

Preparation and Properties of Poly(vinyl alcohol)/Vinyltrimethoxysilane (PVA/VTMS) Hybrid Films with Enhanced Thermal Stability and Oxygen Barrier Properties

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Abstract: To enhance the thermal stability and barrier properties of pure poly(vinyl alcohol) (PVA), a series of poly(vinyl alcohol)/vinyltrimethoxysilane (PVA/VTMS) hybrid films were prepared *via* a sol-gel process, and their physical properties were investigated as a function of VTMS content. During the sol-gel process, simultaneous reactions between hydroxyl groups of PVA and silanol groups of hydrolyzed VTMS and self-condensation of VTMS occurred, inducing a cross-linked network structure and greatly enhanced thermal stability and oxygen barrier properties. The glass transition temperature and thermal decomposition temperature ($T_{5\%}$) of the PVA/VTMS hybrid films increased from 72.6 to 84.3 °C and 273.6 to 342.2 °C, respectively, with increasing VTMS content from 0 to 20%. Oxygen transmission rates of the hybrid films decreased from 6.12 to 0.17 cm³/m²×day, and those of the hybrid films incorporating 5%, 10%, and 20% VTMS were suppressed by 65.7%, 95.6%, and 97.2%, respectively, versus a pure PVA film. These are dependent on the chemical structure and morphology of the films with differing initial amounts of VTMS. The chemical affinity for water, intermolecular packing, and rigidity in polymer chains increased with increasing cross-linking by VTMS, leading to enhanced oxygen barrier properties and thermal stability in the PVA/VTMS hybrid films.

Keywords: poly(vinyl alcohol) (PVA), sol-gel process, vinyltrimethoxysilane (VTMS), hybrid films, chemical structure, morphology.

Introduction

Poly(vinyl alcohol) (PVA) is a water-soluble synthetic polymer with high hydrophilicity and biocompatibility and is nontoxic.¹⁻⁵ Furthermore, PVA possesses not only excellent transparency in the visible range but also good barrier properties to oxygen.³ It also has excellent film-forming, emulsifying, and adhesive properties, which makes it useful in various industrial fields where it finds applications in paper-coating agents, textile sizings, adhesives, carriers in drug delivery, and as a component of biomedical and flexible packaging films.¹ However, its poor resistance to water molecules, originating from hydroxyl groups in the repeating unit of PVA, restricts its use in many applications.^{1-4,6} Most recently, PVA-based organic-inorganic hybrid films have been developed to improve PVA's properties and further explore its applications.¹⁻⁷ Most PVA-based hybrid films are prepared by the exfoliation and/or intercalation of clay,^{2,3} and by the sol-gel method using silane-coupling agents such as Si(OR)₄ or RSi(OR')₃ in the PVA matrix.⁴⁻⁷ These PVA/silica hybrid materials pre-

pared *via* a sol-gel method have yielded fascinating properties such as abrasion resistance, antistatic and antifogging properties, barrier properties, and permselectivity; further, they have been used as coating materials on polymeric substrates and hybrid films in a wide variety of industrial areas.⁴⁻⁹

However, the key issue for preparing organic-inorganic hybrid films is preventing aggregation while uniformly dispersing inorganic particles in a polymer matrix.^{2,4,5,8} Specifically, the sol-gel process in a PVA matrix offers the possibility of combining organic components with inorganic materials at molecular or nanometer levels by covalent or hydrogen bonding.^{4,9} This bonding between hydroxyl groups of PVA and silanol groups of hydrolyzed Si(OR)₄ or RSi(OR')₃ can effectively produce new materials having the advantages of organic materials, such as light weight, flexibility, and good film formability, as well as those of inorganic materials, such as high strength, barrier properties and chemical resistance. It is well known that the physical properties and applications of hybrid materials are strongly dependent on changes in the chemical structure and morphology, originating from the composition.^{2,4,10-13}

To develop PVA/silica hybrid films with good thermal stability and enhanced gas barrier properties of the PVA, vinyltri-

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methoxysilane (VTMS) as a silane precursor was inserted into the PVA matrix, resulting in the formation of poly(vinyl alcohol)/vinyltrimethoxysilane (PVA/VTMS) hybrid films. The chemical structure, morphology, and physical properties of these films were characterized by Fourier transform infrared (FTIR) spectroscopy, contact angle, wide-angle X-ray diffraction (WAXD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), oxygen transmission rate (OTR) studies, and water resistance pressure analysis.

Experimental

PVA/VTMS Hybrid Films. For the formation of the PVA/VTMS hybrid films, fully hydrolyzed PVA F-17A (98.0-99.5% degree of hydrolysis) was supplied by OCI Co., Ltd. (Incheon, Korea). VTMS and hydrochloric acid (HCl) were purchased from Aldrich Chemical Co. and were used without further purification. First, PVA (2 g) was dissolved in deionized water (50 g) with stirring at 90 °C for 5 h to give a PVA solution, and then the solution was cooled to room temperature. VTMS in various amounts of 0-20 wt% was added to the PVA solution under stirring. HCl was added into the resulting solution followed by additional stirring for 2 h. Then, each mixture solution was bar-coated onto a glass substrate using a bar-typed automatic films coating apparatus (KIPAE E&T Co., Ltd., Hwasung, Korea) that can accurately control film thickness and velocity. This provided the PVA/VTMS hybrid films with uniform thickness on the glass substrate. The coated films were dried in a vacuum oven at 80 °C for 24 h. The film thickness was maintained at about 60±1 μm to aid in evaluating the physical properties.

Characterization. To characterize the chemical structure of the PVA/VTMS hybrid films, FTIR spectra were recorded on a Spectrum 65 FTIR spectrometer (Perkin Elmer Co. Ltd., Massachusetts, USA) from 400 to 4000 cm⁻¹ using attenuated total reflection (ATR) mode. UV-visible spectra of the hybrid films were recorded with a single-beam OPTIZEN 2120UV spectrometer (Mecasys Co., Daejeon, Korea) in the range of 200 to 800 nm, and a blank glass plate was employed as a reference. To determine morphologies and topologies of the hybrid films, WAXD and SEM analyses were used. To identify the crystalline structure in the hybrid films and the dispersed state over a fairly large sample volume, WAXD patterns were collected on a D/MAX-2500H X-ray diffractometer (Rigaku Co. Ltd., Tokyo, Japan) with a nickel-filtered CuK_α (λ=1.5406 Å) radiation source. The radiation source was operated at 40 kV and 45 mA, and data were collected in the 2θ range from 2° to 60° at 0.02° intervals with a scan speed of 1.0°/min.

The top and fractured surfaces of the PVA/VTMS hybrid films were obtained using a Quanta 250 SEM (FEI Co. Ltd., Oregon, USA). The dispersion of silica particles on the external surface of the PVA/VTMS hybrid films was observed using a map scan spectrum of the energy dispersion of X-rays (EDX)

for the hybrid films, recorded in an Oxford EDX system.

The thermal properties of the PVA/VTMS hybrid films were investigated using a TGA 4000 thermogravimetric analyzer (Perkin Elmer Co. Ltd., Massachusetts, USA) and a Q10 differential scanning calorimeter (TA Instrument Co. Ltd., Delaware, USA). All of the thermal properties were measured under a nitrogen atmosphere, and the heating rate was 10 °C/min for TGA and 20 °C/min for DSC.

Oxygen transmission rates (OTRs) of the PVA/VTMS hybrid films were measured with an OTR 8001 oxygen permeability tester (Systech Instruments Co. Ltd., Illinois, USA) at 23 °C and 0% relative humidity. The water-resistance pressure (mm) tests of the PVA/VTMS hybrid films were carried out according to a conventional method.¹⁴ Sample films were made in a round shape with a diameter of 30 mm and then used to seal the mouth of a long round tube with graduations in millimeters (tube diameter: 8 mm). After the tube mouth was sealed with the film, it was filled drop-wise with deionized water. As soon as the deionized water permeated through the film, the height of the water column was recorded.

Contact angles and surface energies of the PVA/VTMS hybrid films were measured using a Phoenix 300 contact angle goniometer (SEO Co. Ltd., Suwon, Korea). The sessile drop method was used with deionized water and methylene iodide as proving liquids. A droplet of each water and methylene iodide was gently placed on the film and observed through the eyepiece by applying the θ/2 method. The contact angles of five drops were averaged, and surface energies by the harmonic-mean equation were calculated using the contact angles for water and methylene iodide on the PVA/VTMS hybrid film.^{15,16}

Results and Discussion

In preparing the hybrid films, VTMS was first hydrolyzed in the presence of water and acid catalyst to produce transitional VTMS silanols.^{4,5,7,9} Then, these unstable and highly reactive silanol molecules were subjected to a condensation reaction with the hydroxyl groups on the PVA chains to form cross-linking bridges of Si-O-C, resulting in the formation of the PVA/VTMS hybrid films. In addition, the silanol molecules may simultaneously undergo a self-condensation reaction to form Si-O-Si bonds.^{4,5,7,9} All of these will lead to the formation of a cross-linking network in the PVA matrix, restricting the mobility of PVA and altering the physical properties of the hybrid films. The proposed reaction scheme is depicted in Figure 1 and was confirmed *via* FTIR spectra.

Figure 2(a) and (b) shows the spectra of a pure PVA film and the PVA/VTMS hybrid films containing 5 and 20 wt% VTMS. The peak around 1595 cm⁻¹ is characteristic of the C=C groups of VTMS. Peaks at 971 cm⁻¹ originated from the stretching of Si-O-C bonds, confirming the formation of a Si-O-C cross-linking network between the hydroxyl groups of PVA chains and the silanol groups of hydrolyzed VTMS.^{5,9}

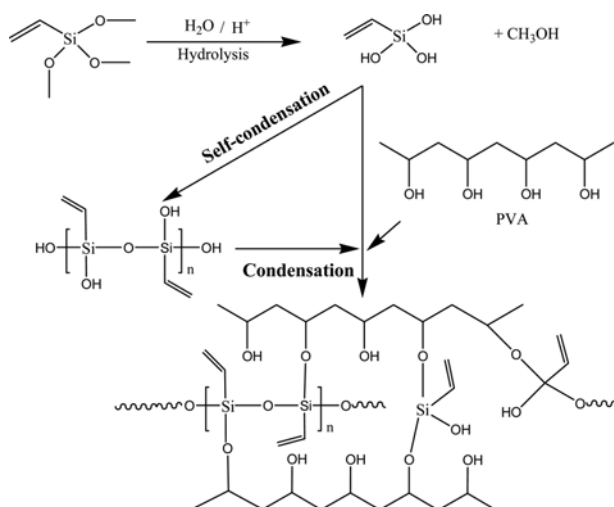


Figure 1. Condensation reaction scheme for the PVA/VTMS hybrid films.

With increasing VTMS content, the peak at 1012 cm^{-1} associated with the stretching of Si-O-Si bonds increased, indicating the self-condensation reaction of silanol groups.^{5,7} A characteristic strong and broad band appeared around 3300 cm^{-1} in the PVA spectra, corresponding to -OH stretching vibrations of the hydroxyl groups; this peak slightly decreased in intensity with increasing VTMS content. This indicates that the hydrophobicity of PVA slightly increased both by the condensation reaction between the -OH groups in PVA and the silanol groups in hydrolyzed VTMS, and by the self-condensation reaction in silanol groups of VTMS, both of which form covalent cross-links between polymer segments.¹⁷

Film Morphology. The morphology of the PVA/VTMS hybrid films was characterized using WAXD, as shown in Figure 3. Pure PVA showed a strong diffraction peak located on the broad halo in the range of $2\theta=15^\circ\text{-}25^\circ$, which indicates that PVA is a semi-crystalline polymer. For the pure PVA, one diffraction peak for an orthorhombic lattice centered at $2\theta=19.5^\circ$ can be attributed to PVA (101) reflection, corresponding to a mean intermolecular distance of 4.57 \AA calculated using Bragg's law.^{5,18} Another diffraction peak with low intensity was found at about $2\theta=40.5^\circ$, indicating the presence of PVA (220) reflection. All of the PVA/VTMS hybrid films showed similar patterns with PVA, and the peak intensity of $2\theta=19.5^\circ$ decreased with the introduction of VTMS into PVA.^{5,18,19} This indicates that the network structure formed between VTMS and hydroxyl groups of PVA prevents the formation of crystalline regions in the PVA matrix, leading to a decrease in the degree of crystallinity in PVA. With increasing VTMS content, however, a new peak at around 10° appeared and appeared to increase with VTMS content. This indicates the presence of new structural ordering with a spacing of about 9.6 nm in the PVA/VTMS hybrid films by VTMS. This structural ordering is attributed to the intermolecular spacing of the silsesquioxane components with a mixture of cage and

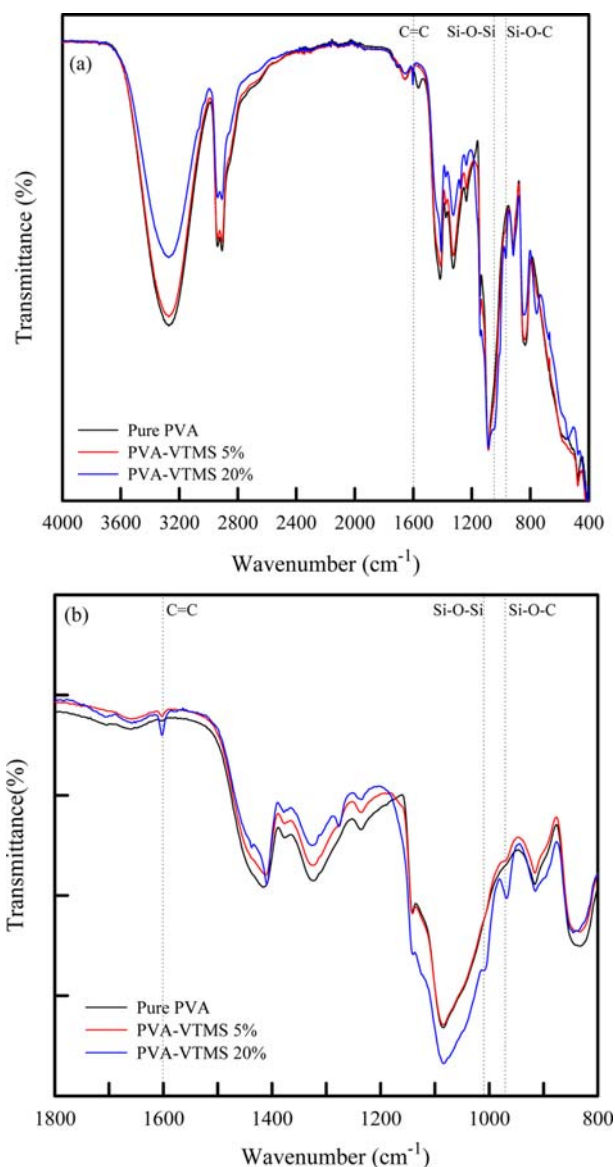


Figure 2. (a) FTIR spectra of pure PVA film and PVA/VTMS hybrid films. (b) FTIR spectra from 800 to 1800 cm^{-1} of pure PVA film and PVA/VTMS hybrid film.

ladder-like structures, which are produced by the self-condensation reaction of silanols in hydrolyzed VTMS.^{5,7,20} The quantity of silsesquioxane components increased with increasing VTMS content. This intermolecular ordering may lead to enhancements in physical properties such as thermal stability and barrier properties at a relatively high content of VTMS.

Figure 4 shows SEM images of the top and fractured surfaces of the PVA-VTMS hybrid films with different VTMS content. The pure PVA exhibited a smooth and homogeneous top surface, while the hybrid films with more than 5% VTMS contained some particulates, which increased with increasing VTMS content. For the fractured surfaces, pure PVA showed a slightly uneven surface, while the hybrid films with rela-

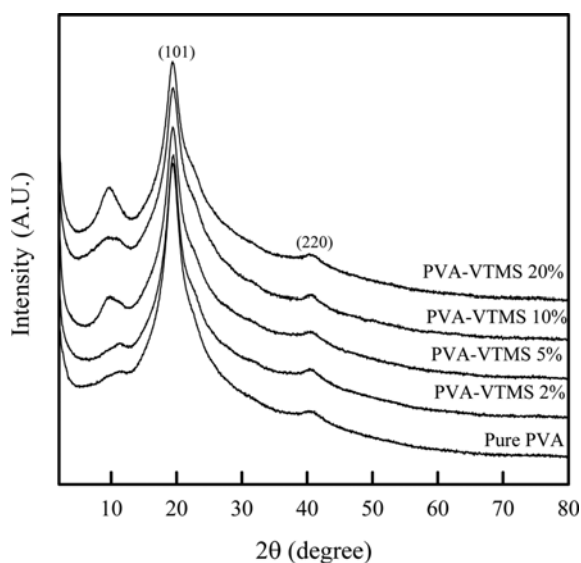


Figure 3. WAXD curves of the PVA-VTMS hybrid films.

tively high VTMS content had some cavities and a rough surface. This SEM result indicates that the compatibility between PVA and VTMS was quite good at relatively low VTMS con-

tent due to chemical bonds and strong chemical interactions formed between PVA and VTMS. However, some particulates formed on the surface, and some cavities in the inner matrix of the hybrid films were observed at high VTMS content. Most likely the self-condensation of VTMS silanols leads to particulate formation at a high VTMS content.^{5,9} The EDX mapping spectra presented in Figure 5 show the dispersion-aggregation phenomenon of silica on the external surface of PVA/VTMS hybrid films. The white color spots over the dark background indicate the location of silicon (Si) atoms in the PVA matrix. As expected, a PVA/VTMS 2% hybrid film showed the lowest silica content and the largest average distance between these spots. With increasing VTMS content, the number of spots increased and the average distance decreased. EDX results demonstrated uniform and homogeneous distribution of silicon atoms within the PVA matrix, regardless of the particulates observed in SEM.

Thermal Stability of the Hybrid Films. The strong interfacial interaction and network structure obtained by introducing inorganic VTMS into PVA increases the thermal stability of pure PVA by preventing the segmental motions of the PVA polymer chains.^{1,6,13} DSC and TGA analyses were performed in a nitrogen atmosphere to investigate how the VTMS con-

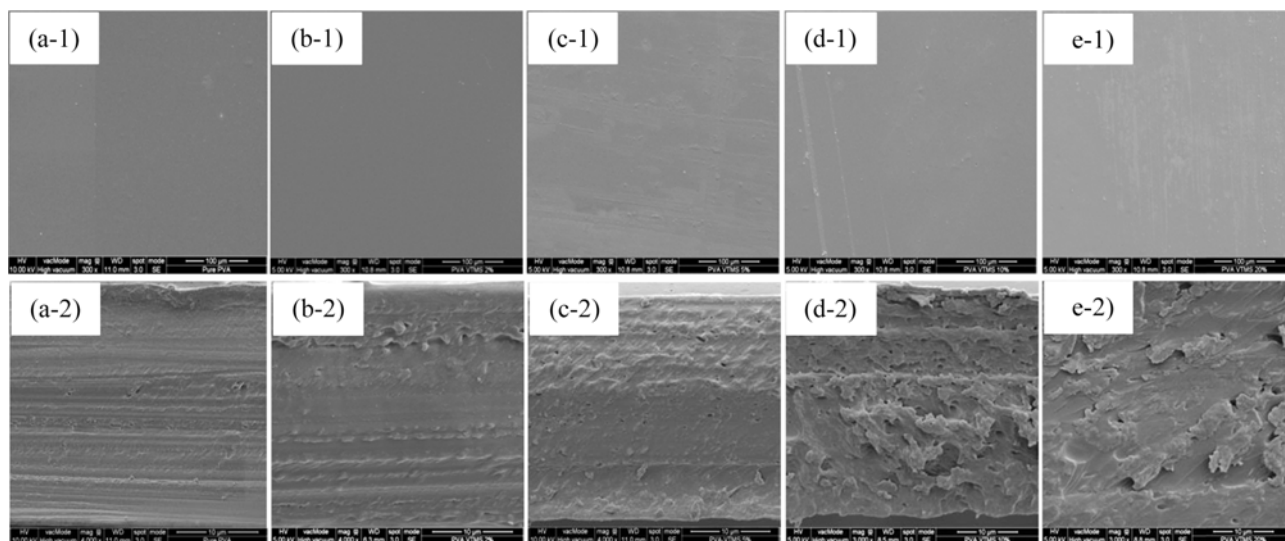


Figure 4. SEM images of the PVA-VTMS hybrid films: (a) pure PVA, (b) PVA/VTMS 2%, (c) PVA/VTMS 5%, (d) PVA/VTMS 10%, and (e) PVA/VTMS 20%.

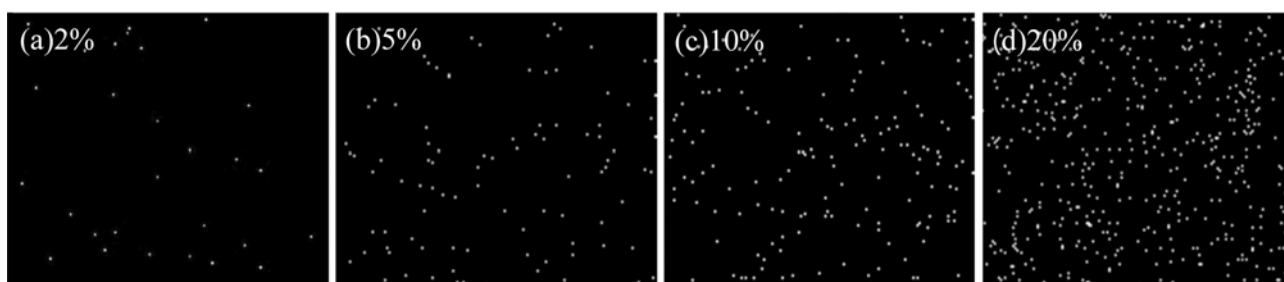


Figure 5. EDX map scanning spectra of silicon (Si) for the PVA/VTMS hybrid films with different VTMS contents.

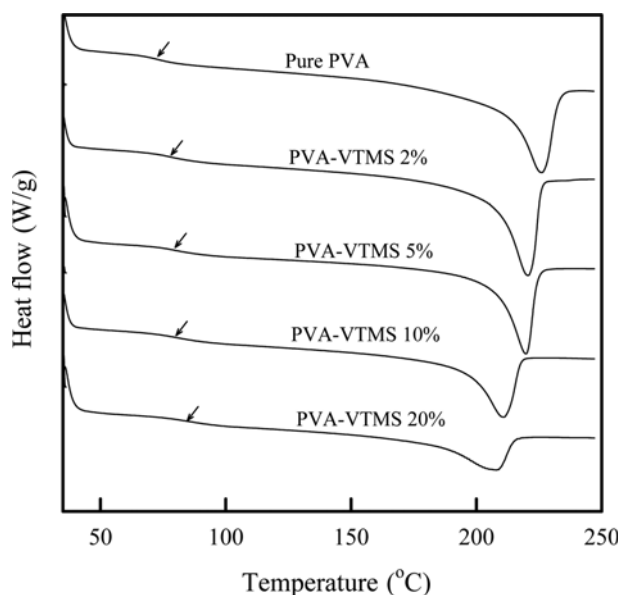


Figure 6. DSC thermograms of the PVA/VTMS hybrid films.

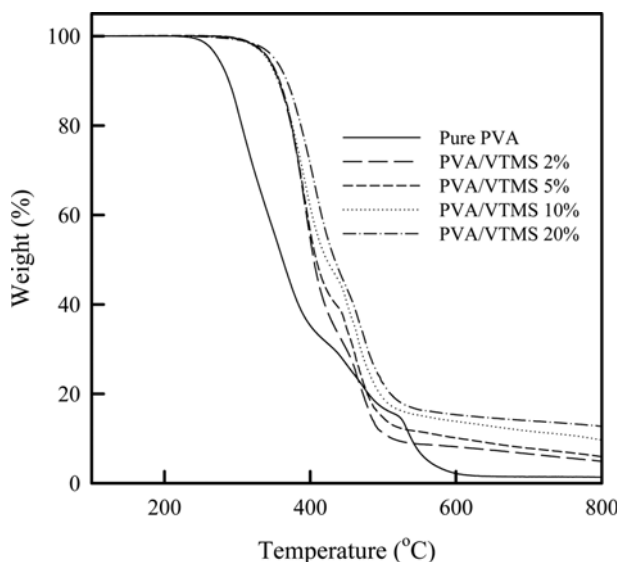


Figure 7. TGA thermograms of the PVA/VTMS hybrid films.

tent affects the thermal stability of the PVA/VTMS hybrid films. Their thermograms are depicted in Figures 6 and 7, respectively, and the results are summarized in Table I.

The DSC curve of pure PVA presents an endothermic peak

at 226 °C corresponding to the melting of the PVA crystallites. This endothermic peak was shifted to lower temperature and became smaller as the VTMS content increased. That is, the enthalpy for melting (ΔH_m) decreased from 71.2 to 36.9 J/g. These DSC results indicate that new crystalline phases do not exist in the PVA/VTMS hybrid films, and the domain size and amount of PVA crystallites decrease linearly with VTMS amount.³ This is consistent with the WAXD results. The Si-O-C bonds formed between the linear PVA chains and VTMS play a role in preventing the formation of a crystalline region, thereby increasing the amorphous region in the PVA matrix. Meanwhile, the pure PVA exhibits a glass transition temperature (T_g) of 72.6 °C. As expected, the PVA/VTMS hybrid films show T_g values of 78.0–84.3 °C, which are higher than that of pure PVA. The T_g value of a polymer represents the amorphous regions of a polymer and is therefore a useful technique to study changes in these regions.²⁰ The strong interaction and chemical cross-linking between VTMS and PVA lead to more compact packing of the molecules, resulting in lower free volumes in the amorphous regions of PVA.

As shown in Figure 7 and Table I, the TGA thermograms show that the degradation pattern and thermal stability are dependent upon the VTMS content. Before TGA analysis, an inert state in the furnace of TGA was first established by purging the N_2 gas, and the experimental sample was added. To minimize the water and oxygen effects of samples, experimental samples were dried by elevating the working temperature from 30 to 120 °C at 10 °C/min in N_2 atmosphere and maintaining the working temperature at 120 °C for 30 min in an N_2 atmosphere. PVA showed a three-step degradation process, whereas all of the hybrid films showed a two-step process, indicating that the introduction of VTMS influences the thermal decomposition patterns of the PVA/VTMS hybrid films. Furthermore, even small amounts of VTMS were very effective in improving the thermal stability of PVA. PVA showed 5% and 10% thermal decomposition temperatures ($T_{5\%}$ and $T_{10\%}$, respectively) of 273.6 and 288.1 °C, whereas PVA/VTMS 2% showed highly increased values of 342.2 and 356.7 °C, which increased only slightly thereafter with increasing VTMS content. Evidently, the thermal decomposition of the hybrid films shifts toward a higher temperature range than that of PVA, indicating an enhancement of thermal stability in the PVA/VTMS hybrid films. This enhancement in the thermal stability and change in the decomposition pattern were ascribed

Table I. Thermal Properties of the PVA/VTMS Hybrid Films

Sample Code	DSC			TGA			
	T_g (°C)	T_m (°C)	ΔH_m (J/g)	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	Residue (%)
Pure PVA	72.5	226.0	71.2	273.6	288.1	362.1	1.4
PVA-VTMS 2%	78.0	220.5	67.2	342.2	356.7	404.9	4.9
PVA-VTMS 5%	79.2	219.8	52.9	343.1	358.0	408.3	5.9
PVA-VTMS 10%	79.7	210.9	46.0	347.6	359.8	422.6	9.7
PVA-VTMS 20%	84.3	208.0	36.9	350.8	368.1	433.5	12.7

to the high heat resistance and structural change exerted by the VTMS, which originated both from the condensation of VTMS with hydroxyl groups of PVA and strong interfacial interactions between VTMS and PVA.

Oxygen Barrier and Water-Resistant Properties. Good oxygen barrier properties are critical for achieving a long protective life for packaging products.^{21,22} The reduction of oxygen permeation can suppress internal damage and improve long-term performance. Therefore, barrier films must prevent or at least decrease the oxygen transfer between the product and the surrounding atmosphere. PVA is well known to have excellent barrier properties to various substances including oxygen due to its crystallinity and strong intermolecular forces.^{6,21} However, PVA is very sensitive to moisture, which plasticizes the polymer and reduces not only the mechanical strength but also the gas barrier properties.^{15,21,23} Therefore, it is very important to enhance both the gas barrier properties and the resistance to water in PVA films for versatile applications. For PVA/VTMS hybrid films incorporating VTMS prepared by a sol-gel process, the oxygen transmission rate and water-resistant pressure were investigated as functions of VTMS content. The results are depicted in Figures 8 and 9.

As shown in Figure 8, the oxygen permeability of the PVA/VTMS hybrid films was strongly dependent upon the amount of VTMS. Pure PVA films showed an OTR value of $6.12 \text{ cm}^3/\text{m}^2 \cdot \text{day}$, and the PVA/VTMS hybrid films exhibited values in the range of 4.96 and $0.17 \text{ cm}^3/\text{m}^2 \cdot \text{day}$. The oxygen permeabilities of the hybrid films incorporating 5%, 10%, and 20% VTMS were suppressed by 65.7%, 95.6%, and 97.2%, respectively, relative to the pure PVA film. OTR decreased substantially to 10 wt% VTMS loading and then decreased only slightly with further VTMS increase. This indicates that the oxygen diffusion in pure PVA film is highly retarded by the incorporation of VTMS into PVA, resulting in enhance-

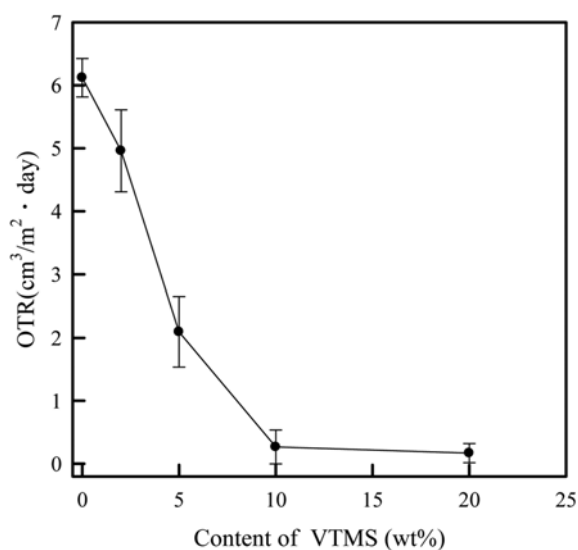


Figure 8. Oxygen transmission rates of the PVA/VTMS hybrid films.

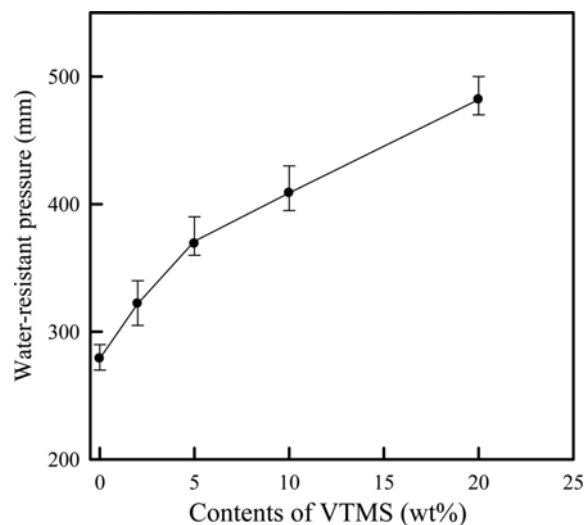


Figure 9. Water-resistance pressures of the PVA/VTMS hybrid films.

ment in the oxygen barrier properties of PVA. Figure 9 shows the relationship between the water-resistant pressure (mm) of the PVA/VTMS hybrid films and the VTMS content. The water-resistant pressure of the PVA/VTMS hybrid films increased linearly, demonstrating that the water-resistance of pure PVA was increased by introducing VTMS.

Overall, the oxygen barrier properties and water-resistant pressure results revealed that the incorporation of VTMS leads to a simultaneous reduction in the oxygen transmission rate and enhancement in water resistance. Such findings indicate a decrease in both the potential capacity of the PVA matrix to absorb permeant molecules and the ability of those molecules to diffuse through the polymeric material. These barrier properties and water resistance may be attributable to variations in the chemical structure and morphologies in films,^{2,4,10-13} which originate from the differences in the compositions of PVA and VTMS and their chemical reactions, in this study.

According to the solution-diffusion mechanism, the amorphous region increases, which favors the diffusion of components and results in an increase in permeation.^{19,24} As described in the DSC and WAXD analyses, although the size and amount of PVA crystallites decreased with increasing VTMS content, the strong interaction of VTMS and PVA, the chemical reaction of PVA and VTMS, and the self-condensation reaction of VTMS increase the cross-linking density of the hybrid films and intermolecular chain ordering with increasing VTMS content. These increases produce a more compact packing structure in the amorphous regions of PVA in the hybrid films, which results in reduced free volume of the amorphous regions and increased film density.^{5,23} Furthermore, films containing higher amounts of VTMS seem to be much more rigid due to increased cross-linking density, which also contributes to a decrease in gas permeability by hindering the ability of diffusing gas molecules to incor-

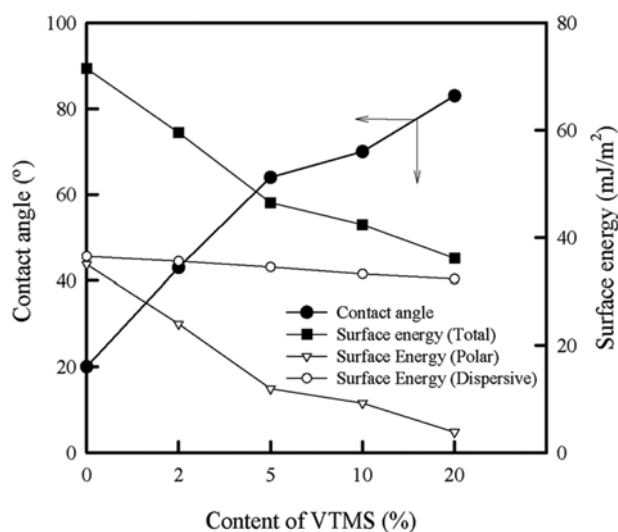


Figure 10. Contact angles and surface energies of the PVA/VTMS hybrid films.

porate into polymer chains. This morphological change from pure PVA to PVA/VTMS hybrid films will result in reduced oxygen permeation in the hybrid films, with a simultaneous increase in the resistance to water in the PVA film.

Contact Angle. The outermost surface characteristics of the hybrid films with different VTMS contents were investigated by water contact angle and surface energy analysis. As shown in Figure 10, the contact angle changed from 20.0° to 83.0° and appeared to increase linearly with increasing VTMS content. This implies that the hydrophobicity of the pure PVA film was greatly enhanced by increasing VTMS content. For the PVA/VTMS hybrid films, the surface energies were determined by means of the contact angle measurements with the aid of a series of organic solvents with known surface energies.¹⁵ The total surface energy of a solid is considered to be equal to the sum of the dispersion and polar components, and their values are shown in Figure 10. The surface energy of pure PVA is 71.5 mJ/m². All the other PVA/VTMS hybrid films with VTMS had lower surface energies. With increasing VTMS content, the polar energy decreased considerably. It was expected that numerous hydroxyl groups would form during the condensation reaction between PVA and VTMS, which would induce relatively hydrophilic surfaces in the hybrid films. However, these contact angle results did not follow this expectation. From the contact angle results, it can be inferred that the hydroxyl groups formed by hydrolyzed VTMS were consumed by reaction with those of PVA and their self-condensation reaction, resulting in hydrophobic surface characteristics. Based on both the chemical affinities and the surface energies, the resistance to water increases with increasing VTMS content.

Optical Properties. For coating or film applications, the transparency of the PVA/VTMS hybrid films is an important property, and it was investigated by photographic images

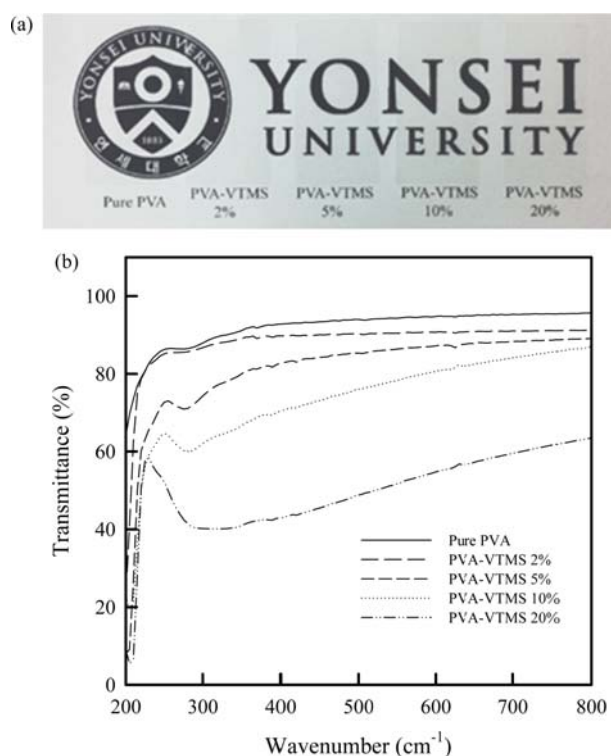


Figure 11. (a) Photographic images and (b) UV-visible spectra of the PVA/VTMS hybrid films.

and UV-visible spectroscopy of the hybrid films (thickness = 60 ± 1 μm), as shown in Figure 11(a) and (b), respectively. Though all samples were somewhat transparent, the films became darker with increasing VTMS content. Light transmittance spectra in the visible light regions (200–800 nm) were slightly affected by the low VTMS loading in the hybrid films. However, the spectra of the hybrid films with high contents of VTMS exhibited lower optical clarity, indicating that there is strong light scattering and/or absorption by particulates formed during self-condensation, resulting in lower transparency of the UV-visible light.

Conclusions

Five different PVA/VTMS hybrid films were successfully prepared *via* a sol-gel method, and their physical properties were investigated as a function of the VTMS content. The hybrid films were formed by reaction between hydroxyl groups of PVA and silanol groups of hydrolyzed VTMS, and self-condensation reaction of VTMS, resulting in a cross-linked network structure and changes in the microstructure of the films. Although the size and amount of PVA crystallites decreased with increasing VTMS content, the cross-linking density and intermolecular chain ordering of the hybrid films increased with increasing VTMS content. The glass transition temperature and thermal decomposition temperature ($T_{5\%}$) of the PVA/VTMS hybrid films increased from 72.6 to 84.3 °C

and 273.6 to 342.2 °C, respectively, when VTMS content was increased from 0 to 20%. Oxygen diffusion in pure PVA film is highly retarded by the incorporation of VTMS. The oxygen permeability of the PVA/VTMS hybrid films was strongly dependent upon the chemical structure and morphology of the films originating from the amount of VTMS, and the OTR decreased from 6.12 to 0.17 cm³/m²-day. From the point of view of chemical structure, the chemical affinity to water and surface energy decreased with increasing VTMS content. Additionally, the intermolecular packing order and rigidity in polymer chains increased with increasing cross-linking by VTMS, inducing enhanced oxygen barrier properties and thermal stability in the PVA/VTMS hybrid films. These properties of the PVA/VTMS hybrid films make them potential candidates for versatile applications as coatings, films, and packaging materials.

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