

A New Modified Silicone–TiO₂ Polymer Composite Film and its Photocatalytic Degradation

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ABSTRACT: The photodegradation of the silicone surfactant–TiO₂ composite films was characterized by FTIR, Raman spectroscopy, and scanning electron microscope. After photocatalytic degradation, the FTIR Si–O–Si peak intensity of the composite film remained unchanged, implying no cleavage of Si–O–Si bond. The above Si–O–Si peak intensity is sensitive to the polyoxyethylene chain length of the composite. The PEG10000-silicone composite is more resist-

ant to photodegradation than those composites with lower molecular weight of constituent PEGs. The wetting rates of the silicone surfactant–TiO₂ composites showed that modified silicone composite films exhibited hydrophobic nature.

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Key words: polysiloxanes; composites; surfactants; photochemistry; irradiation; degradation

INTRODUCTION

Silicone surfactants are useful for various applications in which their high surface activity and silicone character provide performance advantages.¹ Foaming, wetting, emulsification, water repellent, and phase behavior are basic properties relevant to the manufacture of plastic foams, as spreading and wetting agents, and in personal care products of applications.^{2–4}

The TiO₂ films coated on various substrates promise to have a high commercial potential in the environmental applications such as self-cleaning, antibacterial, and waste water purification containment.^{5–8} Gao and Liu⁹ claimed the possibility of supporting TiO₂ and activated carbon particles on silicone rubber (SR) films to increase the collision possibility of pollutants with TiO₂ photocatalysts. The immobilized TiO₂ has good crystallinity and powder size. Moreover, the nearby activated carbon provides a high concentration environment of the organic target around the TiO₂ particles by adsorption and in this way the photo-oxidation rate is enhanced.

Nakashima et al.^{10,11} had studied the photocatalytic decomposition of estrogen by TiO₂ which immobilized on quartz beads. It is well-known that most organic compounds are oxidized to CO₂ by TiO₂ photocatalysis because of the strong oxidizing power of photo-generated holes. There are a few studies on the photocatalytic degradation of polymer–TiO₂

composites.^{12,13} They investigated the photocatalytic degradation of PVC–TiO₂ composite films. Their PVC–TiO₂ composite was prepared by directly embedding TiO₂ into PVC. From the viewpoint of solid-phase photocatalytic degradation, a well-dispersed and uniformly mingled microstructure of polymer–TiO₂ composite is highly desired. Zan et al.¹³ reported that the presence of TiO₂ nanoparticles in polystyrene film greatly promotes the photocatalytic degradation of the composite. The organic modification by grafting polymer on the surface of TiO₂ particles has been proved to be an effective way to obtain good dispersion of TiO₂ nanoparticles in polymer films.

In this study, silicone surfactant–TiO₂ composite film is formed through bonding the silicone surfactant to the hydroxyl groups at the surface of the fine particles of the photooxidation catalyst. Thus, the catalyst particles of the composite would not escape from the film surface, imparting good photodegradation resistance and antifouling properties to the composite.

EXPERIMENTAL

Materials

Chemicals were purchased from ACROS (USA). All the solutions were prepared with deionized water. Titanium oxide was obtained from Onid Technology. The transmission electron micrographs (TEM) of TiO₂ showed that the particles ranged in 2–10 nm diameter.

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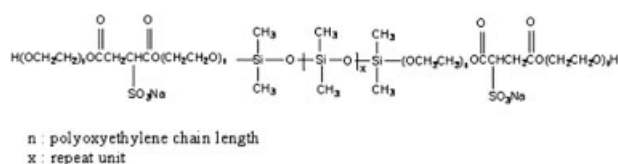


Figure 1 Structure of the silicone surfactant.

Preparation of silicone surfactants-TiO₂ composite films

A series of water-soluble polymeric surfactants were prepared by the reaction of organopolysiloxane with hydroxyl-terminated polyester, as described previously.^{14,15} The structure of the silicone surfactants can be represented as shown in Figure 1. After adding 10 wt % of TiO₂ and 0.5 wt % of MgCl₂, the mixture solution was heated to 95°C for 2 h in an oven.

Photolysis and characterization of the silicone surfactants-TiO₂ composite films

All the films were irradiated under a 20W UV-lamp with an emitting light of 365 nm wavelength. The distance between the sample and the lamp was 20 cm. An UV-vis spectrophotometer (Shimadzu UV-2100) and a FTIR spectrometer (ATR-FTIR Perkin Elmer Cetus Instruments, Norwalk, CT) were used to monitor the spectral transmittance or absorbance changes of the composite films before and after irradiation. Spectra were measured at a resolution of 4 cm⁻¹ and 32 scans were recorded per sample. The surface morphological images of the composite film pretreated by Pt deposition were examined by a scanning electron microscope (SEM, model S-3000N, Hitachi).

RESULTS AND DISCUSSION

Photocatalytic degradation of the composite silicone films

The functional groups in composite silicone films were monitored by IR and Raman spectroscopies. Figure 2 showed the changes in FTIR spectra of the silicone surfactant-TiO₂ films with irradiation time. FTIR spectra displayed characteristic bands at 3400–3600 cm⁻¹ for OH groups, 2780–3000 cm⁻¹ for CH stretching, 1350–1470 cm⁻¹ for CH bending, 1550–1800 cm⁻¹ for C=O stretching, and 1050–1150 cm⁻¹ for C–O stretching. The transmittance of the OH groups gradually increased and then decreased with irradiation time. The CH stretching peak intensity in the composite film showed decrease and shifted to 2970 cm⁻¹ with irradiation. When the irradiation continued for 8 h, the 1738 cm⁻¹ peak increased appa-

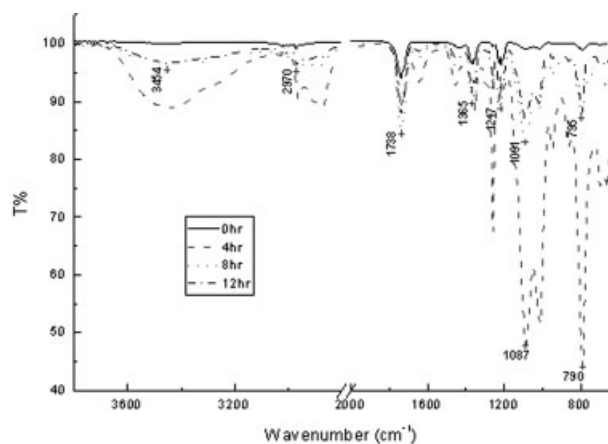


Figure 2 FTIR spectra of PEG2000-silicone-TiO₂ composite films after different times of UV irradiation.

rently. The absorption around 1087 cm⁻¹ shifted to 1091 cm⁻¹ and became narrower, due to the weaker vibration of C–O band. The vibration of intensities of OH and C–O peaks indicate that the composite film of ester group (–COOR) decomposed into carboxylic acid group (–COOH) and hydroxyl group (–OH), leading to the weakening and shifting to higher frequency of the C=O peak.¹⁶ The bands at 1450 cm⁻¹ can be assigned to Si–O–Si bending vibration and the peak intensity does not apparently shift after 12 h, indicating that Si–O–Si linkage is not degraded under irradiation.

Figure 3 showed the change in FTIR spectra of the respective PEG2000-silicone-TiO₂ and PEG10000-silicone-TiO₂ composite films before and after 12 h UV irradiation. The absorption intensities of all the functional groups of the PEG2000-silicone-TiO₂

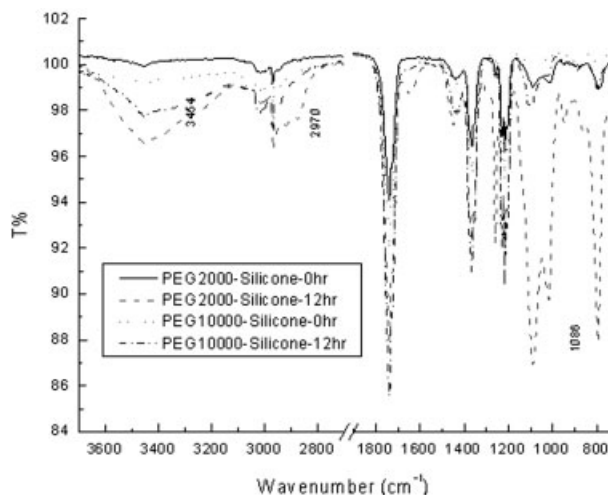


Figure 3 FTIR spectra of PEG2000-silicone-TiO₂ and PEG10000-silicone-TiO₂ composite films before and after 12 h UV irradiation.

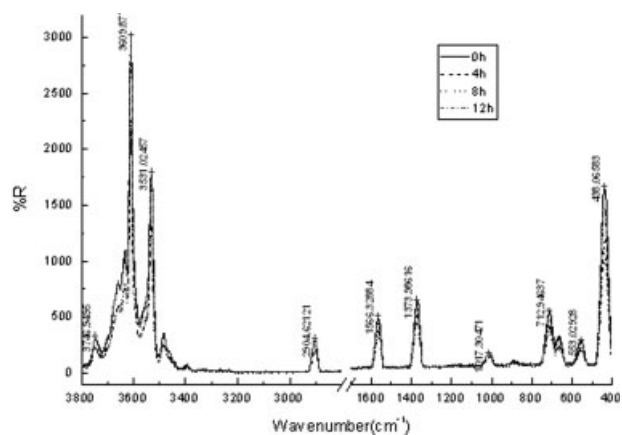


Figure 4 Raman spectra of PEG2000-silicone-TiO₂ composite films after different times of UV irradiation.

composite film gradually increased with irradiation time. The PEG10000-silicone-TiO₂ composite exhibited the similar behavior, but the spectrum change before and after irradiation was smaller than that of PEG2000-silicone-TiO₂ composite. The composite film containing longer polyethylene chain length exhibited worse cleavable ability. The PEG10000-silicone-TiO₂ composite film exhibited better photodegradation resistance than PEG2000-silicone-TiO₂ composite. This is due to the enlargement of the hydrophilic portion (polyoxyethylene chain) of the surfactant molecule, resulting in a decrease in cleavable group per unit surfactant.

Raman spectra of the composite films at different irradiation times are shown in Figure 4. The band at 438 cm⁻¹ is assigned to the stretching vibration of Si-O-Si linkage. The other bands are 1374 cm⁻¹ for -CH₂ bending, 1566 cm⁻¹ for -CH₃ bending, and 3531-3610 cm⁻¹ for O-H stretching vibration. These vibration frequencies of the composite film increased with irradiation time. It showed that the

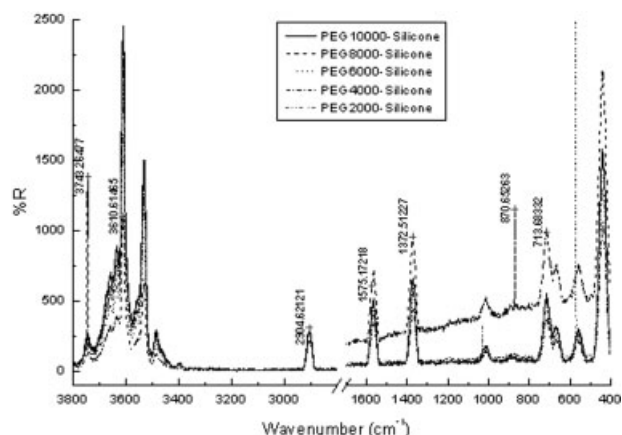


Figure 5 Raman spectra of silicone surfactant-TiO₂ composite films containing different constituent PEGs after 8 h UV irradiation.

ester group (-COOR) was decomposed into carboxylic acid group (-COOH) and hydroxyl group (-OH), and was oxidized into H₂O.

Figure 5 showed the Raman spectra of modified silicone-TiO₂ composite films containing different constituent PEGs after 8 h UV irradiation. The intensity was sensitive to the chain length of the polyoxyethylene of these composite films except that PEG2000-silicone-TiO₂. An increase in the chain length resulted in an increase of the hydroxyl group peak. The intensities of C-H vibrations at 1563-2906 cm⁻¹ of all composites do not change. The PEG10000-silicone-TiO₂ composite possessed the maximum photodegradation resistance among these composites. This is believed to be a hydrophilic system in which electrons and holes form at the surface of the fine photocatalyst particles that have been exposed to light.¹⁷ In addition, the presence of numerous hydroxyl groups at the surface of the fine particles of the photooxidation catalyst, allows the particles to bond securely to the PEG10000-silicone-TiO₂ and not be carried away from the coat, thus

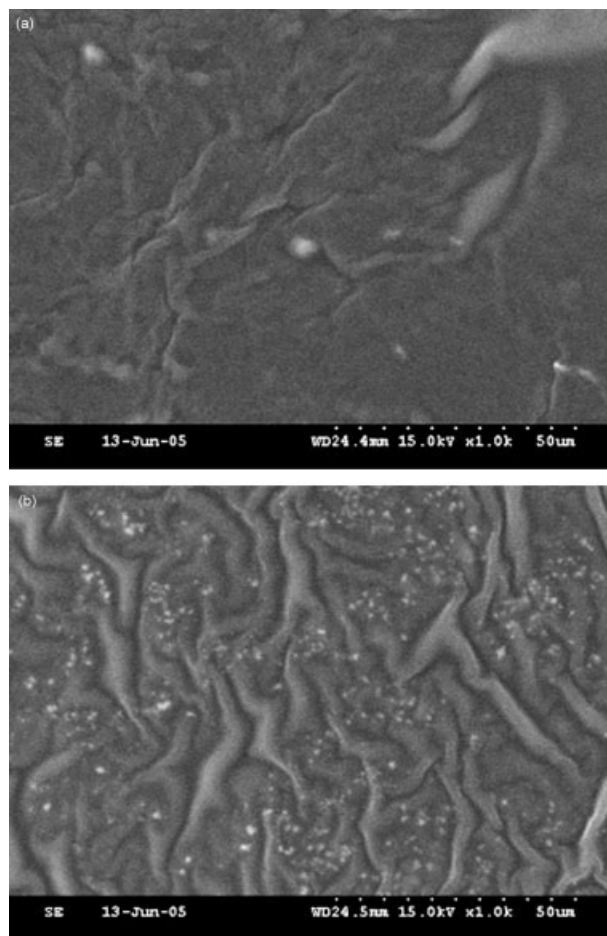


Figure 6 SEM images of composite films: (a) silicone surfactant-TiO₂ film before irradiation, (b) silicone surfactant-TiO₂ film irradiated for 24 h.

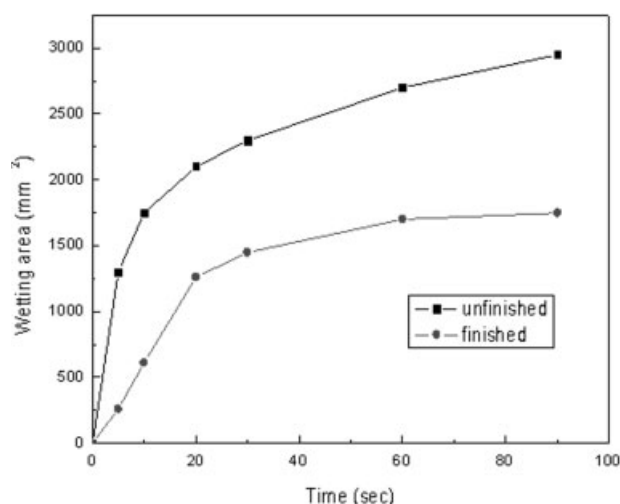


Figure 7 Wetting rates of fabrics coated with modified silicone-TiO₂ composite after 24 h UV irradiation.

making it possible to semipermanently sustain the photodegradation resistance properties.

Figure 6 shows the surface morphologies of PEG2000-silicone-TiO₂ composite film before and after irradiation. Many wrinkles were formed on the surface of the film after 24 h irradiation, nevertheless the surface still maintained its integrity.

Wetting rates of the composite silicone films

We used water absorption measurements to evaluate the wetting rates of the silicone-TiO₂ composite. Figure 7 shows the wetting area of pieces of fabrics coated with the composites at various irradiation times. The silicone-TiO₂ composite imparted a lower wetting ability to the fabrics. This result, we believed that the degradation of silicone-TiO₂ composite would lead to the formation of a water-insoluble silanol moiety and two water-soluble moieties after UV irradiation at different lengths of time. The hydrophobic silanol moiety would readily aggregate and deposit onto the fiber as a hydrophobic film.^{3,4,18}

This film, which consists of hydrocarbon chains attached to and oriented on the fiber surface through polar groups, imparts hydrophobicity to the fabrics.

CONCLUSIONS

Under irradiation of UV light, the ester groups of silicone surfactant composite films decomposed into carboxylic acid groups and hydroxyl groups as revealed by FTIR and Raman spectroscopes. The intensity was sensitive to the chain length of the constituent polyoxyethylene of these composites. The PEG10000-silicone composite exhibits better photodegradation resistance than other composite containing lower chain length of PEGs.

References

- Hill, R. M. *Curr Opin Colloid Interface Sci* 2002, 7, 225.
- Shenai, V. A. *Chem Text Auxiliaries* 1976, p 200.
- Bernhard, S. *Int Text Bull Dyeing/Printing/Finishing* 1995, 41, 50.
- Grish, C.; *Text Chem Colorist* 1995, 27, 21.
- Kandavelu, V.; Kastien, H.; Thampi, K. R. *Appl Catal B* 2004, 48, 101.
- Tsai, S. J.; Cheng, S. *Catal Today* 1997, 33, 227.
- Belhekar, A. A.; Awate, S. V.; Anand, R. *Catal Commun* 2002, 3, 453.
- Kwon, C. H.; Shin, H.; Kim, J. H.; Choi, W. S.; Yoon, K. H. *Mater Chem Phys* 2004, 86, 78.
- Gao, Y.; Liu, H. *Mater Chem Phys* 2005, 92, 604.
- Nakashima, T.; Ohko, Y.; Kubota, Y.; Fujishima, A. *J Photochem Photobiol A* 2003, 160, 115.
- Nakashima, T.; Ohko, Y.; Tryk, D. A.; Fujishima, A. *J Photochem Photobiol A* 2002, 151, 207.
- Cho, S.; Choi, W. *J Photochem Photobiol A* 2001, 143, 221.
- Zan, L.; Tian, L.; Liu, Z.; Peng, Z. *Appl Catal A* 2004, 264, 237.
- Liu, H. J.; Lin, L. H.; Chen, K. M.; *J Appl Polym Sci* 2002, 86, 3005.
- Liu, H. J.; Lin, L. H.; Chen, K. M.; *J Appl Polym Sci* 2003, 88, 1236.
- Xie, Y.; Chen, F.; He, J.; Zhao, J.; Wang, H. *J Photochem Photobiol A* 2000, 136, 235.
- Wark, M.; Tschirch, J.; Bartels, O.; Bahnemann, D.; Rathousky, J. *Microporous Mesoporous Mater* 2005, 84, 247.
- Lin, L. H.; Chen, K. M. *Colloids Surf A* 2006, 275, 99.