실리카/EVOH 하이브리드 나노 물질의 상 미세구조

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Phase Microstructure of Silica/EVOH Hybrid Nano Materials

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1. Introduction

In current, organic-inorganic hybrid coating on polymer substrate film has been attempted to improve the barrier property due to inorganic silicate network and to provide various surface characteristics like abrasion resistance, antistatic, antiadhesive, and antifogging properties through chemical functionalization of coating materials.[1,2] The incorporation of organic polymer into the inorganic silicate network may prevent the crack formation of the coating layer during gelling process due to increased flexibility, and also provide the function of organic polymer itself. Organic-inorganic hybrid coatings on various polymer films for obtaining high gas barrier property have been reported.[1,3,4] These researches have been performed using poly(vinyl alcohol), poly(vinylpyrrolidone), and poly(vinyl acetate) as the organic polymer since these polymers have an ability to form hydrogen bonds with the silanol groups of the silicate network, and also to form a homogeneous solution with silica precursors.[5] In this study, the incorporation of ethylene-vinyl alcohol copolymer(EVOH) as the organic component into silica network was attempted to prepare organic-inorganic hybrid coating solution through sol-gel method. The EVOH with high resistance to the permeation of oxygen molecules has been utilized as high barrier polymer for the application of packaging materials.[6] In addition, the various kinds of silane coupling agent such as vinyltriethoxysilane(VTES), ɣ-glycidoxypropyltrimethoxysilane(GPTMS), 3-aminopropyl-triethoxysilane(APTES) have been used to enhance the interaction between organic segments and the inorganic network.[7,8] In this work, 3-isocyanatopropyltriethoxysilane (IPTES) as the coupling agent was added into coating solutions to obtain transparent hybrid gels without phase separation by enhancing interfacial adhesion between organic and inorganic phases via strong chemical bonds. The microstructure of the hybrid silica/EVOH materials prepared by sol-gel method was investigated by varying the IPTES content.

2. Experimental

Tetraethoxyothosilicate(TEOS) was used as an inorganic silicate precursor. Ethylene-vinyl alcohol copolymer (EVOH, EP-F101), obtained from Kuraray Co., was used as an organic polymer. A mixture of TEOS, distilled water, and ethyl alcohol was stirred for 1 hr to hydrolyse the TEOS 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. Certain amount of of EVOH was thoroughly dissolved in a mixture of water and EtOH with appropriate composition. The modified EVOH solution was prepared by adding the IPTES coupling agent into the EVOH solution followed by stirring for 3 hr at 60℃. This modified EVOH solution was mixed with the partially hydrolysed TEOS sol and then the mixture was stirred for 2 hr at room temperature to produce silica/EVOH hybrid nanocomposites. The obtained sol was cast onto Petri dishes covered with polyimide film and dried for 10 days at room temperature. The filter was covered on gels to prevent contamination from impurities in the air. The samples were dried in a vacuum oven at 60 ℃ for 24 hr prior to instrumental measurements.

Fourier transform infrared spectroscopy(FT-IR, JASCO-430) was used to examine the bonding mechanism via reaction between EVOH and IPTES, which ultimately affect the interaction between two phases. The sample was prepared by KBr dilution. The ratio of KBr to gel was 200. The morphology of hybrid composite was observed by Field-Emission Scanning Electron Microscopy(FE-SEM, JSM-6700A). The transparency of the hybrid coating film was examined by UV-visible spectrometer in the visible-light wavelength range of 200-800 nm.

3. Results and Discussion

For the preparation of hybrid materials with improved performance, one of the major variables is to control the phase separation between organic and inorganic phases. The phase behavior affecting the performance of the hybrid materials depends greatly on the interaction between organic and inorganic components. Thus some research has been conducted to enhance the compatibility between two phases by employing silane coupling agents. We have reported the preparation of silica/EVOH system by using γ-glycidoxypropyltrimethoxysilane(GPTMS) as a coupling agent to obtain the hybrid materials with improved compatibility.[9] But, the GPTMS has a limitation in enhancing the adhesion between EVOH segments and silicate network, because it induces only hydrogen bonding between epoxide group of GPTMS and hydroxyl group of EVOH. In this work, therefore, the addition of IPTES was attempted to enhance the compatibility efficiently via the formation of covalent bonding between organic EVOH and inorganic silica network.

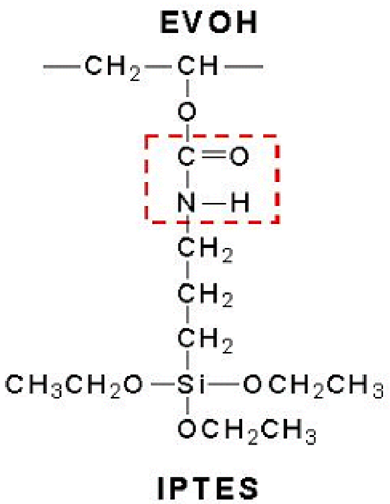


Fig. 1 The modified EVOH prepared by reaction with IPTES.

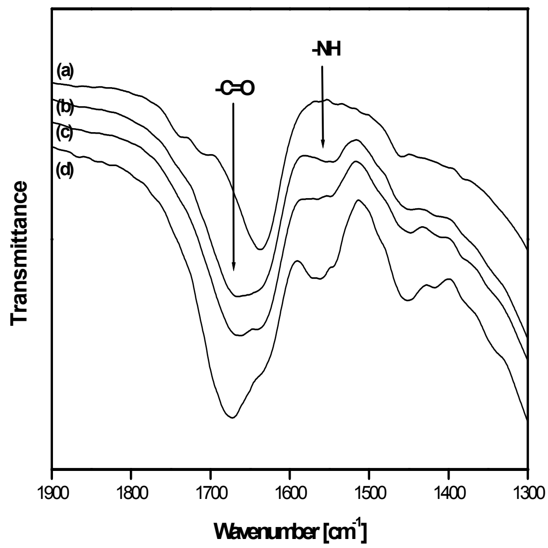
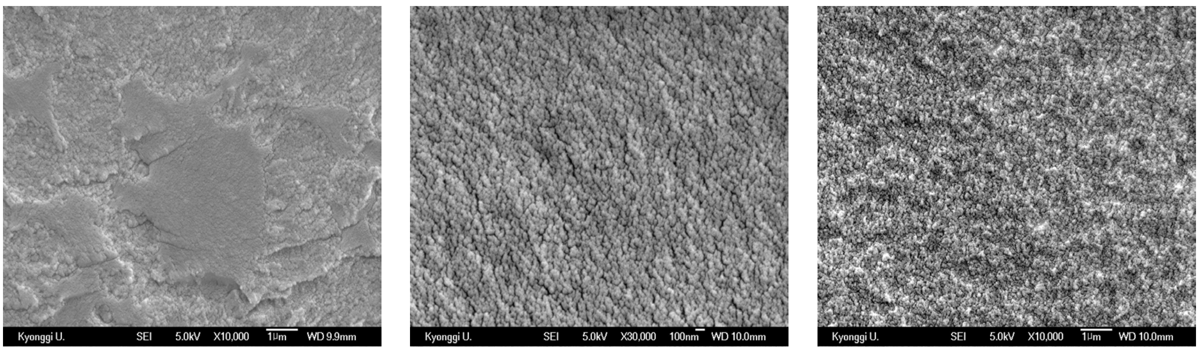


Fig. 2 FT-IR spectra of silica/EVOH hybrid gel with IPTES contents of (a)0 mol, (b)0.004 mol, (c)0.006 mol, (d)0.012 mol.

The modified EVOH as shown in Fig. 1 represents the formation of covalent bonding between hydroxyl group of EVOH and isocyanate group of IPTES through chemical reaction.

The FT-IR spectrum of the prepared silica/IPTES/EVOH hybrid gel is shown in Fig. 2. The characteristic bands of amide appeared at 1675 cm-1 for carbonyl(C=O) unit and at 1540 cm-1 for amine(-NH). This FT-IR results reveals that EVOH resin has reacted with 3-isocyanatopropyltriethoxysilane(IPTES), resulting in strong interaction adhesion between organic EVOH phase and inorganic silica network.

The compatibility of organic polymer and inorganic silica phase greatly influences mechanical, barrier, optical properties, and phase morphology of 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. Fig. 3 is the field-emission scanning electron microscopy(FE-SEM) photographs of the hybrid gel samples with various IPTES contents. With little IPTES content of 0.003 mol, a slight microphase separation can be observed from the photograph, furthermore, there existed a severe phase separation without IPTES (not shown in the figure). However, for the hybrid gel samples with IPTES content of 0.006 mol (Fig. 3-b), no phase separation occurred and the surface was very smooth. In addition, it was confirmed that silica/EVOH hybrid gel with more stable and finer phase morphology could be produced if IPTES with amount of 0.06 mol was added. The micro or macro phase separation could be prevented by enhancing the compatibility of the silica/EVOH hybrid materials via incorporating silane coupling agent capable of inducing covalent bonding. However, with excess contents of IPTES above 0.012 mol, a slight microphase separation was observed. This phenomena might be due to the cluster formation resulting from chemical reaction between isocyanate group of IPTES and hydroxyl group of silanol.



(a) (b) (c)

Figure. 3. Phase morphology of silica/EVOH hybrid gel with IPTES contents of (a) 0.003mol, (b) 0.006mol, (c) 0.012mol

The phase morphology or degree of phase separation influences greatly the transparency of hybrid materials. Fig. 4 shows the relative light transmission as a function of light wavelength for various IPTES contents in the hybrid thin films. As shown in this figure, light transmission through the film is increased up to IPTES content of 0.006 mol, and then decreased after 0.006 mol. This result for transparency is found to be matched with the result of morphological analysis. From these results, we can confirm 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.

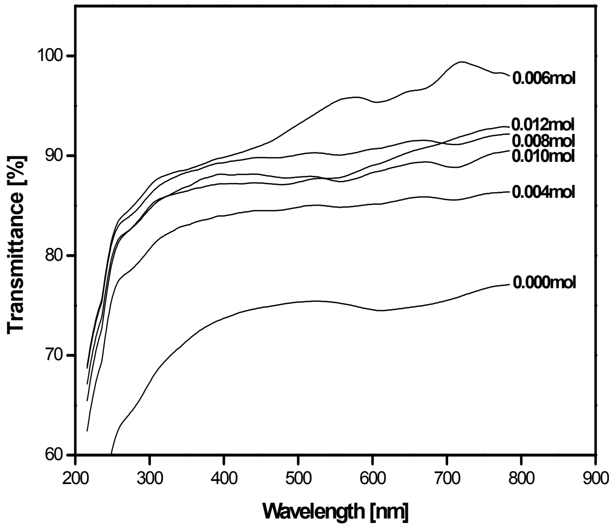


Figure. 4. Light transmission of silica/EVOH hybrid coating film prepared by various IPTES contents

4. Conclusion

Silica/EVOH hybrid nano-materials with well-controlled phase morphology could be produced by employing IPTES as a silane coupling agent. The formation of covalent bonding in the modified EVOH was confirmed from FT-IR measurements. It was revealed that there existed an optimum level of silane coupling agent(IPTES) content to obtain organic-inorganic hybrid nanocomposites with improved phase morphology and transparency.

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