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Photocatalytic of titanium dioxide hybrid polyurethane by miniemulsion polymerization

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Abstract : Polyurethane nanoparticles were synthesized by using condensation miniemulsion polymerization. The miniemulsion technique was employed to produce nanoparticle in range 50 to 500 nm in diameter. 1,12-Dodecanediol and isophoronediisocyanate were polymerized in water base in the present of titanium dioxide (TiO_2) from 1wt%-10wt%. The encapsulated-TiO_2/Pu hybrids nanoparticles were obtained. The mechanical properties, morphology, crystal structure and photocatalytic activity of TiO_2/Pu hybrids were investigated. The diameter of the hybrid particles were measured using dynamic light scattering. The results show that the hydrodynamic diameter of TiO_2/Pu hybrids were in range 164nm-219nm. The morphology of TiO_2/Pu hybrids were observed byscanning electron microscope. The SEM micrograph presented the well-defined structure. The crystal structures were analyzed by XRD. The photoactivity of TiO_2/Pu hybrids-coated on nonwoven fabric presented the colorless of methylene blue solution.

Keywords: polyurethane nanoparticles, miniemulsion polymerization, titanium dioxide, photocatalytic;

1. Introduction

During the pastfew years,hydrophobic polyurethane (Pu) dispersions have been reportedandreviewed in many publications.[1,2]Because ofthey can be formulated for coatings andadhesives in a wide range of applications. Furthermore, the preference of the properties of hydrophobic polyurethane (Pu) are abrasion resistanceand easy film formation. However, there are some limitations to process because of the incompatibility between the polyurethane and the other polymer such as acrylic polymer.The phase separation, gel formation, or discoloring upon storage are generally found after blend system. Therefore, the idea of the small size of the nanoparticalsare expected that to improve that limitation.[2]

The miniemulsions polymerization technique is a unique type of water-base and oil-base emulsion, which resulting in a small size of the nanoparticlesusually in the range of 50nm–500nm.Generally,the nanoparticles are characterized their droplet size and relative stability.The high shear is generally applied to create the nanosizedof the droplets.[3]

Nanotitanium dioxide (TiO_2) applications for the photocatalytic properties has been reviewed from the perspective of both structural designs and novel applications. The surface areas of the nanotitanium is also significantly impact factor of the photocatalytic performance and the properties of TiO_2 materials.[4,5]

The new advantage of the combine technique between polymer and inorganic nanomaterials is lead to improvement the properties of the new materials. This is call “hybrid polymer”. In term of hybrid polymer is usually applied in many fields such as nanoparticles, nanocomposites andtextile industrials.[2,6]

In recent years several reports have been appeared in the literatures on production of hybrid polymerswith copolymers or hybrid structures including polymers formed by different techniques. Production of hybrid polymers have been reported using miniemulsion polymerization such as polyurethane/acrylic hybrid nanoparticles[2]. Therefore, in this paper we describe the production of hybrid polymer of polyurethane (Pu)/titanium dioxide hybrid polymer via miniemulsion polymerization

technique. The photocatalytic behavior of the hybrid polymer was also investigated through self-cleaning properties.

2. Experimental

2.1 Materials

Isophoronediisocyanate (IPDI, 98%), 1,12-dodecanediol (99%), hexadecane (HD, >99%) and sodium dodycylsulfate (SDS, ACS reagent, 99%) were purchased from Sigma-Aldrichat the highness purity.Titanium dioxide (TiO_2, anatase, 99+%) was supply from US Research Nanomaterials.All samples were used as received. All other chemicals were used as supplied by the companies.

2.2. Preparation of Polyurethane miniemulsion

The sodium dodycylsulfate was dissolved in deionized water. Then, the mixture of isophoronediisocyanate, 1,12-dodecanediol, hexadecane and titanium dioxide (1wt%-10wt%) were added into deionized water. The mixture was stirred for 15 minutes under nitrogen gas and homogenized for 15 minutes. After that the reaction temperature was raised up to 60°C for 4 hours. Then, the reaction was terminated in ice-water bath.

2.3. Characterization

Dynamic light scattering was recorded on Delsa^{TM}NanoC particle analyzer equipped with 30mW 658nm laser diode operated at the angle 165°from Beckman Counter, USA. Differential scanning calorimeter thermogram was performed on Netzsch 200 F3 from Netzsch, Germany. The SEM images were observed on JSM-7600F from Jeol, Japan. The samples were coated with palladium prior observed. The X-ray diffractometer patterns were performed on X´Pert Pro MPD model pw3040/60 with Cu-Kα X-ray source from PANalytical, The Netherlands. The diffractometer was scanned from 2θ=5°-80° with a scanning rate of 0.01cm^{-1}. The photoactivity of TiO_2/PU were monitored bydecolorization of methylene blue on the TiO_2/PU coated-nonwoven under UV-A irradiation from Philips, the Netherlands. The methylene blue was prepared at 15 ppm. The UV light intensity was 5.22 mW/cm^2.

3. Results and discussion

3.1. The diameter of TiO_2/Pu hybrids

Polyurethane nanoparticles were carried out by condensation miniemulsionpolymerization. The reaction ratio of two monomers isophoronediisocyanate and 1,12-dodecanediol was 1:1 ratio. The titanium dioxide was encapsulated in polyurethane by using miniemulsion polymerization. The TiO_2/Pu hybridswere obtained. The diameter of TiO_2/Pu hybrids were measured by using dynamic light scattering technique. The results show that the hydrodynamic diameter of pristine Pu was about 164nm, as seen in Fig. 1. Therefore, the diameter of the TiO_2/Pu hybridswere slightly increased with TiO_2 contents from 3wt% to 7wt%. The diameter of Pu hybrid, however, dramatically raised to about219nm with 10wt% TiO_2 content.

3.2. The morphology of the TiO2/Pu hybrids

The morphology of the TiO_2/Pu hybrids were observed on scanning electron microscope. The TiO_2/Pu hybridswere prepared on Al stub. The SEM images were presented in Fig. 2. The results show that the TiO_2/Pu hybridswerewell-defined structure with sphere shape. The diameter of the TiO_2/Pu hybrids were slightly increased with TiO_2 contents.

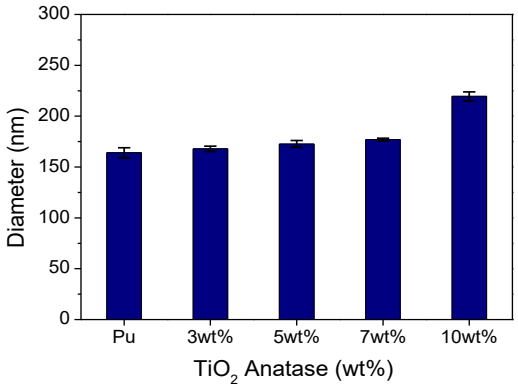

Fig. 1. Diameter of the TiO_2/Pu hybrids with 3wt%-10wt% of TiO_2 contents.

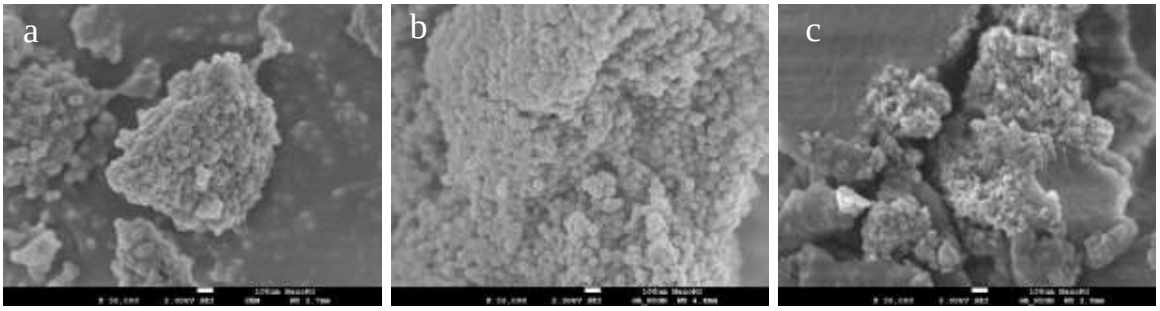

Fig. 2. SEM images at mag. 50,000 of a)pristine Pu b) 5wt% TiO_2/Pu hybrid and c) 10wt% TiO_2/Pu hybrid. The scale bar was 100nm.

3.3. Crystal structureof TiO_2/Pu hybrids

In order to understand the incorporation of polyurethane with titanium dioxide, the XRD technique was introduced to analyze TiO_2/Pu hybrids with 1wt%-10wt% of TiO_2. As seen in Fig. 3, the peak of TiO_2 was presented at 2θ= 25° and 48°, indicating TiO_2 in the anatase phase.[7] The peak of polypropylene nonwoven was shown at 14.4°, 17.2°, 18.9°, 21.2°and 25°.[8] The XRD diffraction pattern of TiO_2 in Pu hybrid was found at 2θ= 25°and 48°, as seen in Fig. 4. Moreover, the intensity of the TiO_2 XRD spectra were slightly increased with TiO_2 contents. Itis confirmed that TiO_2 encapsulated in polyurethane hybrid.

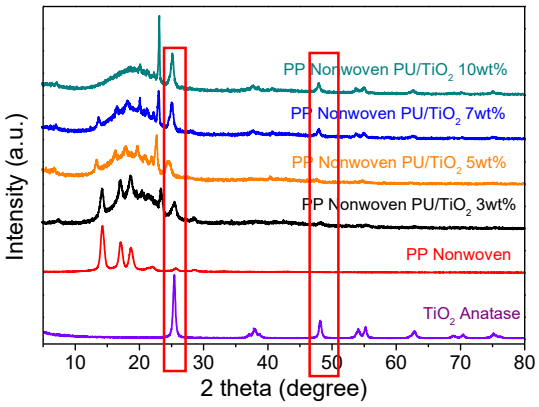

Fig. 3. XRD diffraction pattern of pristine Pu and TiO_2/Pu hybrids with TiO_2 3wt%-10wt%.

3.4. Photocatalytic activity

The photocatalytic activity of the TiO_2/Pu hybrids were studied. The Puhybrids were coated on the polypropylene (PP) nonwoven fabric and dried in oven for 24 hrs. Then, The methlyene blue solution which was prepared at 15ppm stainned on TiO_2/Pu hybrid-coated nonwoven. It was radiated with UV-A wavelength 365 nm and the light intensity was 5.22mW/$cm^2$for 120 mins. The decolouration of methylene blue was monitored. The results show that methylene blue on 10% TiO_2/Pu hybrid was

completely decomposed after 60 mins of radiation time. After 120 mins, in contrast, dry methylene blue presented on pristine Pu-coated fabric. It is concluded thatself-cleaning characteristic of TiO_2/Pu hybrid-coated nonwoven was successfully completed within 120 mins.

Time (mins)	0	20	40	60	80	100	120
Nonwoven Pu (control)							
Nonwoven Pu/TiO_2 10wt%							

Fig. 4. The Photography of photoactivity of pristine Puand 10wt% TiO_2/Pu-coated nonwoven staining with MB under 120 mins of radiation time.

4. Conclusion

The polyurethane hybrid TiO_2 were successfully synthesized via condensation miniemulsion polymerization. The particle sizes were explored using DLS and SEM technique. Therefore, the particle sizes of the TiO_2/Pu hybrid were slightly increased with amounts of TiO_2. The TiO_2/Pu hybrid-coated on the nonwoven fabrics were studied the self-cleaning activity by vanishing of the methylene blue solution. The degradation of methylene blue under UVA was under 120 mins of illumination time.

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