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Characterization of Silica/EVOH Hybrid Coating Materials Prepared by Sol-Gel Method

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Abstract : In this study, the silica-based hybrid material with high barrier property was prepared by incorporating ethylene-vinyl alcohol (EVOH) copolymer, which has been utilized as packaging materials due to its superior gas permeation resistance, during sol-gel process. In preparation of this EVOH/SiO_2 hybrid coating materials, the (3-glycidoxy-propyl)-trimethoxysilane (GPTMS) as a silane coupling agent was employed to promote interfacial adhesion between organic and inorganic phases. As confirmed from FT-IR analysis, the physical interaction between two phases was improved due to the increased hydrogen bonding, resulting in homogeneous microstructure with dispersion of nano-sized silica particles. However, depending on the range of content of added silane coupling agent (GPTMS), micro-phase separated microstructure in the hybrid could be observed due to insufficient interfacial attraction or possibility of polymerization reaction of epoxide ring in GPTMS. The oxygen barrier property of the mono-layer coated BOPP (biaxially oriented polypropylene) film was examined for the hybrids containing various GPTMS contents. Consequently, it is revealed that GPTMS should be used in an optimum level of content to produce the high barrier EVOH/SiO_2 hybrid material with an improved optical transparency and homogeneous phase morphology.

Keywords : sol-gel, EVOH/ SiO_2 hybrid, coating, microstructure, barrier property

1. Introduction

Silica-based hybrid nano materials with high performance have been produced via sol-gel process by combining organic polymer with inorganic silicate at molecular scale. This hybrid materials have been mainly utilized for the application of coating materials to improve gas barrier property of polymer substrate and also to provide various surface characteristics including scratch resistance, antistatic, antipollution, and antifogging properties[1-5]. In particular, among these characteristics, the barrier property has been reported to be remarkably improved due to inorganic silicate network with intrinsic superior barrier property. Therefore, many researches on the improvement of barrier property of the hybrid coated film have been attempted via sol-gel process based on silicon alkoxide as a silicate precursor[6-8]. In preparation of this hybrid

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material with improved barrier property, the organic polymer has been also used due to its remarkable characteristic in the flexibility, tackiness, and formability. It has been known that the organic polymer incorporated with inorganic silicate network can contribute to inhibition of the crack formation within the coating layer during drying process due to stiffness of the silicate network, and also to improvement of the adhesiveness with polymer substrate to be coated.

The organic polymers such as poly(vinyl alcohol), poly(vinylpyrrolidone), and poly(vinyl acetate) have been used to prepare silica-based hybrid coating materials with high barrier property, because these polymers have an ability to form strong physical bonds with the Si-OH groups existed on the surface of the silica particles[9-11]. Among these organic polymers, water soluble PVA resin has shown to be effective organic component to obtain high barrier hybrid materials, since it has high gas permeation resistance property as well as sufficient hydroxyl groups on its segment resulting in hydrogen bonding with silicate network. However, the other polymers have showed some limitations in enhancing the barrier property due to high gas permeation property of themselves.

In this study, ethylene-vinyl alcohol copolymer (EVOH) was used to prepare EVOH/SiO_2 hybrid coating materials for the application of packaging films with barrier characteristic. The semi-crystalline EVOH resin has been widely used for the application of food packaging materials requiring gas barrier due to very high gas permeation resistance[12]. In general, thermoplastic EVOH resin is used to produce a high barrier film as an one-layer occupied in the multi-layer packaging films using co-extrusion process[13].

Therefore, we have studied for the preparation of silica-based hybrid coating materials with enhanced barrier property through sol-gel reaction process by incorporating EVOH resin as an organic component. In our previous study, EVOH/SiO_2 hybrid coating materials was prepared without addition of silane coupling agent[14]. This hybrid materials have shown to be limited in improving property and phase morphology due to weak interfacial bonding between two phases, resulting from insufficient hydroxyl group capable of forming hydrogen bonding on EVOH segments. Consequently, in this study, (3-glycidoxy-propyl)-trimethoxysilane (GPTMS) as a silane coupling agent was employed during sol-gel process to prepare EVOH/SiO_2 hybrid coating materials with improved interfacial adhesion between organic EVOH phase and inorganic silica phase. In addition, the effects of silane coupling agent, GPTMS on the phase morphology, transparency, surface topology, and barrier property of the hybrid materials were investigated.

2. Experimental

2.1 Materials and preparation

Tetraethoxysilane (TEOS, Acros Organics, 98%) and ethylene vinyl alcohol copolymer (EVOH, Kuraray Co., EP F101) were used as the inorganic silicate precursor and organic polymer, respectively. In order to promote interfacial adhesion between inorganic silica and organic EVOH phases, (3-glycidoxy-propyl)-trimethoxysilane (GPTMS, ACROS Organics, 97%) was used as a silane coupling agent. Hydrocholoric acid (HCl, Samchun Chemical, 37 wt%) as an acidic catalyst was added into reactant mixture to derive sol-gel reaction. Biaxially oriented polypropylene (BOPP, Youl Chon Chemical, Ltd.) film with an average thickness of 40 μm, of which surface was already pretreated with corona, was used as the substrate.

The preparation procedure for the

EVOH/SiO_2 hybrid coating sol is as follows: A mixture of TEOS, distilled water, and ethanol with a molar ratio of 1 : 2 : 2 was stirred for 1 hr to partially hydrolyse the TEOS under initial pH condition of 1.0 by adding HCl catalyst. The EVOH solution with a homogeneous dispersion can be prepared by dissolving appropriate amount of crystalline EVOH in a good solvent mixture system, which was composed of water and ethanol with a particular weight ratio. The EVOH resin was modified by adding the coupling agents of GPTMS into the obtained homogenized EVOH solution followed by stirring for 3 hr at elevated temperature of 60℃. The partially hydrolysed TEOS sol and EVOH solution modified with a GPTMS were then combined and stirred vigorously for 2 hr at room temperature to yield EVOH/SiO_2 hybrid coating sols with various compositions. The contents of silane coupling agent of GPTMS added into hybrids were varied as 0.002, 0.004, 0.006, 0.008, 0.012, 0.015 mol. Meanwhile, the amount of inorganic silicate precursor, TEOS, was fixed at 0.04 mol in all hybrid samples.

This prepared hybrid coating sols were used to coat the BOPP substrate by spin coater (KW-4A). The rotation speed and coating time were 6000 rpm and 30 sec, respectively. The hybrid coated films were dried at 60℃ for 24h in a convection-type drying oven. The hybrid gels were also prepared by casting the hybrid sols onto Petri-dishes on which polyimide film was placed, and then via gelling and ageing process for 15 days at room temperature. The experimental procedure for the preparation of EVOH/SiO_2 hybrid coated films and hybrid gels is shown in Fig. 1.

2.2 Characterization

The oxygen permeability of the coated film was measured by permeation apparatus, which was designed and made according to the standard method of ASTM D3985 in our laboratory. The detailed descriptions of the apparatus and experimental measurements were presented elsewhere[15,16]. Infrared spectra for the hybrid were obtained with a

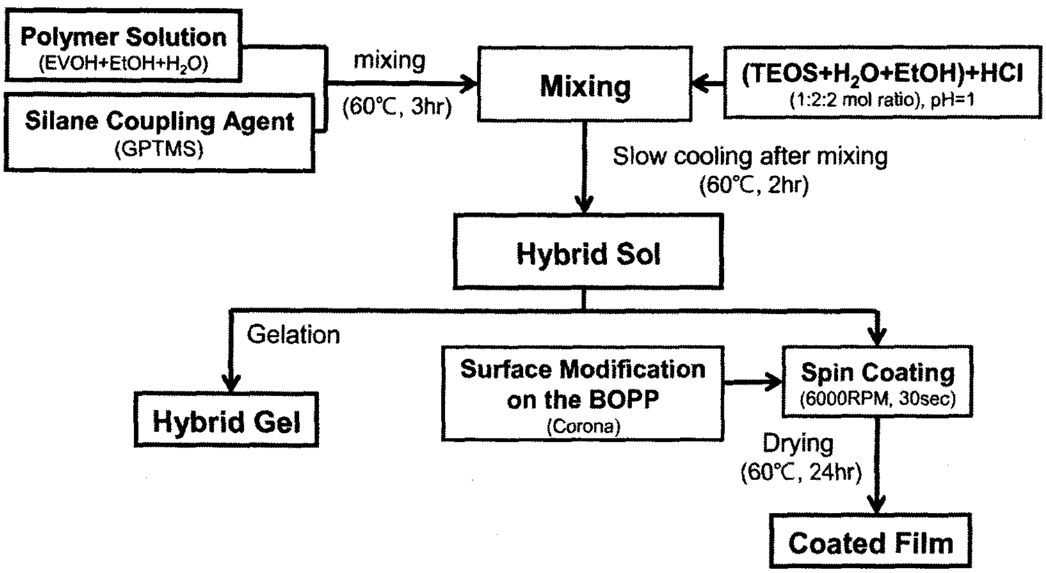


Fig. 1. Experimental procedure for the preparation of EVOH/SiO_2 hybrid gel and coated film using GPTMS coupling agent.

FT-IR spectrometer(JASCO-430). The morphology of fractured surfaces of the hybrid materials were observed by field-emission scanning electron microscope (FE-SEM, JSM-6700A). The surface topologies of the hybrid materials were examined by atomic force microscope (AFM; Nanoscope 3100) in the contact mode with being focused on the micro-domain of 1 ㎛ x 1 ㎛. The photographs for 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 uv-visible spectrometer (UV-VIS, 2120 UV plus) was used to examine the transparency of the hybrid coating film.

3. Results and Discussion

3.1. FT-IR analysis

In order to produce the hybrid materials with enhanced property, the phase interaction between organic and inorganic phase has been recognized as a crucial variable. In this study, therefore, the silane coupling agent GPTMS was employed to induce the interfacial adhesion between EVOH resin and silicate network formed via sol-gel reaction process, resulting in high performance hybrid nano materials with improved homogeneous microstructure. Fig. 2 shows the measured FT-IR spectra of the EVOH/SiO_2 hybrid gel with various GPTMS contents. As shown in the figure, the characteristic broad peak of hydroxyl group from silanol group (Si-OH) of silica and unit of vinyl alcohol of EVOH copolymer appeared at 3434 cm^{-1}. This peak was observed to be shifted gradually to the regime of low wavenumber (3434 cm^{-1} ~ 3415 cm^{-1}) as the GPTMS content in the hybrid gel increased. This chemical shift may be attributable to the additional formation of hydrogen bonding between epoxide functional group of GPTMS and vinyl alcohol group in the EVOH copolymer. The expected physical hydrogen bonding between GPTMS silane coupling agent and EVOH resin is described in Fig. 3. The overall hydrogen bonding formed in the hybrid was intensified due to this additionally formed hydrogen bonding. Therefore, it is confirmed that the increase of GPTMS content can induce the increase of degree of hydrogen bonding, leading to improved phase compatibility in the EVOH/SiO_2 hybrids.

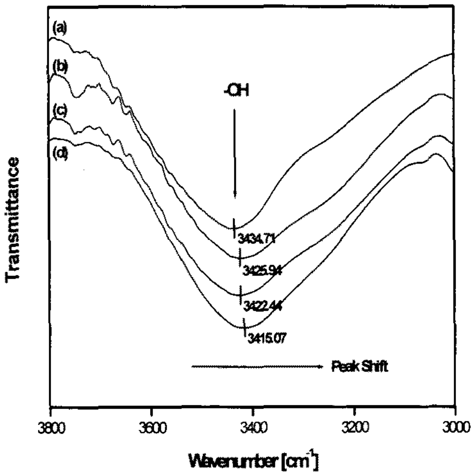


Fig. 2. FT IR spectra of the EVOH/SiO_2 hybrids with various GPTMS contents of (a) 0 mol, (b) 0.004 mol, (c) 0.008 mol, and (d) 0.015 mol.

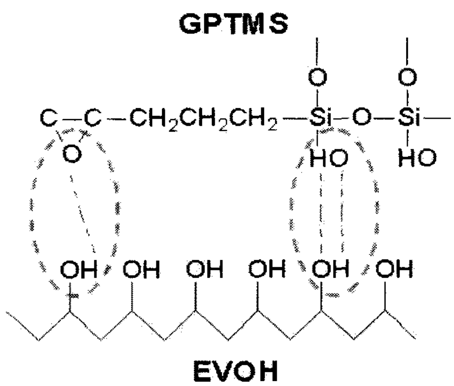


Fig. 3. The physical interfacial bonding in the EVOH resin modified with GPTMS.

3.2 Morphology and surface topology

The improved phase attraction between organic and inorganic component affects greatly the formation of homogeneous morphology of the hybrid materials, leading to enhanced optical, thermal, mechanical, and barrier properties. In this study, the phase morphology of the fractured hybrid gels was observed to evaluate the phase interaction that is associated with the occurrence of microphase separation in the hybrid system. Fig. 4 shows the micrographs taken with FE-SEM for the EVOH/SiO_2 hybrid gels containing various GPTMS contents. As shown in the micrographs, a high degree of phase separation was observed for the hybrid gels without addition of GPTMS or with low content of 0.002 mol. On the other hand, it can be seen that homogeneous microstructure with finely dispersed silica particles is generated in the case of hybrid gel with 0.006 mol of GPTMS. This may be ascribed to the increased degree of hydrogen bonding between organic EVOH resin and inorganic silicate network in the hybrid containing GPTMS at more than 0.006 mol. However, when GPTMS at content lower than 0.006 mol was added, heterogeneous microstructure exhibiting microphase separation was observed due to insufficient physical attraction between two phases, as shown in Fig. 4 (a-c).

Fig. 5 displays the AFM images of the surface topology for the pure BOPP substrate and films coated by pure silica and EVOH/SiO_2 hybrid without coupling agent and that containing 0.006 mol of GPTMS. The RMS value, which is a measure of surface roughness, for the pure BOPP substrate was found to be relatively high as

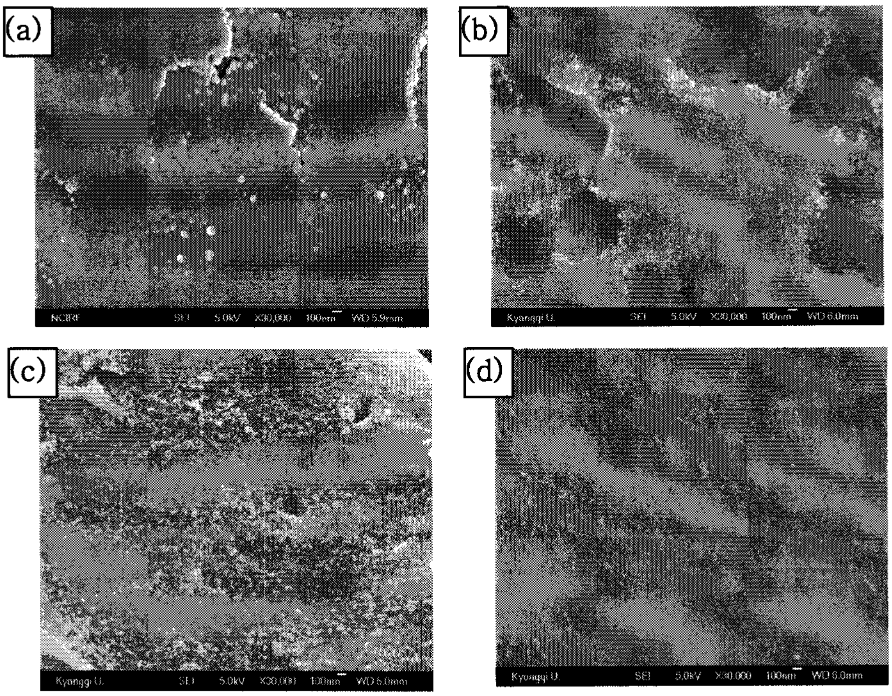


Fig. 4. Phase morphology of the EVOH/SiO_2 hybrids with various GPTMS contents of (a) 0 mol, (b) 0.002 mol, (c) 0.004 mol, and (d) 0.006 mol.

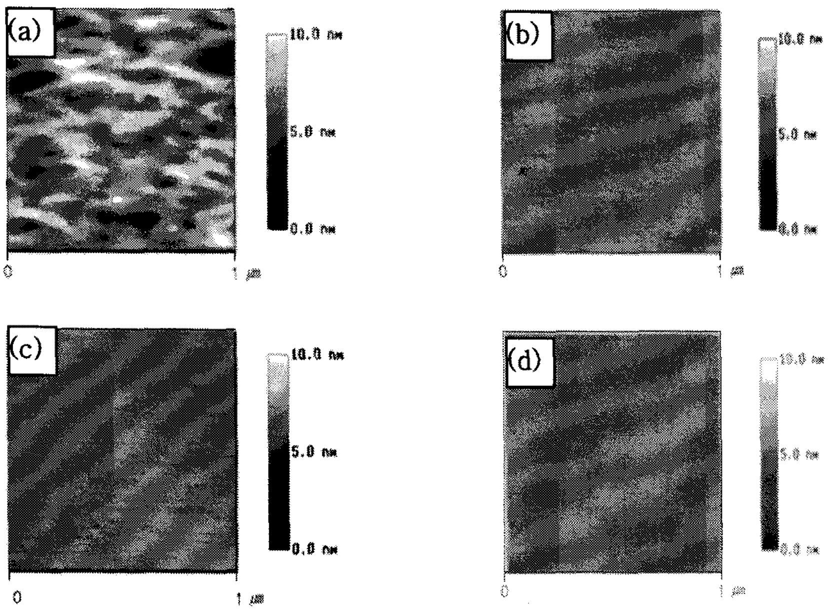


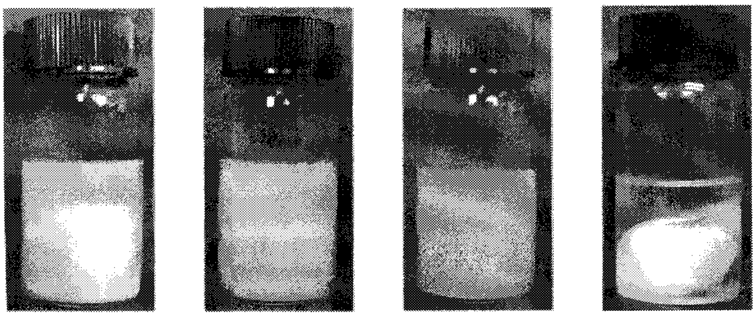
Fig. 5. Surface topology of (a) BOPP substrate, (b) pure silica coated film, and films coated by EVOH/SiO_2 hybrid with GPTMS content of (c) 0 mol and (d) 0.006 mol.

3.41nm due to a large number of pinholes and channels formed during film extrusion processing. However, remarkable reduction in the RMS value was observed by coating on the surface of the BOPP substrate with EVOH/SiO_2 hybrid sols. The RMS value of hybrid without addition of silane coupling agent was measured to be 0.35 nm, while that of hybrid with addition of GPTMS was slightly reduced to a value of 0.25 nm. This improvement in surface smoothness may be attributed to the efficient packing into micro-pinholes and channels existing on the surface of pure BOPP substrate by the stable hybrid sols with dispersion of nano-sized silica particles.

3.3. Optical transparency of hybrids

In this study, the phase interaction in the hybrid was also evaluated by investigating the optical transparency of the hybrid materials. In general, the optical transparency of hybrid material is associated with the state of phase morphology which is prominently governed by the degree of microphase separation. In the hybrid nano material system without microphase separation, a high degree of transparency can be obtained due to uniformly dispersed silica particle with nano-scale dimension, while phase-separated microstructure results in translucent or opaque hybrids due to micrometer scale domain size of the silica cluster dispersed in the matrix.

Fig. 6 shows the pictures, which were taken with digital camera, displaying the state of the EVOH/SiO_2 hybrid gels with different GPTMS contents. These hybrid gels were prepared through gelation and ageing process involving continuing physical and chemical changes from hybrid sols. As shown in the figure, the optical transparency of the hybrid gel was improved as the added GPTMS content was increased from 0 mol to



(a) (b) (c) (d)

Fig. 6. Digital photographs showing the state of the EVOH/SiO_2 hybrids gels with different GPTMS contents of (a) 0 mol, (b) 0.002 mol, (c) 0.006 mol, and (d) 0.015 mol.

0.006 mol. However, when GPTMS was added in the excess amount of 0.015 mol, phase-separated gel state was observed in the hybrid gel. It can be deduced that excess amount of GPTMS can cause polymerization reaction of epoxide ring contained in the GPTMS, resulting in occurrence of microphase separation in the hybrid due to the solubility difference between formed epoxy resin and dissolved EVOH molecules. It should be noted that although the GPTMS was added in the optimal content, the transparent hybrid gel could not be obtained, implying that there is limitation in enhancing the phase attraction between two phases in the hybrid system only with physical interaction such as hydrogen bonding.

Fig. 7 represents the measured light transmittance as a function of visible light wavelength for the films coated by hybrid with different GPTMS contents. As expected, the trend of transparency variation of the hybrid gel with various GPTMS content was reflected in this result for the coated film. It can be seen that low degree of transparency was observed for all coated films, furthermore the light transmittance rate of the film coated by hybrid containing optimal GPTMS content of 0.006 mol was also measured to be lower than 76 % in all visible light range of 400 - 700 nm.

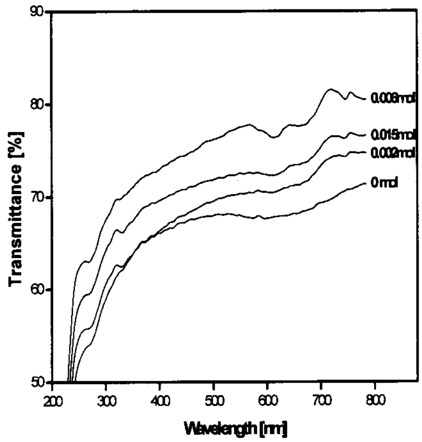


Fig. 7. Light transmittance of films coated with EVOH/SiO_2 hybrids containing various GPTMS contents.

3.4 Oxygen barrier property

In order to produce mono-layer coated BOPP film with improved gas barrier property, EVOH/SiO_2 hybrid materials prepared through sol-gel process were used as a coating sols. The gas barrier property of the coated film was evaluated in terms of measured oxygen permeability. The relationship between barrier property of hybrid coated film and composition of hybrid sol was investigated in association with morphological property and optical transparency. Fig. 8 represents the measured oxygen permeability of the hybrid coated film with varying IPTES content. The permeability unit (ccmm/$m^2$24hatm) means the oxygen gas volume (cc) permeated through the coated film with an effective area of m^2 and thickness of mm for 24h under the pressure difference of 1 atm. As displayed in the figure, the oxygen permeability is reduced as the GPTMS content is increased up to 0.006 mol, which may be due to the regular arrangement of nano-sized silica particles caused by enhanced interfacial attraction between organic and inorganic phase. At more than 0.006 mol of GPTMS content, however, the permeation behavior is reversed, i.e. oxygen permeability is increased with increasing of GPTMS content. This permeation behavior can be evidenced by optical transmittance of hybrid gel and coated film as presented previously. The addition of GPTMS with

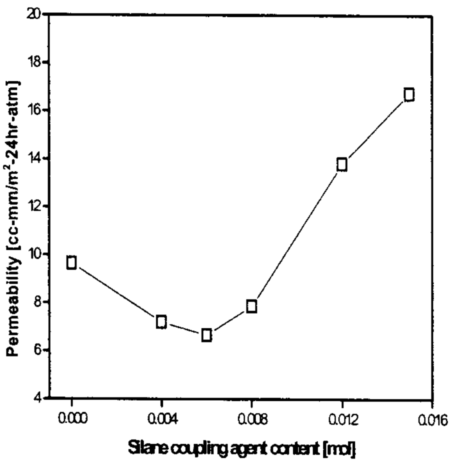


Fig. 8. Oxygen permeability of the EVOH/SiO_2 hybrid coating films as a function of GPTMS contents.

excess amount into hybrid sol yields a hybrid with phase separated microstructure, ultimately resulting in poor barrier property of the coated film. It was revealed from this result that there existed an optimal content of GPTMS silane coupling agent (0.006 mol in this study) to obtain EVOH/SiO_2 hybrid coated film with improved barrier property.

4. Conclusions

Using sol-gel method, silica-based hybrid materials was prepared by incorporating ethylene-vinyl alcohol (EVOH) copolymer as an organic component. Addition of silane coupling agent, GPTMS, containing functional epoxide ring contributed to the enhancement of interfacial interaction between organic EVOH phase and inorganic silica phase in the hybrid due to increased extent of physical hydrogen bonding between two phases. The occurrence of additional hydrogen bonding was confirmed by the measured FT-IR spectra. In addition, GPTMS used in this study influenced significantly the phase microstructure as well as optical property of the nano-structured hybrid materials. The generation of micro-phase separation phenomena in the EVOH/SiO_2 hybrid was found to be dependent on the content of silane coupling agent added into the hybrids. The hybrid coated film with an improved barrier property could be obtained by using silane coupling agent, GPTMS, in an optimal level content, exhibiting homogeneous phase morphology without micro-phase separation.

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