Effect of Surfactant on Morphology, Light Absorption, Surface Chemistry, Thermal and Mechanical Properties of Polyvinyl alcohol/TiO\textsubscript{2} Composite Films

Sirinan Ratchawong\textsuperscript{1}, Sirirat Wacharawichanant\textsuperscript{1*}, Siriporn Tanodekaew\textsuperscript{2}

\textsuperscript{1}Department of Chemical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University Nakhon Pathom 73000, Thailand

\textsuperscript{2}National Metal and Materials Technology Center, 114 Thailand Science Park, Paholyothin, Klong 1, Klong Luang, Pathumthani 12120 Thailand

*E-mail: sirirat.che@gmail.com

Abstract:

The aim of this work is to study the effect of surfactant (sodium dodecylbenzene sulfonate, SDBS) on morphology, light absorption, surface chemistry, thermal properties and mechanical performance of polyvinyl alcohol (PVA)/TiO\textsubscript{2} composite films. The composite films were prepared by a solution casting method associated with a sonication process for improving the dispersion of TiO\textsubscript{2} particles. The weight ratios of TiO\textsubscript{2}:SDBS at 1:1 and 1:2 were used to prepare the composite films. The results show that the TiO\textsubscript{2}:SDBS ratio of 1:1 successfully improved the dispersion of TiO\textsubscript{2} particles in PVA matrix, whereas the TiO\textsubscript{2}:SDBS ratio of 1:2 caused strong micelle-induced depletion forces leading to particle aggregation. The tensile properties of PVA/TiO\textsubscript{2} composite films were improved with the addition of SDBS. The films showed strong absorption of TiO\textsubscript{2} in the UV region. FT-IR spectra of PVA/TiO\textsubscript{2} composite films containing 5\%wt TiO\textsubscript{2} with thermal treatment showed a broad band at 1560 cm\textsuperscript{-1} corresponding to the C=C stretching vibration. This suggested dehydration and double-bond formation of PVA under thermal treatment.

1. Introduction

Polyvinyl alcohol (PVA), due to its well-known hydrophilicity, good film forming and physical properties, biocompatibility, and good chemical resistance\textsuperscript{1}, is often chosen as polymer matrices for embedding semiconductor materials such as TiO\textsubscript{2}, ZnO, CdS, etc\textsuperscript{2}. It appears that particle aggregation or poor dispersion of semiconductor in polymeric matrices usually decreases catalytic efficiency\textsuperscript{3}. There are many studies on solving this problem, including the use of surfactant for dispersing particles\textsuperscript{4-5}. Thermal treatment is an alternative method to enhance catalytic stability and decreases the limiting swelling which made the TiO\textsubscript{2} nanoparticles difficult to lose from composite films\textsuperscript{6-7}. Thus, work studied the effect of sodium dodecylbenzene sulfonate (SDBS) addition and thermal treatment of PVA/TiO\textsubscript{2} composite films on the dispersion of TiO\textsubscript{2} particles and catalytic stability.

In this study, PVA/TiO\textsubscript{2} composite films were prepared by solution casting method. SDBS was selected as a surfactant for dispersing TiO\textsubscript{2} particles in PVA matrix. The effect of surfactant on morphology, light absorption, thermal properties and mechanical performance of PVA/TiO\textsubscript{2} composite films was studied. Thermal treatment was carried out and its influence on surface chemistry and mechanical properties of the composite films was examined.

2. Materials and Methods

2.1 Chemicals and materials

PVA (a molecular weight range of 77,000 - 82,000 g/mol) was purchased from Ajax Finechem, Australia. TiO\textsubscript{2} particles (anatase phase) with a mean diameter of 54 nm was produced by sigma-Aldrich.
Company. SDBS (white to cream powder form) was produced by Carlo Erba Reagents Company.

2.2 Preparation of PVA/TiO$_2$ composite films

The PVA/TiO$_2$ composite films with 0.5, 1, and 5%wt of TiO$_2$ were prepared. TiO$_2$ particles were dispersed in SDBS using the weight ratios of TiO$_2$:SDBS at 1:1 and 1:2 in 50 mL DI water. The mixture was heated to 80˚C, added with 2 g of PVA, and then continuously stirred at 80˚C for 3 h. After that, the mixture was sonicated for 1 h before casting onto a petri dish glass. The solvent was evaporated in an oven at 60˚C for 12 h. Finally, the dried composite films were collected with the thickness of ∼80 μm, and characterized. Some PVA/TiO$_2$ composite films were further subjected to thermal treatment at 180˚C for 2 h in the oven before characterization.

2.3 Characterization

The morphology and the dispersion of TiO$_2$ particles in PVA matrix of the composite films were observed by a scanning electron microscopy (SEM, MIRA3, TESCAN, Czech) with an accelerating voltage of 10 kV. The thermal stability and thermal degradation process were characterized using thermogravimetric analysis (TGA, SDT Q600, TA Instruments, UK). UV-Vis spectrophotometer (Cary 5000, Varian, USA) was employed to evaluate UV absorption of the composite films. Fourier-transform infrared spectroscopy (FTIR, Nicolet 6700, Thermo Scientific, USA) was used to measure the functional groups of samples. The mechanical properties were examined using universal tensile testing (EZ-LX model, Shimadzu, Japan) following ASTM D882.

3. Results & Discussion

3.1 Morphology of PVA/TiO$_2$ composite films

Figure 1 shows the morphology at the bottom of PVA/TiO$_2$ composite films observed by SEM. SDBS was found to affect the dispersion ability of TiO$_2$ in PVA matrix. As seen in Figure 1, the composite films without SDBS (Figure 1A, 1D and 1G) show TiO$_2$ aggregation whereas those with the TiO$_2$:SDBS ratio of 1:1 (Figure 1B, 1E and 1H) show a rather uniform TiO$_2$ particle dispersion, especially PVA/TiO$_2$ films containing 0.5 and 1%wt TiO$_2$. However, the dispersion of TiO$_2$ particles became poorer with increasing SDBS to the TiO$_2$:SDBS ratio of 1:2. TiO$_2$ particles tended to aggregate as seen in Figure 1C, 1F and 1I, which was a result of strong micelle-induced depletion forces$^4,^8$ from the higher micelle concentration of SDBS than critical micelle concentration (3.77×10$^{-4}$ M)$^9$. It was also noted that TiO$_2$ dispersion observed between top and bottom of the film with a TiO$_2$:SDBS ratio of 1:1 was likely similar, whereas there are more particles settled at the bottom in those without SDBS and with a TiO$_2$:SDBS ratio of 1:2. This result indicated less dispersion stability of particles at the higher surfactant concentration due to micelle-induced depletion forces.

3.2 UV-visible diffuse reflectance spectroscopy of PVA/TiO$_2$ composite films

UV-vis diffuse reflectance spectra of the composite films are shown in Figure 2A. All samples showed strong absorption in the UV region with higher absorption observed for the film without SDBS, following by the films with TiO$_2$:SDBS ratios of 1:1 and 1:2, respectively. The direct band gap energies ($E_g$) of the film without SDBS and the films with TiO$_2$:SDBS ratios of 1:1 and 1:2 approximated from a Tauc plot$^{10}$ were 3.35 eV (Figure 2B), 3.31 eV (Figure 2C) and 3.31 eV (Figure 2D), respectively. This implies that the addition of SDBS surfactant hardly affected UV absorption of
Figure 1. SEM images of PVA/TiO$_2$ films containing 0.5\%wt TiO$_2$ (A-C), 1\%wt TiO$_2$ (D-F) and 5\%wt TiO$_2$ (G-I); films without SDBS (A,D,G), films with TiO$_2$:SDBS ratios of 1:1 (B,E,H) and 1:2 (C,F,I) of PVA/TiO$_2$ composite films.

TiO$_2$ in composite films since the band gap energy was slightly changed. The band gap energy of the commercial TiO$_2$ anatase phase is 3.23 eV. The band gap energies of all composite films are higher than that of the commercial TiO$_2$ anatase phase. It indicates the good response and high reactive of the films in UV region due to the quantum confinement effects.\(^{11}\)

3.3 Thermal properties of PVA/TiO$_2$ composite films

The thermal properties of PVA/TiO$_2$ composite films were investigated by TGA as shown in Figure 3. The decomposition of the composite films was similar to that of the original PVA film, which involved 3 steps. The first step at around 100°C attributes to evaporation of absorbed water. The second step (200-300°C) attributes to chain scission, and, then, followed by a further breakage polymeric chain in the third step (360-440°C). It was clearly seen that the addition of SDBS could slightly improve thermal stability of the films by decreasing the rate of degradation in the second step which was the predominant decomposition process. As a result, the decomposition temperature of 50 \%weight loss (T$_d$50) was higher with increasing SDBS.

3.4 Surface chemistry of PVA/TiO$_2$ composite films
FTIR was used to obtain information of the surface chemistry of PVA/TiO$_2$ composite films before and after thermal treatment (Figure 4). The peaks of the composite films ranging 630-720 cm$^{-1}$ was attributed to Ti-O stretching.$^{12}$ After thermal treatment, a new broadened peak around 1560 cm$^{-1}$ was present. This peak was assigned to conjugated C=C bond arisen from dehydration and double-bond formation of PVA under thermal treatment.$^7$

![Figure 2](image-url)

Figure 2. Diffuse reflectance spectra of the composite films containing 5%wt TiO$_2$ (A) and their Tauc plots, films without SDBS (B), with TiO$_2$:SDBS ratios of 1:1 (C) and 1:2 (D)
3.5 Mechanical properties of PVA/TiO₂ composite films

Mechanical properties of PVA/TiO₂ composite films without and with SDBS were assessed by stress at break and strain at break as presented in Figure 5. The film with the TiO₂:SDBS ratio of 1:2 presented the poorest mechanical properties due to highly aggregation of TiO₂ as evidenced from SEM images. The mechanical properties of the films were reduced after thermal treatment. The dehydration of PVA under thermal treatment as evidenced from FTIR spectra led to the loss in film
flexibility, especially that of the film with TiO$_2$:SDBS ratio of 1:2.

4. Conclusion

This work presents effect of SDBS on morphology, light absorption, surface chemistry, thermal properties and mechanical performance of PVA/TiO$_2$ composite films. SDBS clearly affected the dispersion of TiO$_2$ particles in PVA matrix, whereas hardly affected the absorption of TiO$_2$ particles. Thermal stability of the composite films also increased with increasing amount of SDBS. A TiO$_2$:SDBS ratio of 1:1, TiO$_2$ particles were evenly dispersed in PVA matrix. As a result, the mechanical properties of the film with TiO$_2$:SDBS ratio of 1:1 was better than those of the films without SDBS and with TiO$_2$:SDBS ratio of 1:2. The film flexibility appeared to decrease after thermal treatment due to dehydration of PVA.

References