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The photocatalytic activities of nano-titanium dioxide on the cotton fabrics for self-cleaning properties

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Abstract

The study of photocatalysis of nano titanium dioxideon the cotton fabrics have been investigatedthrough self-cleaning properties. The mini-emulsion technique was employed to prepare the encapsulation of titanium dioxide nano particles in polystyrene beads prior used. The mini-emulsion was coated on the cotton fabrics using Pad-dry method.The loading amount of TiO2particles into the mini-emulsion were various from 1%wt to 40%wt. The particles sizes of the TiO2-encapsulated polystyrene mini-emulsion were investigated by dynamic light scattering. It was noticed that the particle size of the mini-emulsion was in the range of 100-200 nm. The morphology of treated cotton fabrics were investigated using scanning electron microscopy. The crystal structure of TiO2–encapsulated PS mini emulsion which coated on cotton fabrics were examined by X-ray diffraction spectroscopy. In order to investigate the photocatalytic activities of TiO2 through the self-cleaning characteristics of the cotton fabrics, colorant stains were created on the samples. Coffee stains were used as colorant organic stains. The result shown that the coffee stained on the cotton fabrics significantly showed the improving of the self-cleaning properties under UV radiation.

Keywords: *nano titanium dioxide, mini-emulsion, self-cleaning, encapsulation, photocatalyticoxidationline space.*

1. INTRODUCTION

Hybrid polymer nano materials have received considerable interest from the academic and industrial researchers because of their outstanding properties in the wind range of high value industrials, foods and medicals applications such as anti-microbial, anti-oxidant, anti-bacterial and self-cleaning properties.[1-3] The combination of multidisciplinary technologies such as nanotechnology, biotechnology and polymer

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technology can offer a multi-functionals, versatiles, stable, resistants and non-toxic products. They are difference process to make novel products such as films, sprays/coatings and fibres, to maintain quality, extend shelf-life and deliver hygienic surfaces.[1, 3]

Many attention has been focused on the new materials that can demonstrate photocatalytic behavior under the proper illumination conditions for applications in textile technological fields.[4] For this reason, nano titanium dioxide (TiO_2) has attracted great attention as a semiconductor photocatalyst due to its widely used materials, low cost, good stability, and ease of preparation.[5] One of an interesting application of TiO_2 is self-cleaning ability.[6-8]

Titanium dioxide is present in three crystalline phases: rutile, anatase and brookite. Among these three forms, rutile is more stable than the other two forms. Anatase and brookite, on the influence of heat, would change to rutile. Rutile and anatase structures are tetragonal while brookite structure is orthorhombic.[9] Although some applications such as normal solution filtering do not require the crystalline phase, crystallinity is essential when biocompatible, photocatalytic or semi-conducting properties are desired. Both anatase and rutile have accessible band-gaps; their photoactive nature means that radical species are produced at their surfaces in the presence of sunlight and water. The incorporation of titania nanoparticles with cellulose or cotton surfaces has been reported to produce a self-cleaning phenomenon.[10]

The development of permanent self-cleaning cotton textiles with a life cycle of 25–50 washings or more is an objective sought by the textile industry in the framework of new products classified as technical textiles.[11] Several studies have reported that TiO_2 coating of cotton textiles could be performed using different pretreatments and techniques such as RF-plasma, MW-plasma, UV-irradiation, Dip-Pad–Dry-Cure and dip-coating to improve the adhesion of the coating and the life cycle of washings. [10, 12, 13]

To explore the potential of the encapsulation of TiO_2 with styrene monomer by using mini-emulsion polymerization and then coated on the cotton with this hybrid polymeric material. We also further studied the photosensitivity of this hybrid material after it has been fully polymerized and coated on cotton.

2. EXPERIMENT

2.1 Materials

The styrene monomer (Sty), hexadecane (HD), sodium dodecylsulfate (SDS) and potassium persulfate (KPS) were purchased from Aldrich at the highness purity. Titanium dioxide (97%) CAS# 13463-67 was supplied by Tronox. All samples were used as received. All other chemicals were used as supplied by the companies.

2.2 Preparation of encapsulated-TiO_2/polystyrene miniemulsionpolymerisation (hybrid miniemulsion)

The mixture of titanium dioxide (1-40%wt), styrene monomer (2.5g) and hexadecane (0.104g) was added into the mixture of distilled water (10cm^3) and sodium dodecylsurfate (0.030g). The mixture was stirred under nitrogen gas for 15 minutes. The mixture was sonicated for 15 minutes. After that the potassium persurfate (0.042g) was added into the reaction and the temperature was raised up to 70℃ for 0-48 hours.

2.3 Hybrid miniemulsion coated on cotton fabrics

The cotton were cut into the dimension of 5x5cm^2. The cotton were treated in the oven at 80℃ for 10 minutes to remove the surface impurities. The coating process is called Dip-Pad-Dry method by immersed the cotton in the miniemulsion for 3 minutes with stirred in ambient temperature for 3 minutes. The coated cotton fabric were dried in an oven at 80℃ for 3 minutes.

2.4Characterizations

2.4.1 Dynamic light scattering (DLS)

Dynamic light scattering was performed on DelsaTMNano C particle analyzer from Beckman Counter, USA. DelsaTMNano C particle analyzer equipped with 30mW 658nm Laser diode operated at the angle 165°

2.4.2 Scanning electron microscope (SEM)

The SEM images were recorded by using Jeol JSM-6510 or Jeol JSM-5410LV, Japan. The samples were coated with gold.

2.4.3 X-ray diffraction (XRD)

The XRD pattern were recorded on PANalytical X΄Pert Pro MPD model pw3040/60 with Cu-Kα X-ray source (the Netherlands). The diffractometer was scanned from 2θ=5°-80° with a scanning rate of 0.02cm-1.

2.4.4 Fourier transform infared (FTIR)

The FTIR measurements were conducted using PerkinElmer model Frontier at the resolution 4cm-1 in wave number region 4000-650cm-1.

2.4.5 Self-cleaning Test

In order to investigate the self-cleaning characteristics of encapsulated-TiO2/polystyrene mini-emulsion, colorant stains were created on the samples. Coffee stains were used as colorant organic stains. Aqueous solution of coffee stains was preparation by mixing 5.5g coffee in 50cm3 of deionized water. Stained samples were irradiated using 11.6 mW/cm2 UV-A lamp (365nm wavelength, Philips, the Netherlands. The self-cleaning property was evaluated based on the colour removal of coffee stains on the cotton fabric.

3. RESULTS AND DISCUSSIONS

3.1 Characterization of styrene miniemulsion

3.1.1 Dynamic light scattering (DLS)

The encapsulation of TiO2 in polystyrene nanoparticles were synthesized via miniemulsion polymerization for 4 hours and 24 hours. The loading amount of TiO2 in polystyrene were investigated from 1wt% to 40%wt. The result show that the maximum loading of TiO2 in the polystyrene miniemulsion were 15%wt due to breaking out of the miniemulsion particles at the loading amount of TiO2 more than 20%wt. The hydrodynamic diameters of the encapsulated-TiO2/polystyrene miniemulsion were determined using DLS, as seen in Fig.1. It was found that the diameter of the miniemulsion particles was slightly increased with raising the polymerization time and with loading amount of TiO2 from 1-15%wt. The hydrodynamic diameter of PS miniemulsion was in range 102nm-168nm for 4 hours of polymerization time and 113-180nm for 24 hours of polymerization time.

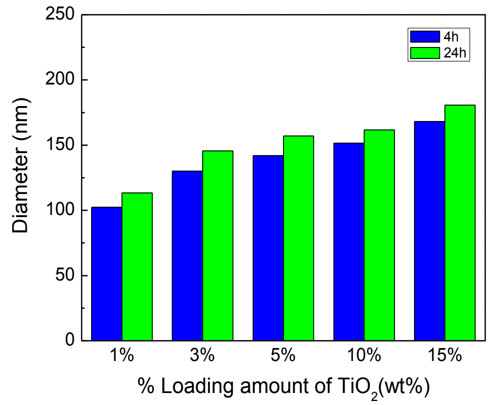

Fig.1. Diameter of encapsulated-TiO2/polystyrene miniemulsion with loading 1-15%wt TiO2

3.1.2 Scanning electron microscope

The morphology of the encapsulated-TiO2 /polystyrene miniemulsion were investigated using of the scanning electron microscope. The hybrid 10%wt TiO2/polystyrene was prepared on the SEM stub and dried in the oven overnight. The result shows that most of the particles were well-define structure and had sphere shape, as presented in Fig.2. The diameter was about 170nm. This is corresponds to the DLS measurement (Fig. 1).

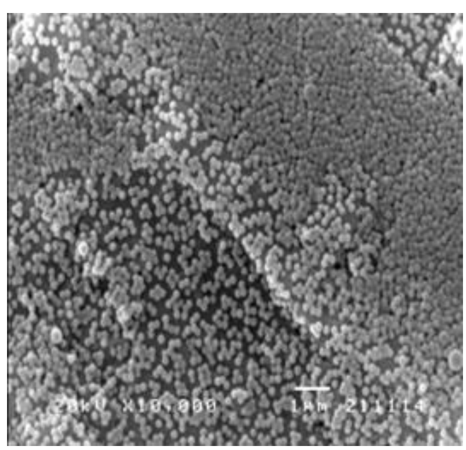

Fig. 2. SEM image of encapsulated-TiO2/polystyrene miniemulsion with 10% TiO2 loading.

3.2 Characterization of cotton coated with encapsulated-TiO2/PS miniemulsion

3.2.1 X-ray diffraction (XRD)

The crystallinity of pristine TiO2 powder and the encapsulated-TiO2 in the PS miniemulsion on the cotton fabric, XRD technique were employed. As seen in Fig.3, peaks of pristine TiO2 are presented at 2θ= 27°, 36° and 55° representing the titania rutile structure.[14] However, the XRD of the miniemulsion on once time coating process was not able to see the TiO2 peaks due to the low loading amount of TiO2 in PS miniemulsion. Although it was coated with miniemulsion 8 times, this peak still dominated with amorphous structure, as demonstrated in Fig.3. [12, 13]

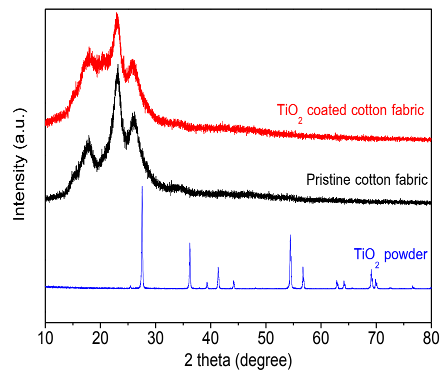

Fig. 3. XRD spectra of pristine TiO2 and cotton coated with encapsulated-TiO2/PSminiemulsion.

3.2.2 Fourier Transform Infrared Spectrophotometer (FTIR)

To confirm the TiO2 on the coated cotton, the Fourier transform infared was investigated the functional-group of the pristine cotton fabric and the encapsulated-TiO2/PS miniemulsion coated on cotton fabric, as presented in Fig.3. The absorption peaks at 696.63 cm-1 was attributed benzene ring folding. The peaks at 757.6 cm-1 were attributed to C-H bending of benzene ring. The C-C stretching of the benzene ring absorptions vibrated at 1492.9 cm-1 and 1600.5 cm-1, respectively. All the absorption bands of the benzene ring and TiO2 in this hybrid particles remained unchanged but the C=O bond vibration at 1712.51 cm-1 deteriorated to the shoulder part in hybrid particles. The absorption band of COO-Ti at 1408.63 cm-1 demonstrates interactions between carboxyl groups and TiO2.[12, 13] These FTIR confirmed that the TiO2 was found on the surface of the coated-cotton.

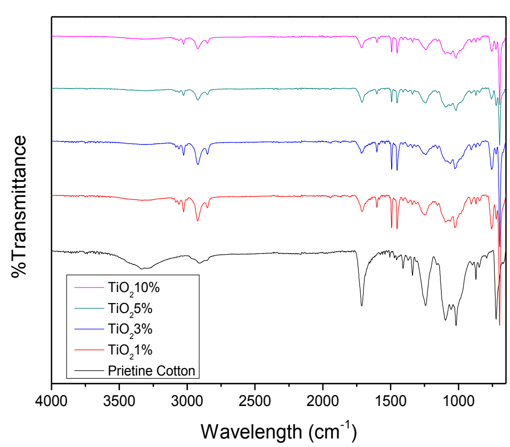

Fig. 4. Shows the FTIR spectra of the pristine cotton fabric and cotton fabric coated with loading 1-10%wt TiO2/PS miniemulsion.

3.2.3 Scanning electron microscope

The morphology of the encapsulated-TiO2/poly-styrene miniemulsion was investigated using of the scanning electron microscope. Fig.5a-4b presents the low magnification of the cotton coated with the hybrid

TiO2/polystyrene with 5% loading of TiO2 and 10% loading of TiO2, respectively. It was noticed that the surface of the cotton fabric was smooth at the hybrid 10%wt TiO2/polystyrene (Fig. 5(b)) than the lower concentration of the TiO2 (5%wt) (Fig. 5(a)).

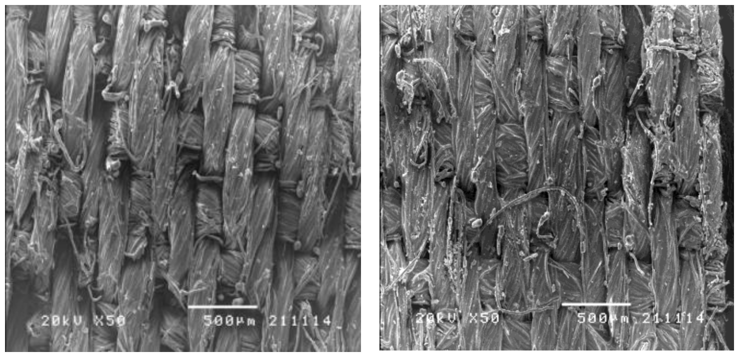

Fig. 5. SEM images of cotton fabric coated with a) the encapsulated-5%wt TiO2/polystyrene miniemulsion at 50x and b) the encapsulated-10%wt TiO2/polystyrene miniemulsion at 50x

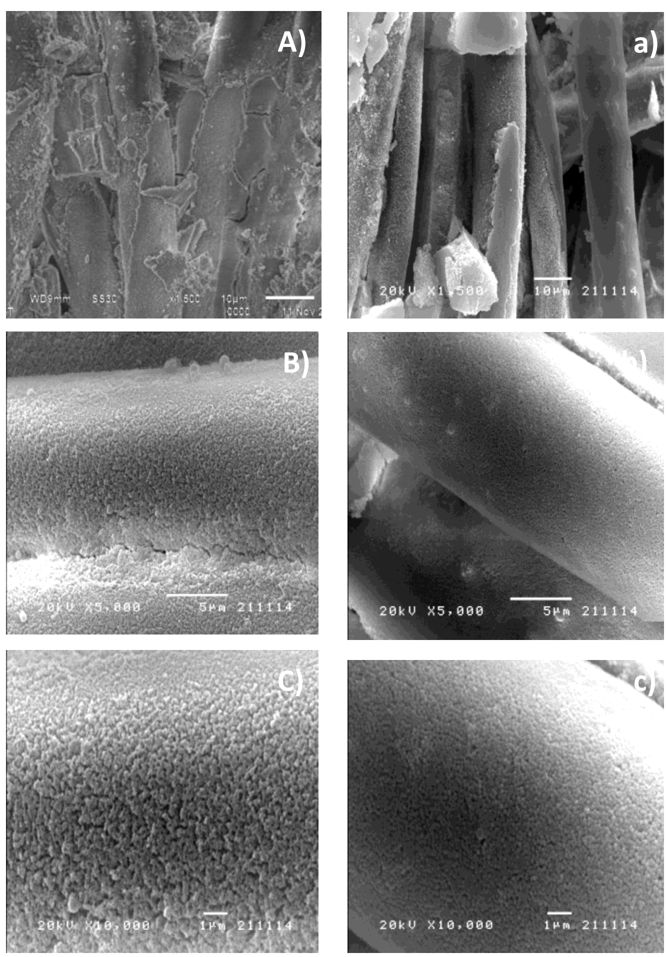

Fig. 6. SEM images of cotton fabric coated with the encapsulated-1%wt TiO2/polystyrene miniemulsion (A-C) and the encapsulated-10%wt TiO2/polystyrene miniemulsion (a-c) at 1500x, 5000x and 10,000x.

As seen in Fig. 5, the SEM images of the cotton coated with encapsulated-TiO2/PS miniemulsion with TiO2 loading 1%wt and 10%wt. The results show that the higher loading of the TiO2 (10%wt) demonstrated the higher density and smooth surface of the coating film while low loading amount of TiO2 (1%wt) had higher porous coating film.

3.2.4 Self-cleaning test

The self-cleaning function was compared through monitoring the removal of coffee stain on fabric under UV-A 11.6 mW/cm2 radiation. The photocatalytic mechanism of discoloration of coffee stain on the pristine cotton fabric and the encapsulated-TiO2/PS miniemulsion coated on cotton fabric at the difference concentration of encapsulated-TiO2/PS miniemulsion were presented in Fig.7.

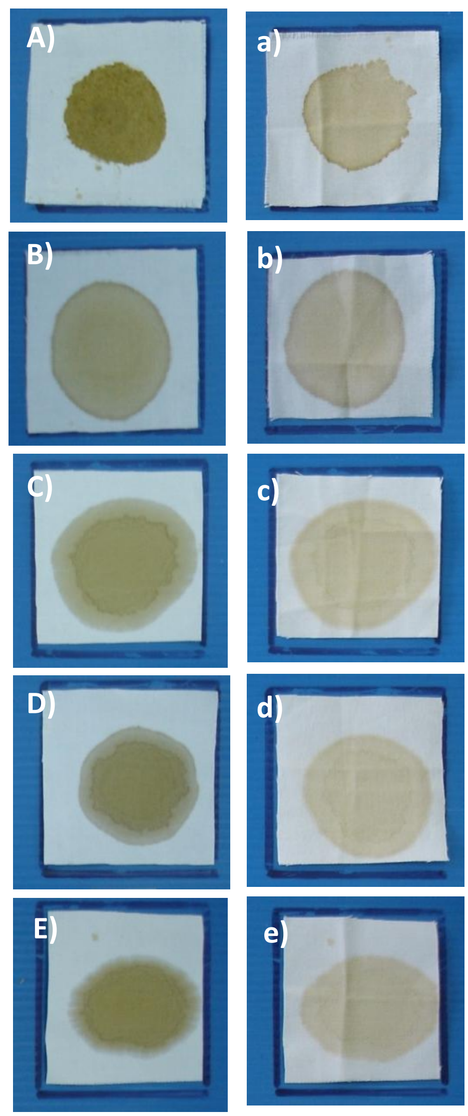

Fig. 7. The photography of the self-cleaning test under UV-A 11.6 mW/cm2 radiation for 84 hr. (Before test: A-E, after test: a-e) when A) Pristine cotton fabric, B) coated with 1%wt TiO2, C) coated with 3%wt TiO2, D) coated with 5%wt TiO2, and E) coated with 10%wt TiO2.

Figure 7 (A and a) were the control, no TiO2 coated on the fabric. The hybrid polymers were coated on the cotton fabric by Dip-Pad-Dry method at the difference load of 1%wt TiO2, 3%wt TiO2, 5%wt TiO2 and 10%wt TiO2 Figure 7 (B-E) and Figure 7 (b-e). After the energy of UV was employed to trigger the photocatalytic decomposition of stains by titanium dioxide particles. Through exposing the stained samples to UV, the photocatalytic properties of titanium dioxide altered the molecular configuration of stains turning them into colourless products (Figure 7 (b-e). The results shown that the colursless of the coffee stain on the fabric significantly correspond to the percent of loaded titanium dioxide in the hybrid polymers at the 84 hours of UV radiation.

4. CONCLUSION

The aim of this study was to development of designing and modifying of nano-TiO2 particles for self-cleaning properties. The miniemulsion polymerization is the selected technique to modified nano-TiO2 particles by encapsulation the nano-TiO2 particles in polystyrene particles. Then the hybrid polymers were coated on the cotton fabric by using Dip-Pad-Dry method. The Variation of the TiO2 content from 1%wt up to 40%wt in the encapsulated of hybrid polymer was study. It was notice that the synthesis was successful. However, the maximum loading of TiO2 in the polystyrene miniemulsion were 15%wt due to the break out of the miniemulsion at the loading amount of TiO2 more than 20%wt. The hydrodynamic diameters of the encapsulated-TiO2/polystyrene miniemulsion were determined using DLS. It was found that the diameter of the miniemulsion particles was slightly increased with raising the polymerization time and with loading amount of TiO2 from 1-15%wt. The hydrodynamic diameter of PS miniemulsion was in range 102nm-168nm for 4hours of polymerization time. The photolycatalytic studied of the coated fabric with hybrid polymer significantly show the improving in self-cleaning properties with increase in the amount of hybrid polymer on the cotton. The FTIR and XRD confirm the present of the hybrid polymer on the cotton fabric. SEM micrographs show the morphology of the hybrid nanoTiO2 at different ratios on the cotton fabric.

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