

Structure and mechanical properties of TiO₂/UHMWPE nanocomposite monofilaments

Wen Wen YU, Jian Gao SHI^a, Lei WANG, Yong Li LIU, Xiao Xue CHEN

East China Sea Fisheries Research Institute, Chinese Academy Fishery Sciences, Shanghai, 200090, China

Abstract. You should leave 8 mm of space above the abstract and 10 mm after the abstract. The heading Abstract should be typed in bold 8,5-point Times. The body of the abstract should be typed in normal 8,5-point Times in a single paragraph, immediately following the heading. The text should be set to 1.15 line spacing. The abstract should be centred across the page, indented 15 mm from the left and right page margins and justified. It should not normally exceed 200 words.

1 Introduction

The ultra high molecular weight polyethylene (UHMWPE) fiber has attracted great attention due to its low density, solubility properties, and superior mechanical properties including high Young's modulus and tensile strength that are favorable for industrial applications[1-4]. Since the 1970s, UHMWPE fibers have been produced by various drawing methods such as solid state hot drawing, solid state extrusion, free growth, surface growth, and gel-spinning. Among them, one of the most successful methods of commercial introduction of high-strength, high-modulus polyethylene fiber is the process of gel-spinning. But, the apparent disadvantage of the gel-spun method is the use of organic solvents that are difficult to recycle and remove.

Melt spinning is an efficient, simple, and nonpolluting method. However, the modulus and strength of melt-spun hot drawn fibers are still much lower than those of gel-spun fiber. Producing high modulus and high strength monofilaments from PE have been one of the challenges in fishing science and technology for a very long time. Yanela Alonso [5] studied the influence of sepiolite content (1, 2, and 3 wt%) and successive drawing steps on the final properties of polyethylene/sepiolite nanocomposite fibers. They found that Young Modulus increases 17 times with drawing in pure PE fibers and 1.5 times because of the presence of sepiolite, and the strength shows similar behavior. Most of the published research has indicated that rigid fillers in composite systems, including filled polyethylene, improved mechanical properties[6-9]. And, the improvement of the mechanical properties in reinforced materials depends on the dispersed states of nano-fillers and interactions between polymer and nano-fillers.

In this paper, TiO₂/UHMWPE nanocomposite monofilament was prepared by reactive extrusion in a

twin-screw extruder and melt spinning. Its morphology and thermal properties were characterized by SEM, DSC and mechanical tensile test.

2 Experimental

2.1. Materials and monofilaments preparation

UHMWPE with an density 950 kg/m³ was supplied by Sinopec Yangzi Petrochemical Company, China. The organically modified TiO₂ was provided from Hangzhou Wanjing New Material Company, China.

TiO₂/UHMWPE hybrid was prepared by reactive extrusion in a twin-screw extruder (Jiangsu, China) at 250 ~ 280 °C from UHMWPE (dried at 80 °C for 12 h) with 3 phr organically modified SiO₂ (dried at 80 °C for 12 h). The mixing speeding is 60 rpm. The extruded strands were pelletized and dried at 80 °C for 24 h to prepare the TiO₂/UHMWPE hybrid. The TiO₂/UHMWPE hybrid was then melt-spun through a 0.5 mm diameter spinneret using a SJ-45C Fiber Spin Line equipped with two drawing roll and a collecting roll (Jiangsu, China). The drawn ratio is 24, and the diameter of TiO₂/UHMWPE nanocomposite monofilaments is about 0.35 mm.

2.2 Characterization

The microstructures of the monofilaments were examined by a JEOL 6360LA scanning electron microscope (SEM) (JEOL Ltd., Japan) operated at an acceleration voltage of 15 kV.

Differential scanning calorimetry (DSC) was applied to investigate the melting and crystallisation behaviour of the monofilaments using a DSC thermal analyser (204F1, Netzsch Instruments, Germany). The samples were scanned at a heating and cooling rate of 10 oC/min in

^a Corresponding author: jiangaoshi666@163.com

nitrogen atmosphere. The degree of crystallinity (X_c) was calculated via the total enthalpy method, according to Eq.

$$X_c = \left(\frac{\Delta H_f^{obs}}{\Delta H_f^0} \right) \times 100 \quad (1)$$

where ΔH_f^{obs} is the observed heat of fusion values. ΔH_f^0 is the specific enthalpy of melting for 100% crystalline polymer. We used ΔH_f^0 value for HDPE 288 J/g.

The tensile properties were studied on an Electron Omnipotence Experiment Machine INSTRON-4466 (Instron Instruments, USA) at a cross-head speed of 300 mm/min according to SC/T 5005-2014 under ambient conditions. At least ten specimens were measured for each sample.

3. Results and Discussion

3.1 Morphology of TiO₂/UHMWPE nanocomposite monofilaments

Figure 1 presents the fracture surface micrographs of TiO₂/UHMWPE nanocomposite monofilaments. The nanocomposite monofilament has a smooth surface. And the SEM images of the fracture surface indicate that the TiO₂ nano particles are well dispersed throughout the polymeric matrix, which could be related to strong interactions between UHMWPE molecular chain and nano-fillers (see Figure 1).

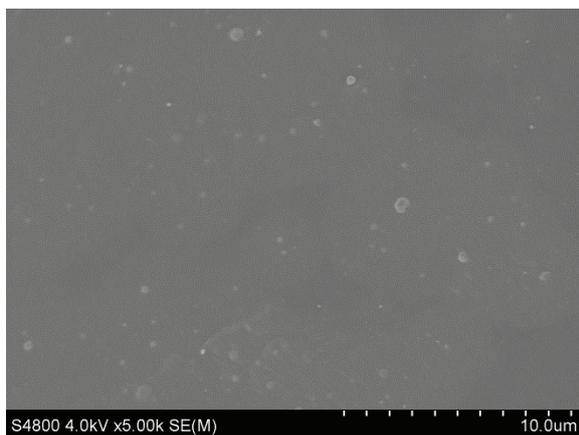


Figure 1 The SEM micrographs of TiO₂/UHMWPE nanocomposite monofilaments

3.2 Thermal analysis of TiO₂/UHMWPE nanocomposite monofilaments

Figure 2 shows the DSC heating and cooling thermograms of TiO₂/UHMWPE nanocomposite monofilaments and UHMWPE monofilaments. The DSC data are summarised in Table 1, including the melting temperature (T_m), percentage of crystallinity and

crystallisation temperature (T_c). It could be noticed from Figure 2 that all monofilaments exhibit a melting peak of the PE component. And the incorporation of TiO₂ causes a increase in T_m and T_c , and reduces the degree of crystallinity of UHMWPE. The percentage of crystallinity for TiO₂/UHMWPE nanocomposite monofilaments decreases by 2.2%. This could be due to some difficulty in chain crystallization brought about by the presence of the TiO₂ in the nanocomposite monofilaments systems.

Table 1 The DSC data of UHMWPE and TiO₂/UHMWPE nanocomposite monofilaments

Samples	T_m [°C]	Percentage of crystallinity [%]	Crystallisation temperature [°C]
UHMWPE	141.2	64.9	116.7
TiO ₂ /UHMWPE	142.6	63.5	117.0

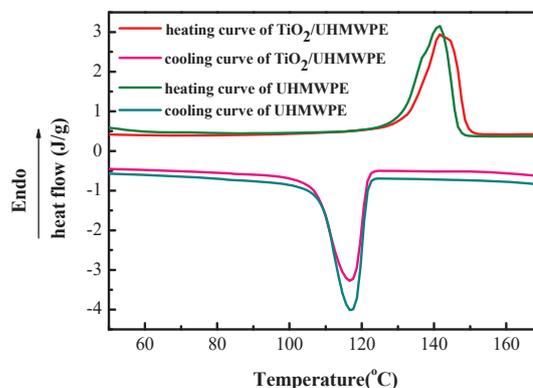


Figure 2 DSC heating cooling thermograms of UHMWPE and TiO₂/UHMWPE nanocomposite monofilaments

3.3 Tensile mechanical properties

The tensile mechanical properties of TiO₂/UHMWPE nanocomposite monofilaments are shown in Fig. 4. Compared with that of UHMWPE monofilaments, the breaking strength and knot strength of nanocomposite monofilaments increases with introducing TiO₂ content. This is probably due to the strong interaction between the UHMWPE molecular chain and nano TiO₂, which make the crack propagation blocked and passivated in the stretching process. It is noted that the TiO₂/UHMWPE nanocomposite fiber has a distinctly superior knot strength which is 32.4% higher than that of the pure UHMWPE fiber. Moreover, the breaking strength and knot breaking strength of the TiO₂/UHMWPE fiber were 7.61 cN/dtex and 8.16 cN/dtex respectively, 46.3% and 56.9% higher than the indexes for the fishing PE monofilament according to the industrial standard SC/T 5005. Elongation is a key factor in the material characteristics and the application properties, and the low elongation rate is another important property for fishing. Elongation at break decreases monotonically with the

addition of nano TiO₂. This could be due to the interaction between the nano TiO₂ and UHMWPE molecular chain, and the monofilaments toughness reduces with the increase of TiO₂ content.

Table 2 The tensile mechanical properties of TiO₂/UHMWPE nanocomposite monofilaments

Samples	Breaking strength /cN·dtex ⁻¹	knot strength /cN·dtex ⁻¹	Elongation at break /%
UHMWPE monofilament	7.61	3.67	15.1
TiO ₂ /UHMWPE nanocomposite monofilaments	8.16	4.86	14.5

4 Conclusion

TiO₂/UHMWPE nanocomposite monofilaments were prepared successfully by melt spinning through a co-rotating screw extruder and drawing at hot water. The TiO₂ nano particles are well dispersed throughout the polymeric matrix. The introduction of TiO₂ increases the melt point, whereas decreases degree of crystallinity of polyethylene. The breaking strength and knot strength of the nanocomposite monofilaments are remarkably improved upon nanofiller addition. The TiO₂/UHMWPE nanocomposite fiber has a distinctly superior knot strength which is 32.4% higher than that of the pure UHMWPE fiber.

Acknowledgements

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References

1. Ward I M. Recent developments in the science and technology of high modulus flexible polymers[J]. *Macromolecular Symposia*, 1995, 100(1):1–14.
2. Huang W, Wang Y, Xia Y. Statistical dynamic tensile strength of UHMWPE-fibers[J]. *Polymer*, 2004, 45(11):3729-3734.
3. Du G, Wang J. The mechanical properties of surface treated UHMWPE fibers and TiO₂ reinforced PMMA composite[J]. *Surface & Interface Analysis*, 2017.
4. Chand N, Kreuzberger S, Hinrichsen G. Influence of processing conditions on the tensile properties of

- unidirectional UHMWPE fibre/LDPE composites[J]. *Composites*, 1994, 25(9):878-880.
5. Alonso Y, Martini R E, Iannoni A, et al. Polyethylene/sepiolite fibers. Influence of drawing and nanofiller content on the crystal morphology and mechanical properties[J]. *Polymer Engineering & Science*, 2014, 56(8):149-149.
6. Mohammadalipour M, Masoomi M, Ahmadi M, et al. Interfacial shear strength characterization of GMA-grafted UHMWPE fiber/epoxy/nano clay hybrid nanocomposite materials[J]. *Rsc Advances*, 2016, 6(48):41793-41799.
7. Yu J R, Luan X N, Hu Z M, et al. Preparation and studies on the structure and properties of ultrahigh molecular weight polyethylene/nano-SiO₂ composite fibers[J]. *Acta Polymerica Sinica*, 2005, 1(5):764-768.
8. Yeh J T, Wang C K, Huang L K, et al. Ultradrawing and Ultimate Tenacity Properties of Ultrahigh Molecular Weight Polyethylene Composite Fibers Filled with Nanosilica Particles with Varying Specific Surface Areas[J]. *Journal of Nanomaterials*, 2015, (2015-9-30), 2015, 2015:1-16.
9. Yeh J T, Yi D, Wang C K, et al. Ultradrawing and ultimate tenacity properties of Ultra-High Molecular Weight Polyethylene composite fibers filled with nanosilica particles with varying specific surface areas[M]// *Applied System Innovation*. 2016.