrid Materials

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**ABSTRACT:** An ethylene/vinyl alcohol copolymer (EVOH) with superior barrier properties was used as an organic component to prepare EVOH/SiO<sub>2</sub> hybrid materials with improved gas barrier properties with a sol-gel method. As a silane coupling agent, 3-isocyanatopropyl triethoxysilane (IPTES) was used to promote interfacial attraction between the organic EVOH segments and the inorganic silicate network in the hybrid. The phase compatibility was evaluated by analysis of Fourier transform infrared spectroscopy and phase morphology and the optical properties of the hybrids. We confirmed that the addition of the silane coupling agent IPTES up to some level of content resulted in enhanced phase compatibility and optical transparency of the nanostructured hybrid material with a homogeneous phase morphology exhibiting no

microphase separation. For the preparation of the monolayer coated film, the biaxially oriented polypropylene substrate pretreated with a corona was coated with the hybrid sols by a spin-coating method. The oxygen permeation behavior through the coated film was examined with various contents of the silane coupling agent IPTES and inorganic silicate precursor tetraethoxyorthosilicate in the hybrid system. Consequently, it was revealed that an optimum range of IPTES and tetraethoxyorthosilicate contents was required to produce high barrier EVOH/SiO<sub>2</sub> hybrid materials with a stable homogeneous microstructure and enhanced optical transparency. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1663–1670, 2010

**Key words:** barrier; coatings; compatibility; nanotechnology

## INTRODUCTION

The sol-gel method has been used to readily produce organic-inorganic hybrid materials at relatively low temperatures. In general, advantageous properties of organic polymers are flexibility, tackiness, toughness, and formability, whereas inorganic glasses have excellent properties of gas permeation resistance, hardness, modulus, transparency, and thermal stability.<sup>1–5</sup> Thus, high-performance or highly functionalized organic-inorganic hybrid materials may be achieved by incorporation of the organic polymer into the inorganic silicate structure through a sol-gel process. In the preparation of hybrid materials by sol-gel processes, the inorganic silicate network based on Si–O–Si bonds is created from an inorganic precursor via hydrolysis and condensation reactions. The detailed reaction mechanism of the sol-gel process is described in the literature.<sup>4,5</sup>

Recently, organic-inorganic hybrid coating of a polymer substrate film has been attempted to improve the barrier properties due to the inorganic silicate network and to provide various surface characteristics, such as abrasion resistance antistatic, anti-adhesive, and antifogging properties through the chemical functionalization of the coating materials.<sup>6–8</sup> The incorporation of an organic polymer into the inorganic silicate network may prevent crack formation in the coating layer during the gelling process because of increased flexibility and may also enhance the adhesion to an organic polymer substrate. Polymer films with barrier properties for the application of food, medical, and cosmetic packaging have been produced with multilayered structures with coextrusion and lamination processes.<sup>9</sup> However, these multiple-layer composite films have some drawbacks, such as difficulties in recycling, high production costs, and a lack of transparency. Recently, a sol-gel silica coating technique was proposed to overcome these shortcomings. This sol-gel coating approach for improving barrier properties has been recognized as fascinating methodology because existing coating equipment for printing can be used without a further investment of equipment.

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Organic–inorganic hybrid coatings of various polymer films for obtaining high gas barrier properties have been reported. As the organic structural units, organically modified trialkoxysilanes, such as methyltriethoxysilane, vinyltriethoxysilane, phenyltriethoxysilane, (3-aminopropyl)triethoxysilane, and (3-glycidoxypropyl)trimethoxysilane, have also been incorporated into silicates resulting from a tetraethoxyorthosilicate (TEOS) precursor to produce organic–inorganic hybrid coating films with high barrier properties.<sup>10–12</sup> However, these hybrid systems have shown some limitations in the enhancement of barrier properties because the coating layer with an increased thickness could not be obtained because of a lack of flexibility and adhesion to the substrate. In addition, studies have been performed with poly(vinyl alcohol), poly(vinylpyrrolidone), and poly(vinyl acetate) as the organic polymer because these polymers have the ability to form hydrogen bonds with the silanol groups of the silicate network and also to form a homogeneous solution with silica precursors.<sup>13–15</sup> Among these polymers, poly(vinyl alcohol) was found to be an effective organic component for suppressing the gas permeability because of its high barrier properties and the sufficient hydroxyl groups on its chain, which induce a strong hydrogen-bonded interface. Meanwhile, the ethylene/vinyl alcohol copolymer (EVOH) has been widely used for the application of packaging materials for food, drugs, and cosmetics because of its superior gas barrier properties.<sup>16</sup> The commercially available EVOH grades contain 56–73 mol % vinyl alcohol. Its excellent barrier properties are attributed to the high cohesive energy density of the resin, which arises from denser intermolecular and intramolecular hydrogen bonding. The physical properties, including the barrier properties, of the EVOH resin are largely dependent on the content of vinyl alcohol in EVOH. Despite the high barrier properties of EVOH, it has not been used for the preparation of organic–inorganic hybrid materials with barrier properties because it does not have sufficient hydroxyl groups to form hydrogen bonding on its chain molecule, and also, it has a difficulty obtaining a homogeneous polymer solution with solvents used in sol–gel processes because of the presence of non-polar hydrocarbon segments consisting of ethylene units.

In this study, EVOH as the organic polymer was incorporated into the silica network to prepare an organic–inorganic hybrid coating solution through the sol–gel method. TEOS was used as an inorganic precursor. To date, there have been no reports in the literature on EVOH/SiO<sub>2</sub> hybrids prepared by the sol–gel method, except our previous study on an EVOH hybrid system without a coupling agent.<sup>17</sup> To produce high-performance EVOH/SiO<sub>2</sub> hybrid

materials by the enhancement of interfacial adhesion between the organic and inorganic phases, silane coupling agents of 3-isocyanatopropyl triethoxysilane (IPTES) were used during the sol–gel process. The phase compatibility and phase microstructure of the hybrid materials with various contents of coupling agent were evaluated in terms of IR spectra and morphological analysis. We studied the barrier properties of biaxially oriented polypropylene (BOPP) films coated with these hybrid materials by investigating the effects of the composition of the hybrid sols and the content of IPTES.

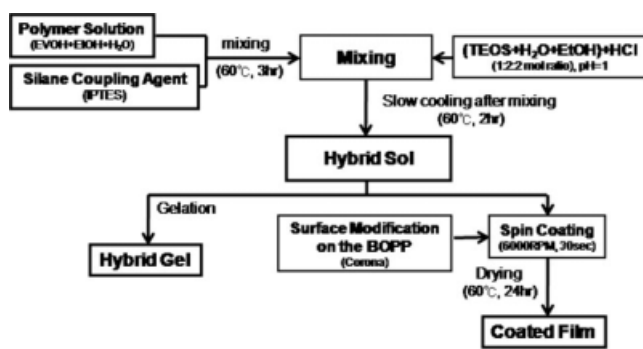
## EXPERIMENTAL

### Materials and preparation

TEOS (Acros Organics, USA, 98%) and IPTES (Aldrich, USA, 95%) were used as the inorganic silicate precursor and the silane coupling agent, respectively. EVOH (32 mol % ethylene content, EP-F101), obtained from Kuraray Co., was used as an organic polymer. Hydrochloric acid (HCl; Samchun Chemical, 37 wt %) was applied as the catalyst. A fluorosurfactant (Zonyl FSO, Aldrich) was used as a wetting agent. BOPP (Youl Chon Chemical, Ltd.) film with a thickness of 40 μm was used as the substrate. The surface of this BOPP film was pretreated with a corona to promote the adhesion between the substrate and the coating layer.

A mixture of TEOS, distilled water, and ethanol (EtOH) was stirred for 1 h to hydrolyze the TEOS under an acid catalyst. The initial pH of the TEOS solution was adjusted to 1.0 by the addition of HCl. The molar ratio of TEOS/water/EtOH was kept at 1 : 2 : 2. The EVOH solution, of which the EVOH/water/EtOH weight ratio was 1 : 6 : 12, was prepared by dissolution of the EVOH resin in a solvent mixture consisting of water and EtOH. The modified EVOH solution was prepared by the addition of the coupling agents of IPTES into the obtained homogenized EVOH solution followed by stirring for 3 h at an elevated temperature of 60°C. This modified EVOH solution was mixed with the partially hydrolyzed TEOS sol, and then, the mixture was stirred vigorously for 2 h at room temperature to produce EVOH/SiO<sub>2</sub> hybrid coating sols with various compositions. Hybrid materials with various contents of the silane coupling agent IPTES (0.003, 0.006, 0.008, 0.012, and 0.015 mol) were prepared. Meanwhile, the amount of the inorganic silicate precursor TEOS was fixed at 0.04 mol in all of the hybrid samples.

The coating was performed on the pretreated BOPP substrate by obtained hybrid coating sols with a spin coater (KW-4A, Chemat Technology, Inc., USA), which was operated at a rotation speed of 6000 rpm and with a coating time of 30 s. In the



**Figure 1** Experimental procedure for the preparation of the EVOH/SiO<sub>2</sub> hybrid gel and coated film.

hybrid-coated film prepared under these conditions, the thickness of the coating layer was measured to be around 1.8  $\mu\text{m}$ . Before spin coating, the wetting agent was added to the hybrid solution with stirring for 10 min. The hybrid-coated films were dried at 60°C for 24 h in a drying oven. In addition to the preparation of coated films, hybrid gels were also obtained by the casting of the hybrid sols onto Petri dishes covered with polyimide film and drying for 15 days at room temperature. The gelling samples were covered by paper filters to prevent contamination from impurities in the air. All of the dried samples were kept in a desiccator to prevent moisture influence before the characterization was performed. The experimental procedure for the preparation of the EVOH/SiO<sub>2</sub> hybrid-coated films and hybrid gels is described in Figure 1.

### Characterization

Fourier transform infrared (FTIR) spectroscopy (model 430, Jasco, Japan) was used to examine the phase attraction between the inorganic silicate and organic EVOH polymer in IPTES-added hybrid materials. To prepare samples diluted by KBr for the FTIR measurements, the hybrid gels were mixed with KBr powder and pressed into pellets with a thickness of less than 1 mm. The weight ratio of hybrid gels to KBr was adjusted to 200. The morphology of the fractured surfaces of the hybrid materials was observed with field-emission scanning electron microscopy (FESEM; model 6700A, JSM). The surface topologies of the hybrid materials were examined with atomic force microscopy (AFM; model 3100, Nanoscope) in contact mode with focus on a microdomain of  $1 \times 1 \mu\text{m}^2$ . The values of the root mean square (RMS), which is considered to be a parameter for surface roughness, were calculated from the roughness profile determined by AFM. The optical transparency of the hybrid-coated film was measured by ultraviolet–visible spectrometry (2120 UV plus, Mecasys, Korea) in the visible-light wavelength

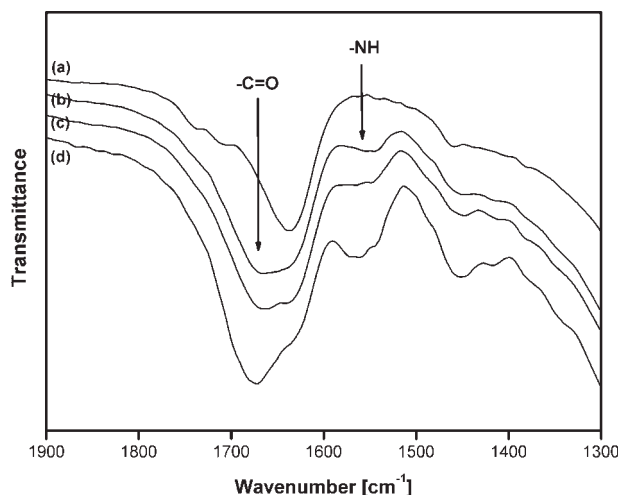
range 200–800 nm. Photographs for the hybrid sols were taken with a digital camera to observe the occurrence of phase separation and to evaluate sol stability of the hybrid sols. The oxygen permeability of the coated film was measured by a handmade permeation apparatus, which was designed and made by our research team according to the standard method ASTM D 3985. The test were performed at room temperature and a relative humidity of 0%. Detailed descriptions of the apparatus and experimental measurements were presented elsewhere.<sup>18,19</sup>

## RESULTS AND DISCUSSION

### FTIR analysis

In organic–inorganic hybrid materials, the nature and microstructure of each consisting component, composition of the hybrid, and interaction between phases are considered significant control parameters that can determine the performance of the hybrids. Among these factors, phase attraction between the organic and inorganic phases is the most crucial to the production of hybrid materials with enhanced properties. Particularly, in hybrid materials obtained by the sol–gel method with a polymeric resin as an organic component, the phase morphology affecting the performance of the hybrid materials depends greatly on the interaction between the polymer chain segments and the formed inorganic particles. The enhanced interfacial adhesion in the hybrid materials produced via a sol–gel process is expected to resist phase separation and induce the phase morphology with a well-dispersed and homogeneous microstructure.

Silane coupling agents have often been used to enhance the compatibility between the two phases in silica-based hybrid systems. In particular, IPTES has been frequently used because it contains a functional reactive isocyanate ( $\text{N}=\text{C}=\text{O}$ ) group, which results in the formation of covalent bonding through a chemical reaction with the organic polymer with another functional group. In this study, therefore, the silane coupling agent IPTES was used to enhance the compatibility efficiently via the formation of strong covalent bonding between the organic EVOH phase and the inorganic silicate network. However, this IPTES was expected to be inefficiently consumed during the sol–gel reaction process because it could react with other components that also contained reactive hydrogen atoms, such as water and EtOH, which were used as solvents in the preparation of the EVOH solution and silica sol. As a result of these competitive reactions of the isocyanate functional group with the solvent mixture and hydroxyl group in EVOH, urea groups and urethane groups could be formed. The urea group could be formed



**Figure 2** FTIR spectra of the EVOH/SiO<sub>2</sub> hybrids with various IPTES contents: (a) 0, (b) 0.003, (c) 0.006, and (d) 0.012 mol.

through the reaction of isocyanate and amine compounds, which was product resulting from the reaction of isocyanate and water. Figures 2 and 3 show the measured FTIR spectra of the EVOH/SiO<sub>2</sub> hybrids with various IPTES contents and the expected molecular structure of the modified EVOH resin, which had a urethane group derived from the chemical reaction between the isocyanate group of IPTES and the hydroxyl group in the segments consisting of vinyl alcohol units in the EVOH copolymer. As shown in the figure, two different characteristic bands appeared in a broad range from 1630 to 1680 cm<sup>-1</sup> for the carbonyl (—C=O) group and from 1530 to 1575 cm<sup>-1</sup> for the amine (—NH) group. These broad bands were attributed to the overlap of each peak corresponding to urethane and urea groups, respectively. Consequently, these FTIR results reveal that the EVOH resin reacted with IPTES, which resulted in strong interaction adhesion between the organic EVOH phase and the inorganic silica network.

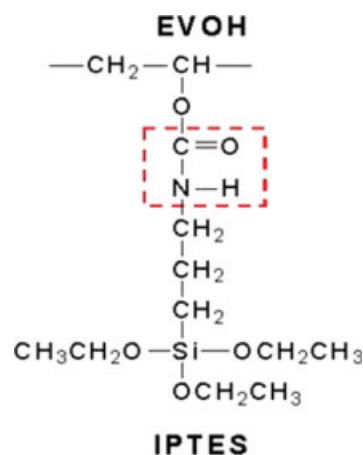
### Phase morphology

The compatibility between the organic polymer and inorganic silica phase greatly influences the mechanical, barrier, optical properties and phase morphology of the organic–inorganic hybrid nanocomposites. In this study, the phase morphology of the fractured surfaces was observed to examine the microphase separation and microstructure of the hybrid gels. Figure 4 presents FESEM photographs of the hybrid gel samples with various IPTES contents. A high extent of microphase separation occurred in the case of the hybrid gels without the addition of the IPTES silane coupling agent. This phenomena was attributed to the weak interaction between the inorganic

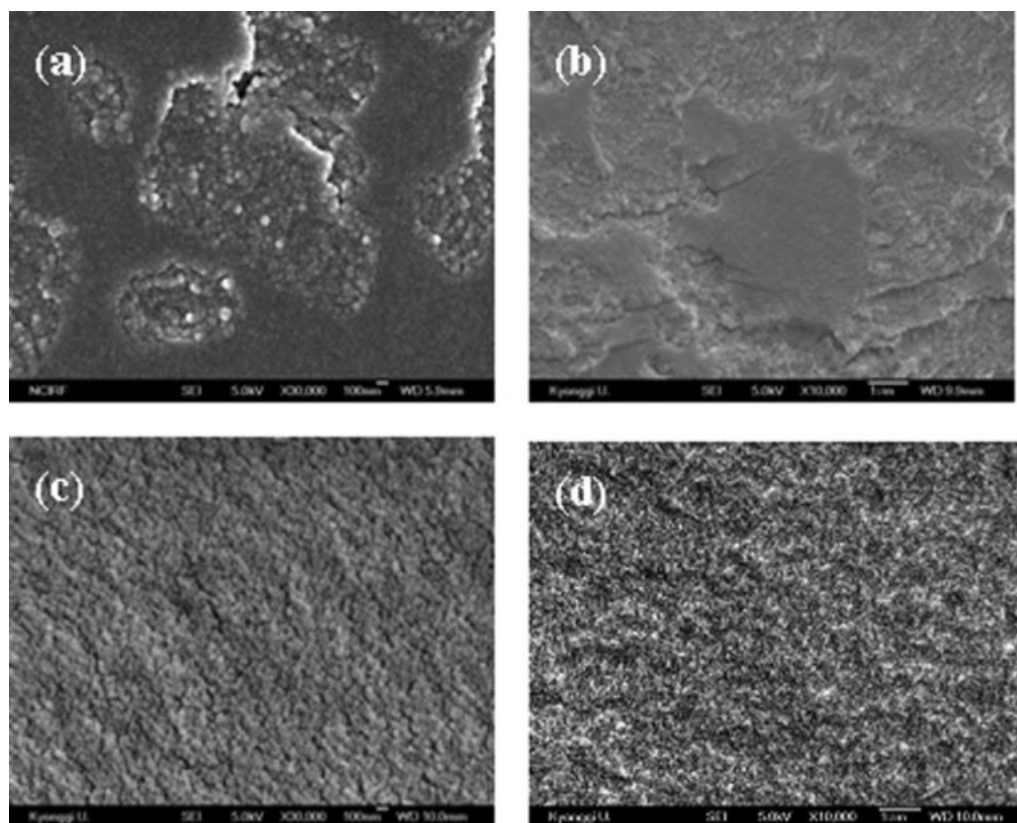
and organic phases, which promoted the formation of silica clusters with a large domain size, which resulted from the coalescence of nanosized silica particles by a chemical condensation reaction between the silanol groups on the silica surfaces and physical interaction among the silica particles. With a small IPTES content of 0.003 mol, a slight microphase separation was also observed because of insufficient interaction bonding between the two phases. For the hybrid gel samples with an IPTES content of 0.006 mol [Fig. 4(c)], however, silica particles with an average size of less than 80 nm were homogeneously dispersed in the EVOH matrix, and no phase separation was found. In particular, despite the addition of an excess amount of IPTES (0.012 mol), a phase morphology similar to that of the hybrid containing 0.006 mol of IPTES was still observed. It was confirmed from morphological analysis that the addition of only a small amount (the molar ratio of IPTES to TEOS + IPTES was 0.15) of the IPTES silane coupling agent capable of inducing covalent bonding yielded a silica/EVOH hybrid material with a more stable and finer phase morphology without phase separation by enhancement of the compatibility between the inorganic silica phase and the organic EVOH phase.

### Transparency of the hybrid gel and coated film

In this study, the phase compatibility was also evaluated in terms of the optical properties of the hybrid gel or hybrid-coated films. The transparency of the hybrid material depends on the phase morphology or degree of phase separation. The phase morphology with an uniformly dispersed particles with a nanometer scale below 100 nm generally induces a high degree of light transmittance through the hybrids and results in transparent hybrids, whereas



**Figure 3** Molecular structure of the EVOH resin modified with IPTES. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 4** Phase morphology of the EVOH/SiO<sub>2</sub> hybrids with various IPTES contents: (a) 0, (b) 0.003, (c) 0.006, and (d) 0.012 mol.

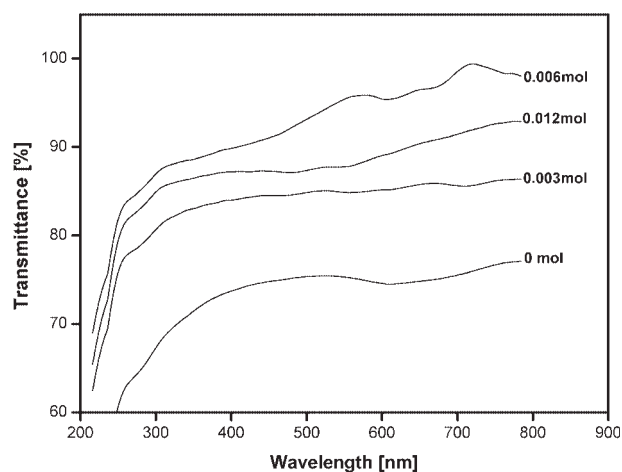
the phase-separated hybrid structure has a greater tendency of scattering the visible light because of a larger dispersed particle size with a micrometer scale, which leads to translucent or opaque hybrids.

Figure 5 shows the pictures displaying the state of the silica/EVOH hybrid gels with different IPTES contents, which were obtained via a gelation and aging process involving continuing physical and chemical changes from hybrid sols. As shown in the figure, when IPTES at contents higher than 0.006

mol was added, highly transparent hybrid gels were obtained. In the case of the hybrid gel without the addition of IPTES, however, the hybrid gel was observed to be heavily milky white, which indicated that a high degree of phase separation took place during gelation because of lack of phase compatibility. In addition, a little increased amount of IPTES at 0.003 mol did not seem to sufficiently contribute to improvement in the interaction between the organic EVOH segments and the inorganic silicate network,



**Figure 5** Digital photographs showing the state of the EVOH/SiO<sub>2</sub> hybrids gels with different IPTES contents: (a) 0, (b) 0.003, (c) 0.006, and (d) 0.012 mol. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 6** Light transmittance of films coated with EVOH/SiO<sub>2</sub> hybrids with various IPTES contents.

which showed little enhancement in the optical transmittance but there was still a translucent state for the hybrid gel.

Figure 6 shows the relative light transmission as a function of visible light wavelength for various IPTES contents in the hybrid-coated films. This result for the optical transmittance of the coated films represented a similar trend to that of the hybrid gel. Light transmittance increased with increasing IPTES content up to 0.006 mol in the entire visible light range of 400–800 nm. Above 0.006 mol of IPTES, all of the coated films were found to be fairly transparent with the measured light transmittance rate at more than 90%. These results for the optical transparency also illustrate that the addition of the IPTES silane coupling agent up to some level of content resulted in improved optical transparency as a result of a more homogeneous and finer microstructure in the hybrids because of increased interfacial attraction between the organic and inorganic phases, as observed in the previous SEM micrographs. From these results, we confirmed that there existed an optimum level of silane coupling agent (IPTES) content (0.006 mol in this study) to obtain organic–inorganic hybrid nanocomposites with improved phase morphology and transparency.

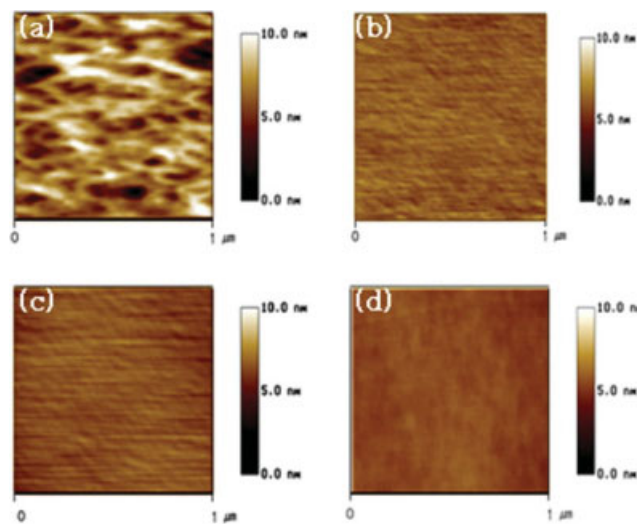
#### Surface topology of the coated films

In general, the optical transparency of the coated films depends on various factors, including the optical properties of each layer in the coated films, the difference in refractive index between the coating layer and the substrate, and the surface topology. Among these factors, the surface topographic structure, which can be predominantly influenced by the phase morphology of the hybrid material, has been recognized as a significant parameter affecting the

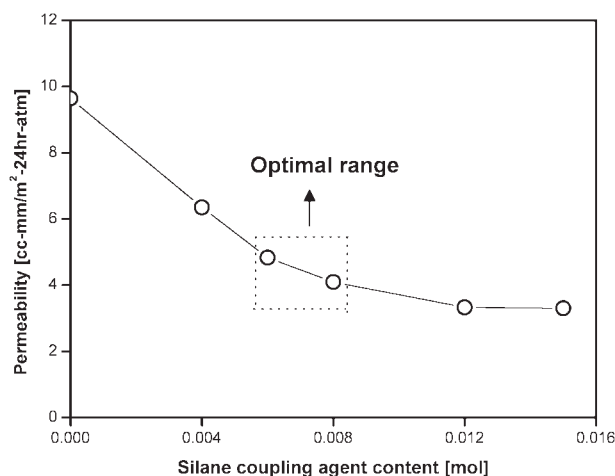
optical properties because the extent of light scattering on the film surface can be varied by the surface roughness. Figure 7 displays the AFM images of the surface for the pure BOPP substrate, films coated by pure silica, and EVOH/SiO<sub>2</sub> hybrids without IPTES and with 0.006 mol of IPTES. As shown in the figure, the pure BOPP film before coating had a large number of micropores or channels present on the surface, which led to surface roughness with an RMS value of 3.41 nm. However, when pure silica or hybrid sols were applied on the surface of the BOPP substrate exhibiting a high degree of roughness, the RMS value dramatically decreased, which resulted in a smooth surface with an unevenness of less than 0.4 nm. This result was attributable to the efficient packing into micropores or channels by the hybrid sols containing silica particles of nanometer size. Particularly, in the case of hybrid-coated films with the addition of the IPTES silane coupling agent, the surface morphology was observed to be remarkably improved because of the homogeneous and fine phase morphology of the hybrids as confirmed in the previous SEM photographs, which exhibited the best conditions for the smoothness with an RMS value of 0.21 nm.

#### Barrier properties

EVOH-based silica hybrid sols prepared via a sol-gel method were used to yield monolayer coated BOPP films with high gas barrier properties. The effects of the amount of incorporated IPTES silane coupling agent and TEOS inorganic precursor on



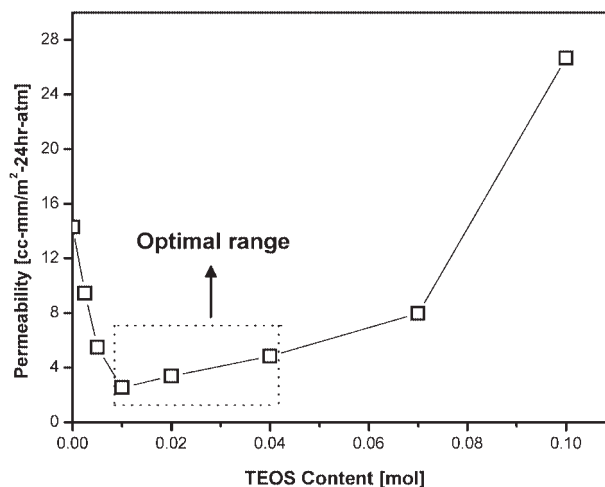
**Figure 7** Surface topology of (a) the BOPP substrate, (b) the pure silica-coated film, and (c,d) the films coated with EVOH/SiO<sub>2</sub> hybrids with IPTES contents of 0 and 0.006 mol, respectively. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 8** Oxygen permeability of the EVOH/SiO<sub>2</sub> hybrid coating films as a function of the IPTES content.

oxygen permeation through the coated films were examined. Figure 8 represents the measured oxygen permeabilities of the hybrid-coated films as a function of the IPTES content. The permeability unit (cc mm/m<sup>2</sup> 24h atm) means the oxygen gas volume (cc) permeated through the coated film with an effective area of square meters and a thickness of millimeters for 24 h under a pressure difference of 1 atm. As shown in Figure 8, in the investigated range of IPTES contents, the oxygen permeability was substantially reduced with increasing IPTES content. The addition of IPTES up to 0.006 mol offered a prominent effect on the reduction in oxygen permeability, but the effect was shown to be minor above 0.006 mol of IPTES; particularly, a variation in permeability was not observed at contents in excess of 0.012 mol. It was confirmed from this result that the IPTES silane coupling agent used in this study provided an efficient contribution to the improvement in interfacial attraction between the organic and inorganic components in the EVOH/SiO<sub>2</sub> hybrid, which resulted in high barrier hybrid possessing morphology with the homogeneous dispersions of nanosized silica, which was confirmed from the SEM observations. However, the addition of IPTES at more than some level of content (0.012 mol in this study) exhibited no more contribution to the increase of the interfacial adhesion between two phases, which resulted in an equilibrium value in the oxygen permeation through the hybrid-coated film. With regard to the optical properties, morphological and topological microstructures, preparation cost, and barrier properties, an optimum range of the IPTES silane coupling agent content (0.006–0.008 mol in this study) was required for addition to the EVOH/SiO<sub>2</sub> hybrid sol during the sol–gel process to obtain a transparent EVOH/SiO<sub>2</sub> hybrid-coated film with high barrier properties.

In addition, the effect of the amount of silica network formed from the TEOS precursor on the permeability of the hybrid-coated film is displayed in Figure 9. For all of the hybrids with different TEOS contents, IPTES was added in the same amount of 0.006 mol, which was established as the optimal content by the previous experimental results. In the range of TEOS contents up to 0.01 mol, the oxygen permeability was dramatically reduced with increasing TEOS content, which was because of the increased amount of the inorganic silica component, possessing superior barrier properties. Furthermore, in the range of TEOS contents from 0.01 to 0.04 mol, the barrier properties of the hybrid-coated films were found to be remarkably enhanced; they exhibited low oxygen permeability (2.54–4.83 cc mm/m<sup>2</sup> 24 h atm). These improved barrier properties were attributable to a stable homogeneous microstructure without microphase separation in the hybrids incorporated with 37.5–70.5 wt % inorganic silica (corresponding to 0.01–0.04 mol of TEOS), which was calculated under the assumption of 100% conversion from the TEOS precursor to the silicate network. On the other hand, an increased oxygen permeability corresponding to poor barrier properties was observed at high levels of TEOS content greater than 0.07 mol (i.e., more than 80.7 wt % silica). It is known that a microcrack in the sol–gel coating layer, within which the silica network is stiff or rigid, can be easily formed by capillary stress generated during the drying process after the coating process.<sup>13,14</sup> The incorporation of the inorganic silica component with an excess amount resulted in microcrack formation in the EVOH/SiO<sub>2</sub> hybrid coating layer positioned on the BOPP substrate because of reduced flexibility. Consequently, the permeability increased because the oxygen molecules easily permeated through these microcracks formed in the coating layer. In



**Figure 9** Oxygen permeability of the EVOH/SiO<sub>2</sub> hybrid coating films as a function of the TEOS content.

addition, the reduction in the barrier properties with excess amounts of the silica component were caused by the lack of interfacial adhesion between the coating layer and the substrate.

### CONCLUSIONS

In this study, the incorporation of EVOH copolymer as an organic component into the inorganic silica phase was attempted to yield hybrid materials with high gas barrier properties with a sol-gel method. The addition of the silane coupling agent IPTES containing functional reactive isocyanate groups resulted in improved phase compatibility in the EVOH/SiO<sub>2</sub> hybrid materials because of the formation of strong covalent bonding between the organic EVOH segments and inorganic silicate network, which was confirmed by FTIR analysis. In particular, EVOH/SiO<sub>2</sub> nanostructured hybrid materials with a homogeneous phase morphology exhibiting no microphase separation and a high degree of transparency were produced by an enhancement in the phase compatibility. In association with the barrier properties, the amount of the silane coupling agent IPTES and the inorganic precursor TEOS used for the preparation of the hybrid sol was revealed to significantly affect the barrier properties of the hybrid-coated films. There existed optimum ranges of IPTES and TEOS contents for obtaining a high barrier hybrid-coated film with a stable homogeneous microstructure and enhanced optical transparency. The existence of optimum ranges in the IPTES and TEOS contents were attributed to the limitation of increasing interfacial attraction between the two phases, despite further addition of IPTES, and microcrack formation at excess contents of TEOS. In conclusion, the barrier properties and optical proper-

ties of the EVOH/SiO<sub>2</sub> hybrid were found to be significantly influenced by the phase microstructure and phase compatibility, which could be controlled by the silane coupling agent added to the hybrid during the sol-gel process.

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