Photocatalytic Properties of Silicone Polyesters Using Calcium Phosphate/Titanium Dioxide

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ABSTRACT: This study uses titanium dioxide treated with calcium phosphate to prepare multilayer structure composites. These products are regarded as photocatalysts. Utilizing polyethylene glycol (PEG)–silicone polyester as an adhesive spread on matrix surfaces, this can provide these products with antifouling properties, good weather resistance, and antibacterial property. It has been observed that UV irradiation has caused changes in the film molecular structure of PEG–silicone polyesters, as well as changes in the surface morphology. These changes in molecular structure have been observed by FTIR and Raman analysis. PEG–silicone polyesters con-tain silicon atoms with both organic and inorganic char-acteristics. This makes fixation of photocatalysts possible and retards oxidation of organic materials in the polyest-ers. The results of FTIR and Raman spectrum analyses indicate films made of these polyesters effectively cover calcium phosphate–titanium dioxide photocatalysts, retard surface cracks, and slow down decomposition, caused by UV light. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 413–419, 2009

Key words: polysiloxanes; composites; surfactants; photo-chemistry; irradiation; degradation

INTRODUCTION

Because titanium dioxide photocatalysts are low priced, nontoxic, highly stable, and low in solubility and have semiconducting properties, they are ideal for producing electric cavities and electron pairs to increase reactions under low-energy ultraviolet irra-diation and they also stimulate adsorbed oxygen and water molecules on their surfaces to turn into active species of O_2 and active free radical $^{\bullet}OH$. These oxidized free radicals can decompose harmful organic and partially inorganic materials into stable and harmless materials. In the process, they disin-fect, destroy odors, and purify the air.[1–4]

How can we spread photocatalysts uniformly on matrices and prevent them from decomposing? Nanoparticles present difficulties for use and a hard inorganic film would not be compatible with a flexi-ble fabric. Therefore the best solution is to incorpo-rate high activity photocatalyst nanoparticles in a flexible film of silicone polyesters and such a photo-catalyst could improve a flexible fabric or other flexible material.[5–7] The catalyst particles of the com-posite would not escape from the film surface and impart good photodegradation resistance to the com-posite. They also put no harmful materials into the environment.[8–10]

Hydrophilic polyethylene glycol (PEG)–silicone polyesters use Si—O—Si in the main chain so that sil-icon atoms can connect organic groups with cross-linking semi-inorganic polymers. Because PEG–sili-cone polyesters have both organic and inorganic properties, they offer good resistance to decomposi-tion. Photocatalysts were added into PEG–silicone polyester solutions and then the effects of the film's molecular weights on the composites properties were investigated. The most simple and common method of application of photocatalysts on textiles is the film-spreading processing method. Therefore, synthetic PEG–silicone polyesters used as adhesives for photocatalysts on various organic matrices, such as plastics, can achieve fixed photocatalytic effects and increase their resistance to decomposition, retard cracking of organic matrices caused by oxida-tion, and increase the lifespan of film resin. The pho-tocatalytic effects also have economic value as finishing processes.

The development of polymer products that de-grade under ambient sunlight irradiation with little formation of toxic byproducts could lead to a

disposal of polymer wastes. Several studies on photodegradation of TiO_2-blended polymer such as polystyrene,[11] polyurethane,[12] and PVC[13] focused mainly on inhibiting the photocatalytic activity of TiO_2 in relation to weathering of the polymer composites. This study uses calcium phosphate mixed with photocatalysts for preparing multilayer structure complexes, utilizing polysiloxane, maleic anhydride, and PEG of different molecular weights to synthesize a series of hydrophilic PEG–silicone polyesters containing silicon adhesives, producing stemlike films. These films with different molecular weights of hydrophilic PEG–silicone polyester have been examined for changes of molecular structure due to photocatalytic reactions, by FTIR and Raman analyses after different UV light exposures.

MATERIALS AND METHODS

Materials

The silicone polyesters were prepared by the reaction of a hydroxyl-terminated polyester (PEG, molecular weight = 2000–10,000) and an organopolysiloxane. The preparation and purification of these products were described previously.[14,15] The following chemicals were used as supplied: magnesium chloride, molecular formula: $MgCl_2$ (reagent grade obtained from Hayashi Pure Chemical Co., Osaka, Japan), titanium dioxide (Anatase), molecular formula: TiO_2 (supplied by Chyuan-Yaw, Taipei, Taiwan), methylene blue, molecular formula: $C_{16}H_{18}ClN_3S$ (reagent grade obtained from Hayashi Pure Chemical Co., Osaka, Japan).

Preparation of calcium phosphate–titanium dioxide composites

Calcium phosphate 100 g was added to about 400 mL sol–gel titanium dioxide and this product formed a composite. The composite was well agitated about 60 min by an electromagnetic agitator. The composite was laid on an ultrasonic vibrator for about 2 h until calcium phosphate was completely absorbed by the titanium dioxide and the liquids left were all transparent. The solvent in the composite was removed by a vacuum device. The product was dried to remove water content in an oven at 150°C for 24 h. The dried product was heated to remove crystalline water, letting the chain bonds between calcium phosphate and titanium dioxide stabilize, in a high temperature oven at 300, 400, 500, or 600°C for 1 h, and composites were regarded as photocatalysts in this study.

Preparation of films composed of calcium phosphate–titanium dioxide composites and PEG–silicone polyesters

PEG–silicone polyesters 10 g and pure water 90 mL were added to the same beaker and agitated adequately

at room temperature until the PEG–silicone polyester dissolved completely into the water. This was the PEG–silicone polyester water solution. Calcium phosphate–titanium dioxide composite 1 g was added to polyester water solution 100 mL; 1 g magnesium chloride was added, and this mixed solution was adjusted to contain 1 wt % of calcium phosphate–titanium dioxide composites. A sample of polyester solution was put on a glass dish. This sample was dried in an oven without light at 90°C for 2 h (or 200°C for 12 h) and the properties of the formed film were observed.

Characterization of photocatalysts

An X-ray diffractometer (Thermo Model ARL X'TRA) was used to examine ordering in silicone polyesters using calcium phosphate/titanium dioxide composites. The X-ray beam was Ni-filtered Cu Kα radiation (wavelength, $\lambda = 0.154$ nm) from a sealed tube operated at 45 kV and 40 mA. The observed peaks occur at positions of 2θ, given by Bragg's law, as follows:

$$d = \lambda/2 \sin \theta_{max}$$

where λ is the wavelength of the incident X-ray.

Photocatalyst capacity to decompose organic materials

Photocatalytic activity of the specimens was evaluated by measurement of degradation of methylene blue. The concentration of dye was 0.01 mmol/L and all the films were irradiated under a 144-W UV lamp, the wavelength of which is 365 nm. The intensity of incident light was 1 mW/cm^2 at the level of sample exposed to radiation. The distance between the sample and the lamp was 20 cm. The photocatalytic activity was analyzed with a UV–vis spectrophotometer (Shimadzu UV-2100). The changes of adsorption strength for methylene blue at its wavelength of 664 nm were inspected and hence the extent of its decomposition could be deduced. Therefore, the capacity to decompose organic materials of photocatalysts $CaPO_4$-TiO_2 (calcium phosphate/titanium dioxide) was estimated by the speed of the decomposition of color.

Comparisons of decomposition activity of PEG–silicone polyester films to photocatalysts

FTIR spectrometer (ATR-FTIR Perkin-Elmer Cetus Instruments, Norwalk, CT) and Raman spectrometer (Renishaw 2000 Raman spectrometer) were used to analyze and compare photocatalysts to PEG–silicone polyester films for changes of molecular structure including both organic materials and silicon atoms.
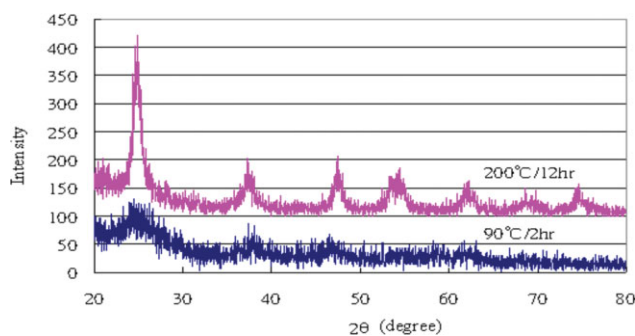
Figure 1 Photocatalyst powder analyzed by X-ray diffraction after heat treatment at a temperature of 90 or 200°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

A scanning electron microscope (SEM, model S-3000N; Hitachi) was used to observe the surface shapes of product films and the influence of photocatalysts on PEG–silicone polyester surfaces.

RESULTS AND DISCUSSION

Structural analyses of photocatalysts

Photocatalysts were prepared by sol–gel method after heat treatment at a temperature of 90 or 200°C, and these products, powders of calcium phosphate–titanium dioxide composites, were analyzed by X-ray diffraction as shown in Figure 1. This diagram shows that the structures of photocatalysts are Anatase shapes, and both extent of crystallization and particle size of the crystals increases with an increase in temperature.

Photocatalysts activity to decompose organic materials

The extent of decomposition of methylene blue[16] by photocatalysts was decided by changes in its characteristic absorbed wavelength of 664 nm, conditions for the wavelength of 365 nm and 144 W of UV light, and irradiation distance of 20 cm. Figure 2
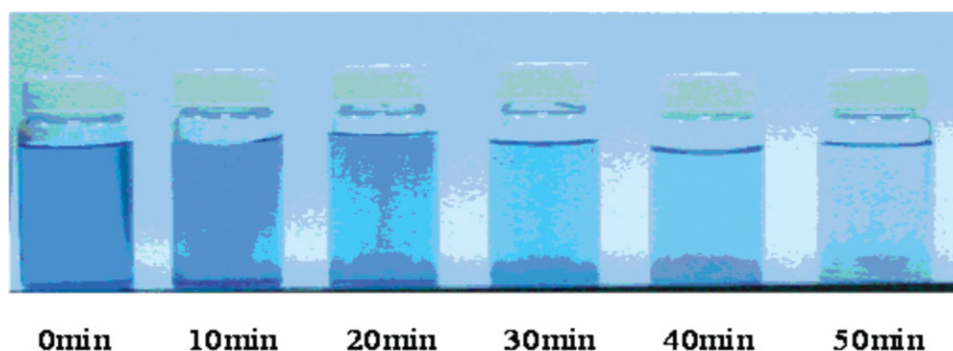

Figure 3 UV spectrum diagram of methylene blue solutions decomposed by photocatalysts at calcined temperature of 600°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

shows the results of methylene blue solution (10 mL) decomposed by photocatalysts. This figure indicates that as times of UV light irradiation increase, colors of methylene blue gradually fade, and photocatalysts are capable of decomposition of methylene blue dyestuffs. Figure 3 is a diagram of characteristic absorbed spectrums, obtained by UV decomposition after photocatalysts calcined at 600°C were used for treatment of a methylene blue solution, and it indicates that as exposure times increase, absorbance values of 664 nm decrease. Figure 4 shows the decomposition conditions of methylene blue, after photocatalysts were calcined at temperature from 300 to 600°C, and these indicate that as calcined temperatures of photocatalysts increase, the decomposition capacities of photocatalysts increase; that is, photocatalysts calcined at 600°C possess the best decomposition effect. Furthermore, the decomposition (%) of methylene blue increases about 65% through its decomposition time of 50 min and this indicates that photocatalysts are obviously capable of decomposition of organic materials.

Figure 2 Results of methylene blue solution decomposed by photocatalysts. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
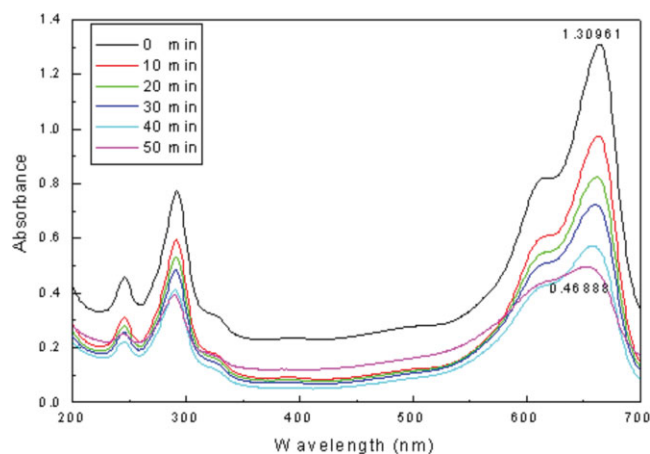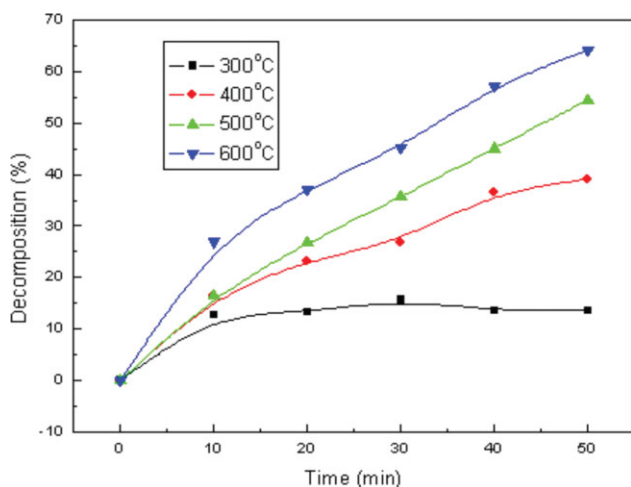
Figure 4 Photodecomposition diagram of methylene blue solutions decomposed by photocatalysts at different calcined temperatures. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

Figure 6 IR spectrum diagram of films composed of PEG2000–silicone polyester and photocatalysts after different UV light exposures. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

The decomposition (%) was calculated as follows:

$$\text{Decomposition}\,(\%)$$
$$= \frac{\text{absorbance of UV light after irradiation}}{\text{absorbance of UV light before irradiation}}$$

The changes in molecular structure of films illuminated by UV light

The structural formula of PEG–silicone polyesters is as shown in Figure 5. These films composed of PEG–silicone polyester and photocatalysts were irradiated by UV light of 365 nm for 10, 20, 30, 40, or 50 min and the changes in these samples compared to the changes of molecular structure in different treated films decomposed by photocatalysts[17–19]; this result is shown in Figure 6. Inspecting the IR absorbed spectrum diagram (Fig. 6) of these treated films, their molecular structures were changed after different exposures to UV light. Due to displacement changes of absorbed spectrum bands for functional group vibration, such as elastic vibrations of O—H
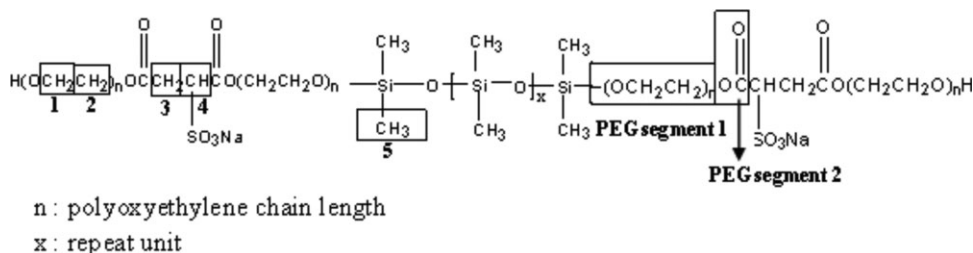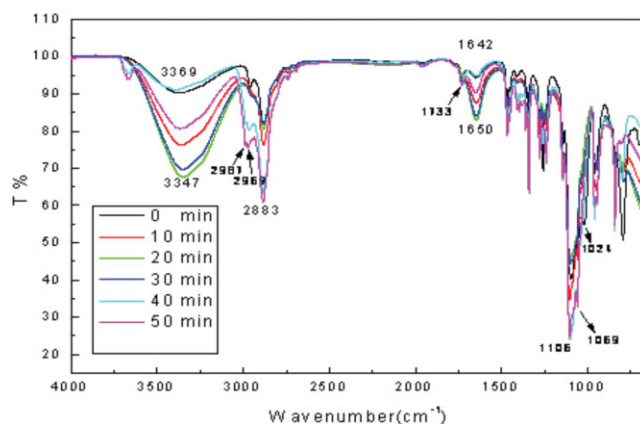
$(3200–3600\ \text{cm}^{-1})$, C—O $(1050–1150\ \text{cm}^{-1})$, C=O $(1550–1800\ \text{cm}^{-1})$, and the same vibration $(2780–3000\ \text{cm}^{-1})$ and winding vibration $(1350–1470\ \text{cm}^{-1})$ of —CH$_2$, —CH$_3$, these results are in accordance with mutual action between photocatalysts and PEG–silicone polyesters.

The chain segments of PEG–silicone polyesters possess at least five kinds of functional groups of —CH that contain the main and characteristic absorbed frequencies, winding vibration $(1380–1470\ \text{cm}^{-1})$, and elastic vibration $(2853–2960\ \text{cm}^{-1})$, and as exposure time of these polyesters increases, the absorption strength of the hydroxyl group increases at elastic vibration of $3200–3600\ \text{cm}^{-1}$. For an increased exposure time of 40 min, the absorption strength decreased and the concentration of hydroxyl groups decreased. The vibration frequencies were changed as the main chains of these polyesters were decomposed by effects of photocatalysts. Figure 6 shows that the wave peak of elastic vibration for —CH$_2$ at a position of $2883\ \text{cm}^{-1}$ was oxidized by photocatalysts, and the ethylene glycol chain segments of these polyesters were decomposed to produce an increase of —CH$_2$ (serial

n : polyoxyethylene chain length

x : repeat unit

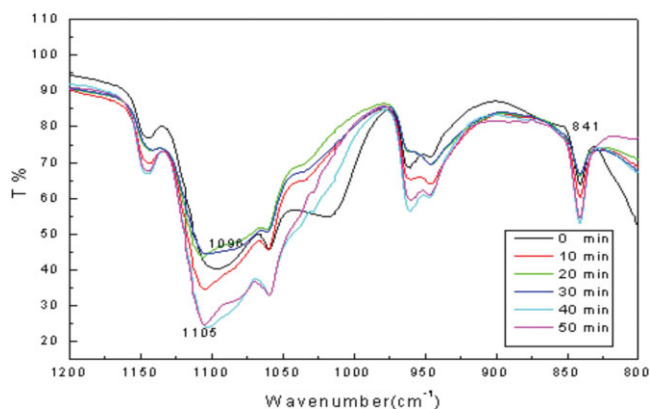**Figure 5** The molecular structural formula of PEG–silicone polyester.

Figure 7 IR spectrum diagram of carbonyl group for films composed of PEG2000–silicone polyester and photocatalysts after different UV light exposures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 8 Raman spectrum diagram of films composed of PEG2000–silicone polyester and photocatalysts after different UV light exposures. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

number 1), which were adjacent to the hydroxyl groups in these molecular structures. Elastic vibration of no symmetry appeared stronger and the obvious absorbed wave peak shifted from 2883 to 2969 cm^{-1} in the spectrum diagram. The relative strength of the shape change vibration for the absorbed spectrum band of —CH can show relative quantities of —CH$_2$ and —CH$_3$, but the absorbed wave peak of symmetric winding vibration for —CH$_3$ of 1450 cm^{-1} on silicone main chains (Si—O—Si) did not produce an obvious shift. These results seem to show that main-chain segments of silicone are not decomposed during the initial period of photocatalytic action.

Figure 7 indicates that elastic and coupling vibration frequencies of no symmetry for carbonyl groups in PEG–silicone polyesters were also shifted from 1096 cm^{-1} before UV exposure to 1105 cm^{-1} after exposure. Therefore, this result may show that carbonyl groups of ester-chain segment are decomposed by oxidation of photocatalysts into products with end-groups in the carboxylic group (absorbed frequency, 1750–1820 cm^{-1}) and in the hydroxyl group (absorbed frequency, 3200–3700 cm^{-1}); after these polyester films were irradiated by different UV exposures, the absorbed frequencies of the carbonyl groups increase in strength and the wave peak shifts toward high frequency.

Figure 8 is a Raman spectrum graph for films composed of PEG2000 (PEG, molecular weight = 2000)–silicone polyesters and photocatalysts after different UV light exposures, and it indicates that the absorbed peak of elastic vibration frequency for the hydroxyl group in the molecular structure increases its strength as UV irradiation time increases. This result may indicate that the ester main chain of this polyester film was decomposed
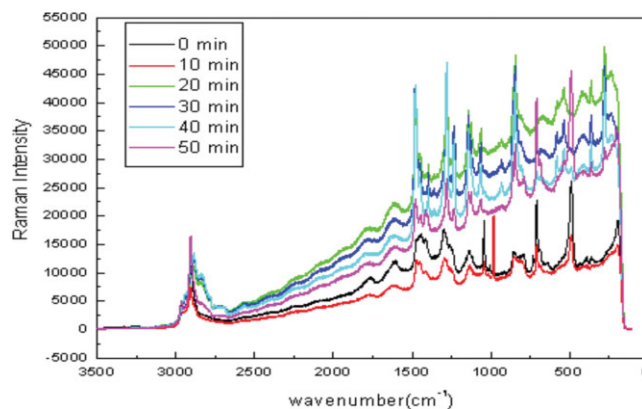
into hydroxyl groups by oxidation and cracking action of photocatalysts according to the action theory of photocatalysts. Figure 9 is a Raman spectrum graph for films composed of PEG10000–silicone polyesters and photocatalysts after different UV light exposures, and because the chain energy of Si—O—Si was stronger and because of its inorganic properties it was not easily oxidized by photocatalysts, these wave peaks were not obviously changed before and after irradiation by UV light. Inspecting Figures 8 and 9, Raman spectrum graphs for PEG–silicone polyesters with different quantities of silicon atoms were compared for changes in molecular structure; that is, the changes of spectrum bands of vibration frequency of —CH and —CH$_2$ (1563–2906 cm^{-1}) could indicate that the higher molecular weight of PEG-chain segments are, the more stable the molecular structure and the changes in its
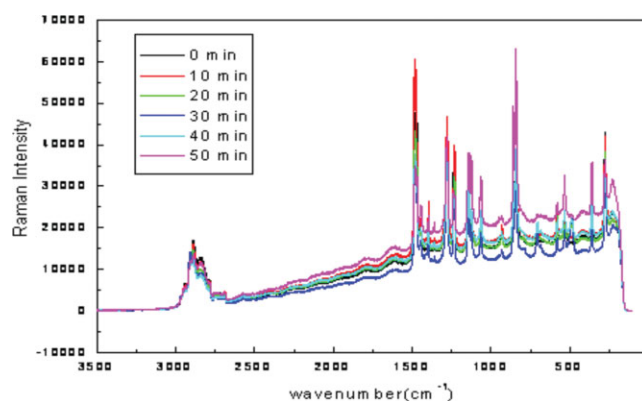

Figure 9 Raman spectrum diagram of films composed of PEG10000–silicone polyester and photocatalysts after different UV light exposures. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

structure caused by photocatalysis decrease, and therefore, the more silicone atoms of this polyester film contains, the more decomposition resistance to photocatalysis it possesses.

SEM analyses of film surfaces illuminated by UV light

Figure 10(a,b) are SEM micrographs of films composed of PEG2000–silicone polyesters and photocatalysts before and after irradiation by UV light; the surface shapes in the two SEM micrographs were not obviously changed before UV exposure and after UV exposure of 1 h. This result indicates that these films could resist decomposition by photocatalysts. Figure 11 is a SEM micrograph of films composed of stearic acid and the same photocatalysts after UV exposure of 1 h; their surfaces reveal a decomposition phenomenon, and this result shows that films containing stearic acid fail to resist decomposition by photocatalysts.
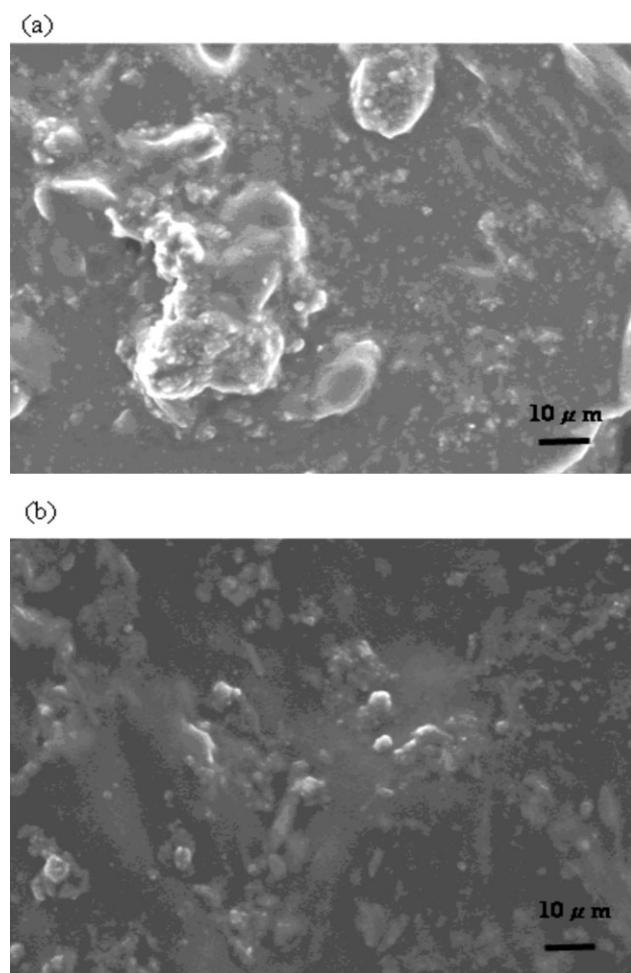

Figure 11 SEM micrograph of film composed of stearic acid and photocatalysts after UV exposure of 1 h.

Figure 10 SEM micrographs of PEG2000–silicone polyester and photocatalysts (a) before UV exposure and (b) after UV exposure of 1 h.

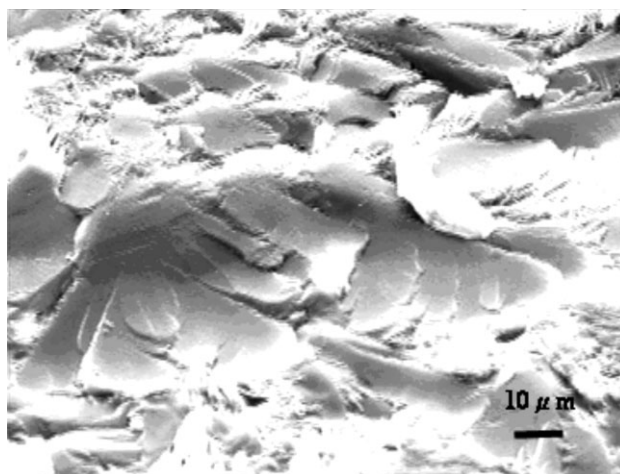## CONCLUSIONS

The results of methylene blue decomposed by photocatalysts show that on increasing exposure times to UV light, decomposition efficiencies increase. Photoactivated Anatase crystals must be prepared by calcining up to a temperature of 400 and 600°C was the best temperature for photodecomposition effect on dyestuffs. PEG–silicone polyesters are organic polymers with O—Si—O in the main chain as a polysiloxane structure, providing characteristic of inorganic materials. They possess a good ability to form films. The results of IR and Raman spectrum analyses show that the ester-chain segments of PEG–silicone polyester films were decomposed into carbonyl groups, hydroxyl groups, and different types of alkyl groups and these results indicate that the higher the molecular weight of these polyesters are, the more stable their molecular structures are and the more resistance to decomposition by photocatalysts they have.

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