PREPARATION AND ANTIBACTERIAL PROPERTIES OF ORGANIC-INORGANIC POLYMER HYBRIDS USING NANO-TIO_2

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Abstract
Organic-inorganic polymer hybrids of were prepared by melt compounding using a twin-screw extruder. Polyamide6 (PA6) was selected due to its fiber performance, while nano-sized titania (TiO_2) was used as inorganic filler due to its function. Silver nano-particles were successfully doped to the PA6/TiO_2 hybrids by immersing them in aqueous silver nitrate solution followed by UV irradiation through photo-depositing mechanism. All the hybrids doped with silver showed excellent antibacterial properties against Escherichia coli, Klebsiella pneumonia and *Staphylococcus aureu* .

1 Introduction
Much attention has been focused on the incorporation of silver nanoparticles into polymers because of possible applications in biomedical fields, sensors, and so on.[1-3] Meanwhile, some researches have reported upon the Ag/TiO_2 nanocomposite system using titania as stabilizers of silver nanoparticles using photo-catalytic properties of TiO_2, which can immobilize Ag nanoparticles in polymer systems through a chemical reduction process of silver ion.[4]

In this work, organic-inorganic hybrids, which consist of polyamide6 (PA6) and titania, were prepared by melt compounding followed by UV photo-reduction of silver ion in silver nitrate solution on the as-prepared PA6/TiO_2 hybrids. Antibacterial properties of the hybrid fibers after photo-deposition of silver were investigated

2. Experimental
1.1 Materials
PA6 was provided by Rhodia (Korea). TiO_2 (Degussa P25, 80% anatase 20% rutile, average particle size of 30 nm) and silver nitrate ($AgNO_3$, Daesung Metal Co. Korea) were commercially available and used without further purification.

1.2 Preparation of PA6/TiO_2 Hybrids
Hybrids of PA6 and nano-TiO_2 were prepared by melt compounding using a twin-screw extruder (Bautec, Korea) at melt state. The temperatures of the six heating zones in the

cylinder from hopper to die were set at 150℃, 190℃, 210℃, 230℃, 240℃ and 250℃, respectively. PA6 chips were dried and mixed with TiO_2 by shaking for effective adhesion of nano-TiO_2 to the surface of PA6 chips homogeneously. The hybrid amount of TiO_2 was controlled up to 4wt%. The hybrid extrudates were quenched in a cooling water bath and cut into small pellets using a pelletizer. The hybrid fibers of PA6/TiO_2 were made by melt spinning using a laboratory spinning machine at 250℃ and ambient cooling.

1.3 Silver Photo-deposition on PA6/TiO_2 Hybrids

For silver photo-deposition, PA6/TiO_2 hybrid fibers were placed into aqueous $AgNO_3$ solution at a concentration 100ppm of Ag ion. The photo-deposition was carried out under UV-light (at 254 nm) for irradiation times of 30, 60 and 120s, respectively. Then silver deposited hybrid fibers were rinsed with distilled water and dried resulting in the hybrid fibers of PA6/TiO_2-Ag.

1.4 Characterization

The existence of TiO_2 in the fibers and photo-deposition of silver after UV irradiation were identified using FE-SEM, EDS (JEOL, 6500F) and XRD (Rigaku, 2000-PC). The photo-deposition amount was measured using a ICP-OES (Varian, 720-ES) for the $AgNO_3$ solution before and after UV irradiation. The thermal and crystalline properties of the hybrid fibers were characterized using DSC (PerkinElmer, PYRIS Diamond DSC).

1.5 Antibacterial Tests

Antibacterial properties of PA6/TiO_2 hybrid fibers before and after silver photo-deposition were evaluated using shaking flask method and paper disc method. *Escherichia coli, Klebsiella pneumonia* and *Staphylococcus aureus* were selected as Gram-negative and Gram-positive bacteria.

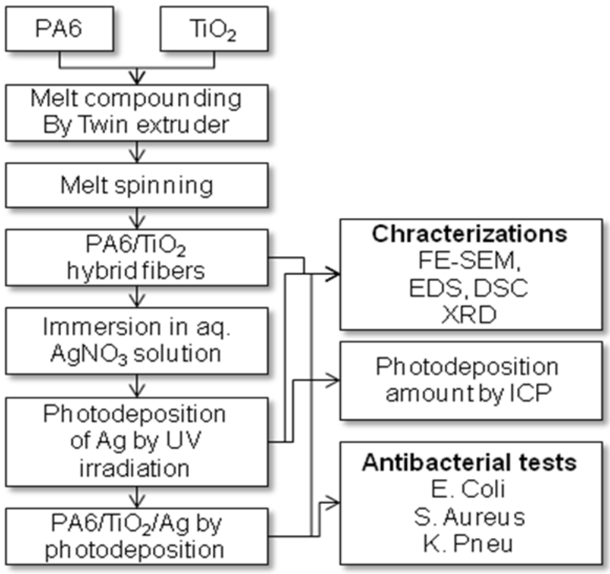

Figure 1. Flow diagram of the study.

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3. Results and Discussion

From the EDS measurement of neat TiO_2 after UV irradiation in the aqueous $AgNO_3$ solution, as shown in Figure 2, it is clear that Ag was photodeposited by UV irradiation through photocatalytic effect of TiO_2 resulting reduction of Ag ion to Ag. The results showed that the photoreduction process was fairly fast under UV irradiation at a wavelength of 254 nm, even under the absence of any capping agent and chemical reducing agent.

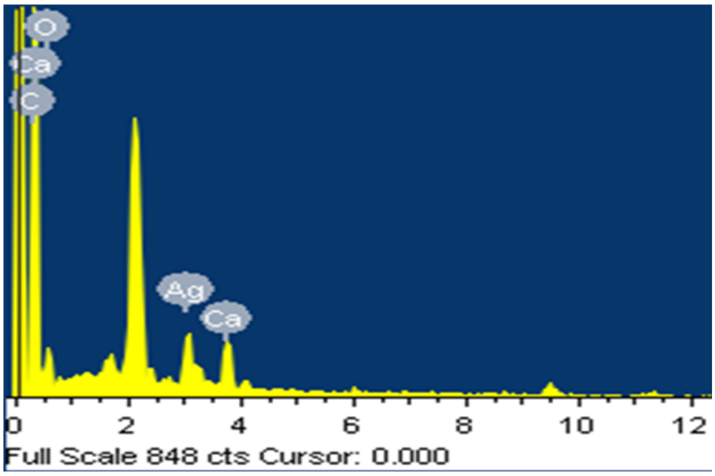

Figure 2. EDS analysis of the PA6/TiO_2 hybrid fibers after immersing in aqueous $AgNO_3$ solution.

The existence of TiO_2 in the hybrid fibers was confirmed from the XRD pattern shown in Figure 3, which was obtained for the fiber with 4wt% TiO_2. The sharp and intense peaks could be assigned to the anatase and rutile phase [4] of P25 titania (the ratio of anatase to rutile is 8:2), which indicates that TiO_2 nanoparticles were well loaded without any chemical and structural modifications into PA6 polymer.

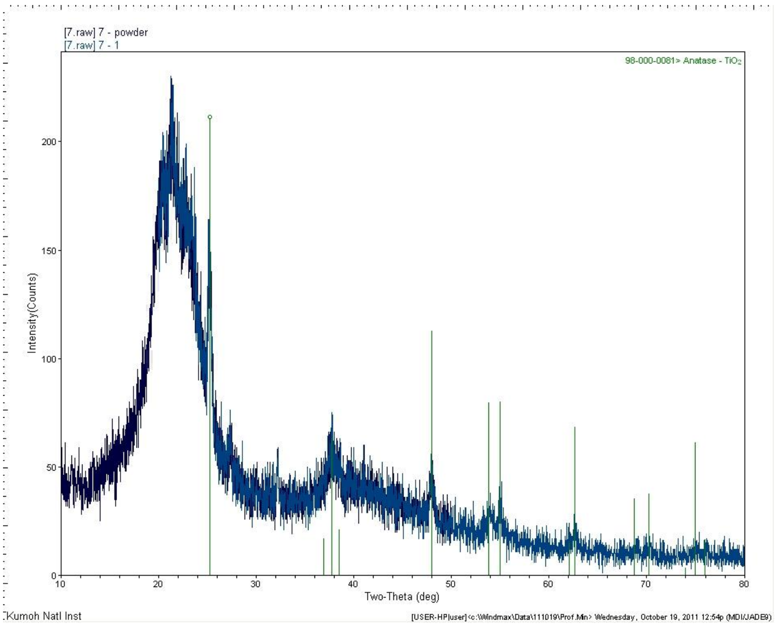

Figure 3. XRD pattern of PA6/TiO_2 hybrid fibers prepared with TiO_2 content of 4 wt%. The vertical lines shows the peak locations of TiO_2 used in the study.

Photographs of agar plates plated with the control cell suspension and those exposed to the hybrid fibers of PA6/TiO_2 and PA6/TiO_2-Ag having 4wt% of TiO_2 with and without UV irradiation for 120s in the aqueous $AgNO_3$ solution, respectively are shown in Figure 4 for Gram-positive and Gram-negative microorganism tests. The absence of colony-forming units on the plates exposed to PA6/TiO_2-Ag hybrid fiber suggests a complete kill, as summarized in Table 1.

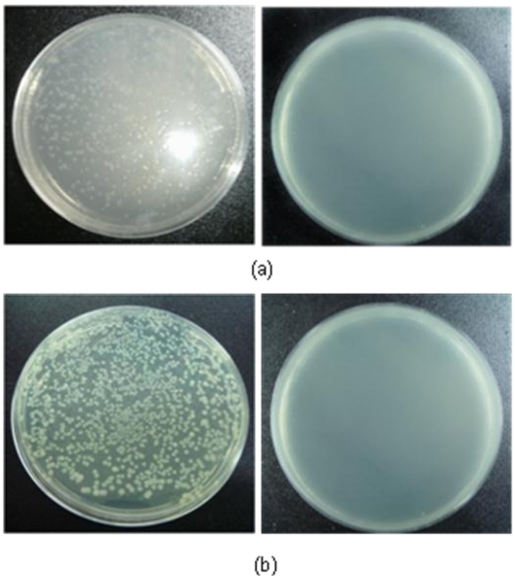

Figure 4. Antibacterial test plates of *E. Coli* (a) and *S. Aureus* (b) of PA6/TiO_2 hybrid fiber having 4wt% TiO_2 with (left) and without (right) UV photodeposition in aqueous $AgNO_3$ solution.

4. Conclusions

Hybrid fibers of PA6 with TiO_2 on which Ag is photo-deposited could be obtained through photo-catalytic reduction in the absence of any organic capping and reducing agents. The hybrid fibers showed excellent antibacterial performance for typical bacteria. Conclusively, the hybrid fibers with the stabilized noble metal nanoparticles are expected to be easily fabricated by this method to be appropriate in biomedical applications.

Acknowledgement

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References

[1] Bakar, M.S.A., Cheng, M.H.W., Tang, S.M., Yu, S.C., Liao, K, Tan, C.T., Khor, K.A., Cheang, P. Tensile properties, tension–tension fatigue and biological response of polyetheretherketone–hydroxyapatite composites for load-bearing orthopedic implants. *Biomaterials*, **24**, 2245-2250 (2005).

[2] Tang, S.M., Cheang, P., Bakar, M.S.A, Khor, K.A., Liao, K. Tension–tension fatigue behavior of hydroxyapatite reinforced polyetheretherketone composites. *Inter. J. Fatig.*, **26**, 49-57 (2004).

[3] Yu, S., Hariram, K.P., Kumar, R., Cheang, P. Aik, K.K. In vitro apatite formation and its growth kinetics on hydroxyapatite/polyetheretherketone biocomposites. *Biomaterials*, **26**, 2343-2352 (2005).

[4] Lim, S.K., Lee, S-K., Hwang S.H., Kim, H. Photocatalytic Deposition of Silver Nanoparticles onto Organic/Inorganic Composite Nanofibers. *Macromol. Mater. Eng*. **291**, 1265–1270 (2006).