

# Photocatalytic Activity of Titanium Oxide-containing Polymer Films.

*Sungwoo Jin, Gwanghoi Koo, Hae-sung Lee, Jinho Jang*

*School of Advanced Materials and System Engineering,*

*Kumoh National Institute of Technology, Kumi, Korea*

*Abstract: Photocatalytic activity of PET and Nylon film containing 0.3% TiO<sub>2</sub> (diameter 300 nm, anatase type) were prepared by melt casting method using a heating press machine. The polymer films were irradiated with different UV energy using a UV/O<sub>3</sub> irradiator. Reflectance in visible region of the irradiated polymer films decreased with increasing UV irradiation and the extent of decrease was more pronounced in Nylon film compared with PET. Also the water contact angle of the polymer films decreased with UV irradiation. The TiO<sub>2</sub> in the polymer films enhanced reflectance decrease and hydrophilicity of PET rather than Nylon. Methylene blue solution was bleached by UV irradiation and the TiO<sub>2</sub> in the films helped to increase the photobleaching effect.*

## **Introduction**

When titanium dioxide is irradiated with UV light, excited electron-hole pairs result in chemical process to degrade organic compounds, particularly environmentally hazardous compounds.<sup>1</sup> Photocatalytic activity of oxidation of TiO<sub>2</sub> has being intensively studied since Ollis and Marinangelli start to investigate in late 1970s.<sup>2</sup> Band gap of TiO<sub>2</sub> is about 3.2eV and photocatalytic reaction proceeds by irradiating UV light of 380nm or less.<sup>3</sup> On UV irradiation, valence electrons (e<sup>-</sup>) of TiO<sub>2</sub> are excited to conduction band producing holes(h<sup>+</sup>) in the valence bands. The electrons and holes migrate to the TiO<sub>2</sub> surface which can induce oxidation/reduction reaction or recombine to generate heat. The electrons in the conduction band can reduce oxidants such as oxygen(O<sub>2</sub> + H<sup>+</sup> + e<sup>-</sup> → HO<sub>2</sub> · ) and the holes in the valence band can oxidate reductants such as water(H<sub>2</sub>O + h<sup>+</sup> → OH · + H<sup>+</sup> ).<sup>4-6</sup> Therefore the photocatalyst can degrade many organic materials because of its higher oxidation ability compared with covalent bond energies of C-C, C-H, C-N, C-O, O-H, N-H.<sup>7</sup> However the strong oxidation power can be serious durability problem when the photocatalysts are incorporated into organic matrix such as polymeric films in spite of desirable functionality of TiO<sub>2</sub> such as self cleaning, disinfection, anti-fogging, decoloration, etc.<sup>8-10</sup> This study is to assess photostability and surface property of polymer films such as polyester and nylon 6 films containing

TiO<sub>2</sub> photocatalysts and photocatalytic degradation capability of the polymer films to methylene blue solution.

## **Experimental**

### **Materials**

Polymer chips(PET and Nylon 6) with and without 0.3% anatase-type TiO<sub>2</sub> (diameter 0.3 μm) were used to prepare thin polymer films up to 200 μm thickness using a heating press machine under a pressure of 1200Pa.

### **UV/O<sub>3</sub> treatment**

Polymer films were irradiated with a UV irradiator(UVO-cleaner, Jelight) of a output intensity of 17.2mW/cm<sup>2</sup>. UV energy was applied by prolonging UV irradiation time from 5.3 to 31.8 J/cm<sup>2</sup> for reflectance and contact angle measurement. For photobleaching experiment, UV energy up to 63.6 J/cm<sup>2</sup> was irradiated.

### **Reflectance and contact angle measurement**

Reflectance of the polymer films were measured with a UV/VIS reflectance spectrophotometer (GretagMacbeth, Coloreye 3100) in the range of 360-700nm. Contact angles of the polymer films were measured by sessile drop method using a static goniometer (Phoenix300, AhTech) attached with a CCD camera. Three test liquids of deionized water, diiodomethane and glycerin were used for the contact angle measurement. Five measurements under standard condition (20°C, 65% RH) were averaged.

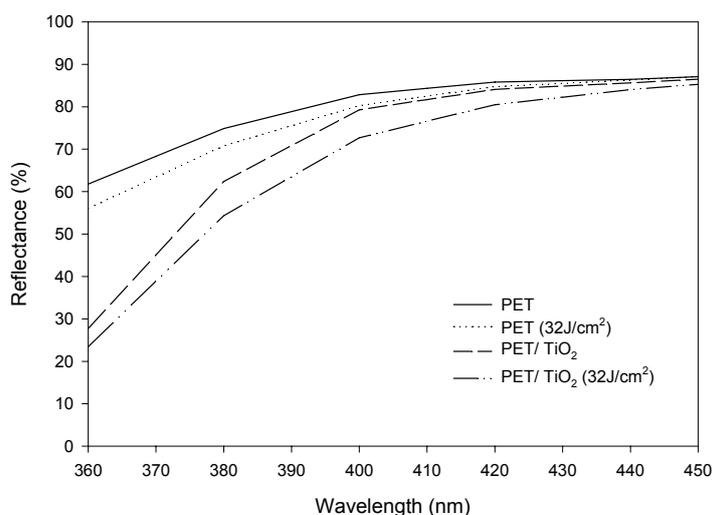
### **Photobleaching measurement**

0.1 mL of aqueous methylene blue solution (20 mg/L) was deposited on the polymer films and the test films were covered with a polyethylene film and then a polystyrene Petri dish. The color of the methylene blue solution was measured with different irradiation time using a portable UV/VIS reflectance spectrophotometer (Minolta JP/CR-11). The color difference (ΔE) of the irradiated sample compared to the untreated was calculated from CIE Lab color system.

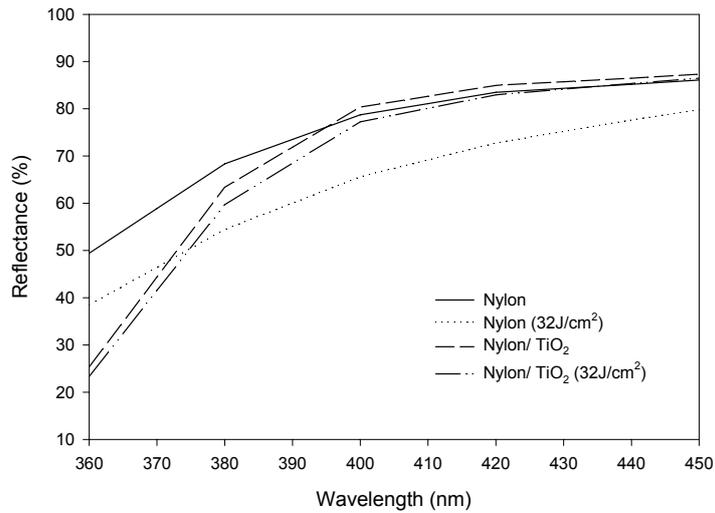
## Results and discussion

### Photostability of PET and Nylon 6 films containing TiO<sub>2</sub> photocatalysts

Reflectance is the light reflected of a sample relative to that of a reference white plate, which is related light. When UV irradiate on the film, PET film shows slight decrease in reflectance due to increased photodegradation as shown in *Figure 1*. The TiO<sub>2</sub>-containing PET film has lower reflectance at lower wavelength due to light absorption of TiO<sub>2</sub> particles and the reflectance of the film also decreased but the extent of decrease was slightly higher than that of unfilled film with prolonged UV irradiation, indicating that the particle enhanced photodegradability of PET due to assisted photocatalytic activity. Nylon films were more susceptible to UV irradiation compared to PET (*Figure 2*). However photodegradation of TiO<sub>2</sub>-containing Nylon films was lower than the unfilled, which was opposite photodegradation behavior compared with PET. The amount of reflectance decrease was more pronounced with unfilled Nylon film compared to TiO<sub>2</sub> containing film, which suggested that UV light absorption effect of TiO<sub>2</sub> in Nylon film surpassed the photocatalytic photodegradation of the polyamide.



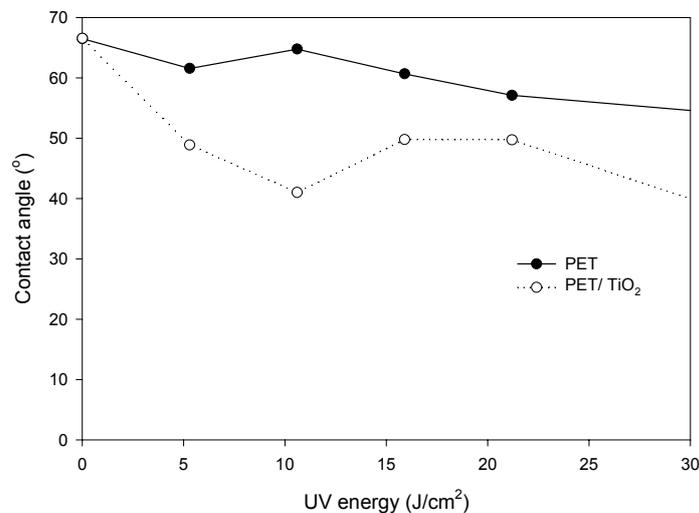
**Figure 1** Effects of UV irradiation on the reflectance of PET and PET/TiO<sub>2</sub> films.



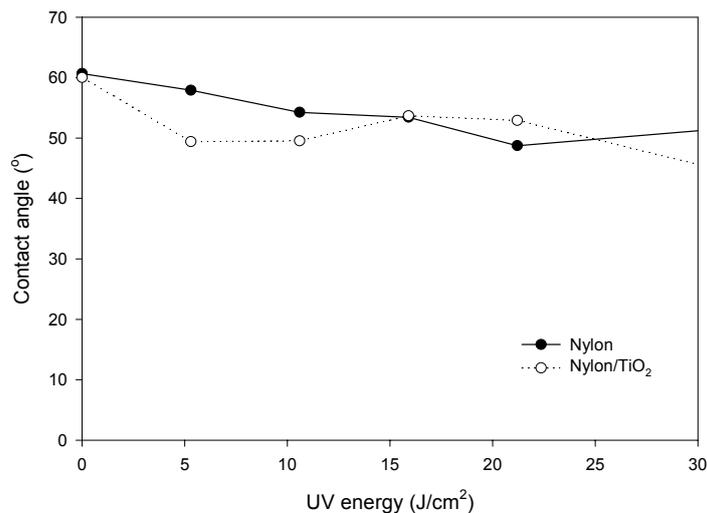
**Figure 2** Effects of UV irradiation on the reflectance of Nylon and Nylon/TiO<sub>2</sub> films.

### Water contact angle measurement

Hydrophilicity of the UV-irradiated polymer films was examined by measuring water contact angle to the polymer films (*Figure 3* and 4). Both PET and nylon films had similar water contact angles irrespective of TiO<sub>2</sub> particle addition. When UV light was irradiated on the films, both unfilled polymer films showed an increased hydrophilicity due to surface photo-oxidation. Also same phenomenon was observed in both TiO<sub>2</sub>-containing films with more pronounced effect particularly at lower UV energy level indicating synergistic contribution of TiO<sub>2</sub> particles to the hydrophilicity. However extent of hydrophilicity increase was more noticeable in the PET/TiO<sub>2</sub> films compared with Nylon/TiO<sub>2</sub> films. The lower water contact angles of the Nylon/TiO<sub>2</sub> films may be resulted from lower photooxidation in the TiO<sub>2</sub>-containing Nylon films compared with PET/TiO<sub>2</sub> films as seen in the reflectance decrease.



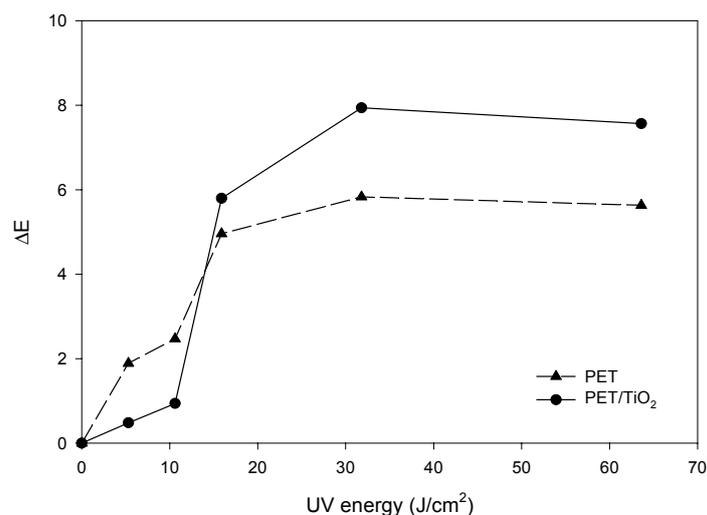
**Figure 3** Water contact angles of UV-irradiated PET and PET/TiO<sub>2</sub> films.



**Figure 4** Water contact angles of UV-irradiated Nylon and Nylon/TiO<sub>2</sub> films.

#### Photobleaching of methylene blue solution

The photocatalytic activity of polymer film can be assessed by observing color change of methylene blue solution which has high color fastness to light. The blue color became weaker upon UV irradiation due to photodegradation of the dyes and color difference ( $\Delta E$ ) increased accordingly due to higher change in lightness ( $\Delta L^*$ ) and color ( $\Delta a^*$ ,  $\Delta b^*$ ). Unsurprisingly the photobleaching effect of TiO<sub>2</sub>-containing PET film was better than that of PET films alone because of excellent photocatalytic activity of TiO<sub>2</sub> as shown in *Figure 5*.



**Figure 5** Color difference ( $\Delta E$ ) of UV-irradiated PET and PET/TiO<sub>2</sub> films.

## Conclusion

Photostability of PET and nylon films to TiO<sub>2</sub> was assessed with UV/VIS light reflectance and the Nylon was found to be more susceptible to the photodegradation than PET. While the PET and nylon film themselves became more hydrophilic on UV irradiation alone, the incorporation of TiO<sub>2</sub> into the films enhance the hydrophilicity increase of both films due to synergistic photooxidation of UV and TiO<sub>2</sub>, producing photooxidated products such as carboxy acid and hydroxyl groups on the film surface, coupled with more facile water adsorption of hydroxylated Ti<sup>3+</sup> on the surface of TiO<sub>2</sub> particles. And the photobleaching of the TiO<sub>2</sub> containing polymer films was better than the polymer film itself.

## References

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