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Morphology, Mechanical and Thermal Properties of PBT-TiO_2 Polymer Nanocomposite

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Abstract. This research aims to study the effects of the TiO_2 in PBT composite fibers on the thermal properties, mechanical properties and photocatalytic properties of the polymer composite. The results showed that the tensile strength of the TiO_2/PBT fibers decreased with increasing in the content of TiO_2 in polymer matrix. The content of TiO_2 in composite fibers did not affect the thermal properties of the fibers but the %crystalline of the composite fibers were increased with content of TiO_2 in the composite fibers. The SEM images demonstrated that the TiO_2 were well dispersed in the composite fibers. Moreover, some aggregation of the TiO_2 in the composite fibers was found at high content of TiO_2. The photocatalytic characteristic of the composite fiber was studied thought out self-cleaning properties. The presents of the content of TiO_2 in the PBT fibers significantly showed the improving of the self-cleaning properties under UV-A radiation. The TiO_2/PBT fibers in the presents of TiO_2 10wt% showed the best results of self-cleaning under 168 hours of UV radiation.

1 Introduction

Polymer-inorganic nanocomposite materials (PINCs) have received considerable interest from the academic and industrial researchers because of their outstanding properties in the wide range of high value industrials. The use of inorganic nanoparticles into the polymer matrix can provide high-performance novel materials that find applications in many fields such as foods, medicals and textile [1, 2]. However, it is well known that different surface properties between the inorganic and the matrix will affect the inorganic/polymer compatibility and their interfacial adhesion. Without such a treatment, a coupling agents are an alternative way. It is known that coupling agents such as silane and olefin grafted maleic anhydride are an effective way to improve its dispersibility in polymer matrix as well, and hence ameliorate the polymer matrix, thus enhancing the properties of the resulting composites [3-5].

Poly(butylene terephthalate) (PBT) is one of the most widely used in automotive, electric, consumer application and textile industry. Besides, PBT also enhances the comprehensive properties of engineering plastic including thermal stability, and excellent processing properties; PBT is very often modified with other polymers and particulate fillers [6].

Many attention has been focused on the new materials that can demonstrate photocatalytic behavior under the proper illumination conditions for applications in solar cell industrial and textile industrial [7, 8]. For this reason, nanotitanium 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 [9]. One of an interesting application of TiO_2 is self-cleaning ability.

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 [10]. Although some applications 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 [11].

The development and modification of titania nanoparticles throughout photocatalytic behavior by the frame work of self-cleaning properties are increasingly an interest from many researchers [12, 13]. However, to date, no research has presented the PBT- TiO_2 fibers which designed with special end-use properties. Therefore, in this research we designed an inorganic nanocomposite fibers which have self-cleaning effect. For this purpose, we have prepared nanocomposite fibers using PBT and nano TiO_2 with varying the concentration of TiO_2

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nanoparticles. HI-LUBE™ and Licowax™ OP were used to improve its dispersibility in polymer matrix.

2 Experiments

2.1 Materials

Poly(butylene terephthalate) (PBT) B4500UN was purchased from BASF corporation. TiO_2 nanoparticles CAS# 13463-67 was supplied by Tronox. HI-LUBE™ was supplied by SINWON chemical Co. Ltd. Licowax™OP powder (LOP) was purchased from Clariant. HI-LUPE™ and LOP™ were used as coupling agents. All samples were used as received. All other chemicals were used as supplied by the companies.

2.2 Preparation of TiO_2 compound

The PBT pellets were dried at 80°C overnight prior used. The 500 g of PBT pellets was mixed with 1wt%, 3wt%, 5wt% and 10wt% of TiO_2 containing HI-LUBE (E) 0.35wt% and LOP (L) 0.15wt%. The glycerol 3 drops were added into the mixture. The TiO_2 was blended with PBT using Twin Screw Extruder. The extruder barrel-temperatures zones were set at 260°C. The screw speed was 80 rpm. The obtained TiO_2/PBT composites were cut into pellet size.

2.3 Preparation of TiO_2/PBT fiber.

The TiO_2/PBT composite pellets were mixed using ThermoHakePolyDrive (Single Screw Extruder). The barrel-temperatures zones were operated at 260°C. The screw speed was 4 rpm. The melting composite exit from the spinneret was draw into the fiber shape. The TiO_2/PBT fiber was obtained.

Table 1. Formulation of composites materials.

Sample Name	Materials	Filler	Additive	PBT %(W/W)	TiO_2 %(W/W)	Additive %(W/W)
A	PBT	-	-	100	-	-
B1	PBT	TiO_2	EBS/ LOP	99	1	0.5
B2	PBT	TiO_2	EBS/ LOP	97	3	0.5
B3	PBT	TiO_2	EBS/ LOP	95	5	0.5
B4	PBT	TiO_2	EBS/ LOP	90	10	0.5

2.4 Characterization

The morphology of the specimens were observed using scanning electron microscope model JSM-5410LV from Jeol, Japan. The cross-sectional fractures were obtained by breaking the specimens after freezing in liquid nitrogen. All of the samples were coated with platinum prior used.

The tensile tests of the fiber composite were performed on Instron 5569 universal testing machine according to ASTM D3822. The speed of the cross head was 30 mm/min.

Thermal properties of the polymer compound were investigated using differential scanning calorimetry model DSC 200 F3 from Netzsch, Germany. The scan were performed from 30°C to 300°C with heating rate and cooling rate 10°C/min under nitrogen atmosphere.

Moreover, the photocatalytic characteristics of TiO_2/PBT fibers were study through out self-cleaning properties of fiber composite by using UV-light. The wine stains were created on the samples. Stained samples were irradiated under UV-A lamp (Philips, the Netherlands), with 365 nm wavelength and light intensity of 11.6 mW/cm2. The self-cleaning property was evaluated based on the wine stain removal from the fibers.

3 Results and discussions

3.1 TiO_2/PBT fiber forming

The TiO_2/PBT composite fibers containing 1wt%, 3wt%, 5wt% and 10wt% of TiO_2 were produced using ThermoHake PolyDrive. Two type of coupling agents HI-LUPE™ and LOP™ were used in this process in order to enhance compatibility and adhesion between TiO_2 and the matrices. The TiO_2/PBT fibers were obtained. The results of the extrusion instabilities of the fibers were investigated. It was found that TiO_2/PBT fibers containing 1wt%-10wt% of TiO_2 demonstrated the smooth skin.

3.2 Scanning electron microscope (SEM)

The images of the cross section of the TiO_2/PBT composite fibers were investigated using Scanning Electron microscope. Figure 2 show the fracture surface of composites with 0.5wt% coupling agent at content of TiO_2 1wt% and 10wt%. It was well known that the coupling agent could be effect on the interfacial properties of composites [3]. The fracture surfaces of the composite fibers were also observed. The results showed that the cross-section images of the composite fibers containing 1wt% and 10%wt TiO_2 were well dispersed, as seen in Figure2. However, the agglomeration of TiO_2 might be occurred at high content of TiO_2 (10wt%). The presence of agglomeration of TiO_2 in the composite fiber, as shown in Figure 2, may create stress concentration points, which in turn reduce the strength of the samples. In addition, this would affect the mechanical and thermal performance of the substrate.

A

B1

B4

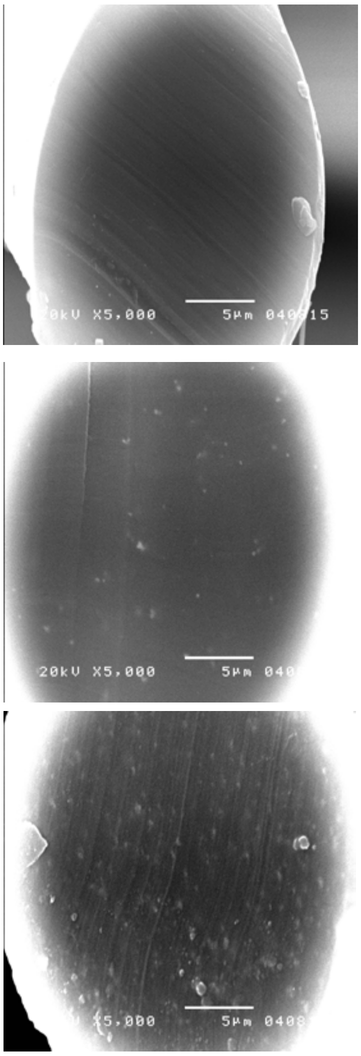

Figure 2. Cross-section SEM images (5000X) of pristine PBT and 1wt% TiO_2/PBT composite and 10wt% TiO_2/PBT composite fiber.

3.3 Thermal properties

The melting temperature (Tm), crystalline temperature (Tc) and %crystallinity of the pristine PBT and TiO_2/PBT fibers composite were explored using Differential Scanning Calorimetry. It was found that the melting temperature of the composites were obtained from heating cycle while the crystalline temperatures were obtained from cooling cycle. There were no significant difference of the melting temperature when increasing the content of TiO_2 from 0wt%, 1wt%, 3wt%, 5wt%, and 10wt% in the polymer matrix as shown in Table 2. Melting temperature of the PBT and their composites was around 224.5°C±0.5°C. The %crystallinity was increased when increasing the content of TiO_2 as presented in Table1. It indicated that high content of nanoTiO_2 may affect the %crystalline. In addition, there is no significant effect of coupling agent on the thermal properties of the fiber composite.

Table 2. Thermal properties of DSC of pristine PBT and TiO_2/PBT composite with various content of TiO_2 from 1wt%, 3wt% , 5wt% and 10wt%.

Sample	Tm (°C)	Tc (°C)	%crystallinity
A	224.8	196.4	25.55
B1	224.5	200.4	19.73
B2	224.7	197.9	23.98
B3	224.2	198.7	30.09
B4	224.9	198.8	33.16

3.4 Tensile Test

The mechanical properties of pristine PBT and TiO_2/PBT composite with various content of TiO_2 nanoparticles from 1wt%, 3wt%, 5wt% and 10wt% were examined using Instron 5569 universal testing machine. The tensile strength and elongation of fibers were demonstrated in Figure 3 and Figure 4, respectively. The results showed that the tensile strength of the TiO_2/PBT fiber composite gradually decreased from 1wt% - 3wt% of TiO_2 in the polymer matrix but it was remain steady up to 10wt% of TiO_2. It might be due to good tensile load transferring at lower content of TiO_2 [11]. Regarding on SEM micrograph of TiO_2/PBT fiber composite, it was noticed that the presence of the agglomeration of TiO_2 in the polymer matrix, as shown in Figure 2, might create stress concentration points which turn to reduce the strength of the samples. Therefore, the mechanical properties of the TiO_2/PBT fiber at the high content of TiO_2 in polymer matrix were poor than the lower content of TiO_2 (Figure 3-4).

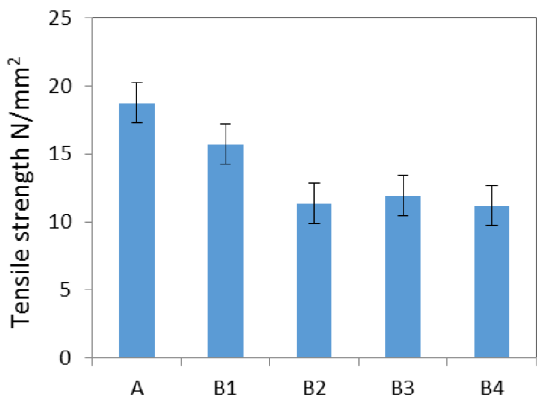

Figure 3. Tensile strength of pristine PBT and TiO_2/PBT composite with various content of TiO_2 from 1wt%, 3wt%, 5wt% and 10wt%.

The %elongation was presented in Figure 4. It was found that %elongation was slightly increased with contents of TiO_2 from 1wt%-3wt% in the fiber composite. Moreover, %elongation of TiO_2/PBT fiber at higher content of TiO_2 from 5wt% was dramatically decreased and it remain steady at 10wt% TiO_2. It was concluded that TiO_2 affected the mechanical properties of the composite fiber at high content of TiO_2.

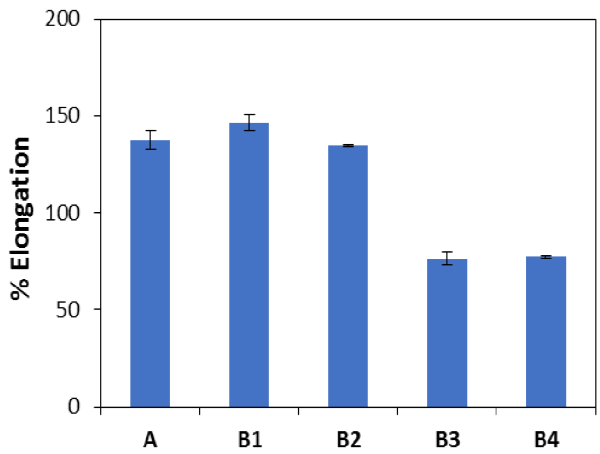

Figure 4. Elongation of pristine PBT and TiO_2/PBT composite with various content of TiO_2 from 1wt%, 3wt%, 5wt% and 10wt%.

3.5 Photocatalytic characteristics of TiO_2/PBT fibers

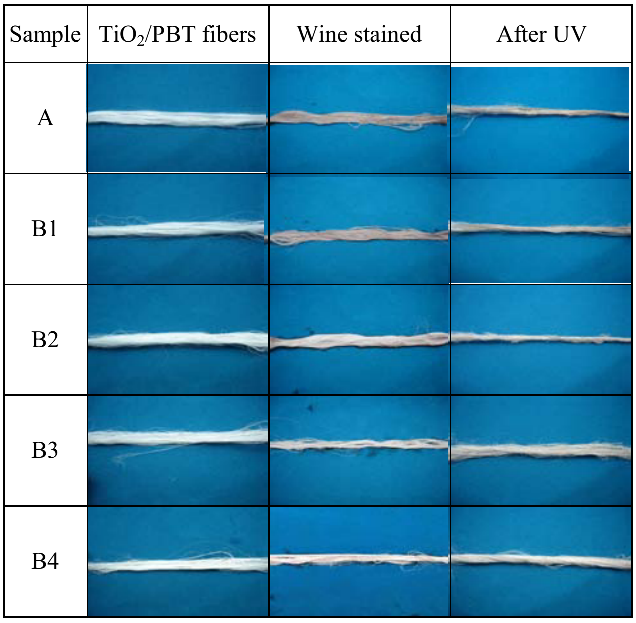

Figure 5. The photography of the self-cleaning test of the pristine PBT fibers and TiO_2/PBT composite fibers containing 1wt%-10wt% of TiO_2 of unstained-wine and stained-wine under 168 hours of UV radiation.

The photocatalytic characteristics of TiO_2/PBT fibers were study thought out self-cleaning properties. The TiO_2/PBT composite fibers stained with wine were investigated under UV-A lamp with 365 nm wavelength and light intensity of 11.6 mW/cm^2. After the energy of UV-A lamp was employed to trigger the photocatalytic decomposition of wine stains by titanium dioxide particles, the photocatalytic properties of titanium dioxide altered the molecular configuration of stains turning them into colourless products, as seen in Figure 5. The result showed that the colorless the composite fibers significantly correspond to the percent of the content of TiO_2 in the PBT matrix. The TiO_2/PBT fiber containing at 10wt% of TiO_2 gave the colorless of the wine stain at 168 hours of UV radiation.

4 Conclusion

The polymer-inorganic nanocomposite materials (PINCs) have been successfully investigated. The effect of the TiO_2 in PBT composite fibers on the thermal properties, mechanical properties and self-cleaning properties of polymer nanocomposite were also studied. The TiO_2 nanoparticles were blended with the PBT at 1wt%, 3wt%, 5wt%, and 10wt%. The TiO_2/PBT composite fibers were obtained from single screw extruder. Variation of the TiO_2 content in the PBT composite fibers resulted in self-cleaning properties of the fibers. With increase in the content of TiO_2 in PBT composite fibers, the self-cleaning properties of the PBT composite fibers gradually increase. SEM micrographs show the fracture surface of the TiO_2 composite fibers and also provides proof of well blending. The tensile properties of the TiO_2/PBT fibers results provide further evident to proof that this composite fibers able to make a textile products.

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References

1. L. Sen, W. Kuan, Z. ZhiRen, S. ChunLian,C. Jiang, W. ZhuoRu, W. XiuFang and P. PiHui, Sci. China Chem., **53,** 605 (2010)
2. M. Bengtsson, N. M. Stark, K. Oksman, Polymer, **49**, 3187 (2006)
3. H. J. O'Donnell and D. G. Bairdt, Polymer, 16, 3113 (1995)
4. A. L. Cattoa and R. Marlene, J. Mater.Sci. and Eng. b 3, **10**, 641 (2013)
5. Y. Xie, C.A.S. Hill, Z. Xiao, H. Militz, C. Mai, Composites: Part A, **41**, 806 (2010)
6. G. S. Deshmukh, D. R. Peshwe, S. U. Pathak and J. D. Ekh, J. Polym. Res., **18**, 1081 (2011)
7. M. Zhang, G. Gao, C.-Q. Li and F.-Q. Liu, Langmuir, **20**, 1420 (2004)
8. A. Bozzi, T. Yuranova and J. Kiwi, J. Photochem. Photobiol., A: Chem., **172**, 27 (2005)
9. R. Fateh, R. Dillert and D. Bahnemann, ACS Appl. Mater. Inter., **6**, 2270 (2014)
10. L. Liu and X. Chen, Chem. Rev., **114**, 9890 (2014)

11. C.-W. Chiu, C.-A. Lin and P.-D. Hong, J. Polym. Res., **18**, 367 (2011)
12. T. Yuranova, R. Mosteo, J. Bandara, D. Laub and J. Kiwi, J. Mol. Catal. A: Chem., **244**, 160 (2006)
13. L. Karimi, M. Mirjalili, M. E. Yazdanshenas and A. Nazari, Photochem. Photobiol., **86**, 1030 (2010)
14. T. Yuranova, D. Laub and J. Kiwi, Catal. Today, **122**, 109 (2007)