

Original research article

## The structure and mechanical property of silane-grafted-polyethylene/SiO<sub>2</sub> nanocomposite fiber rope

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## ABSTRACT

The effect of vinyltrimethoxysilane (VTMS) graft and SiO<sub>2</sub> on the structure and mechanical properties of silane-grafted-polyethylene/SiO<sub>2</sub> (VTMS-g-PE/SiO<sub>2</sub>) nanocomposite fibers and ropes was studied. Scanning electron microscopy (SEM), Fourier transfer infrared (FT-IR), differential scanning calorimetry analysis (DSC) and tensile mechanical tests were performed to characterize the morphology, thermal and mechanical properties of nanocomposite fibers and ropes. The results revealed that the SiO<sub>2</sub> nanoparticles were well dispersed throughout the polymeric matrix. With increasing SiO<sub>2</sub> content,  $T_m$ , the melt peak width and  $X_c$ , degree of crystallinity, of VTMS-g-PE/SiO<sub>2</sub> nanocomposite fibers increased. The breaking load and breaking strength of the nanocomposite fiber ropes were remarkably improved compared to pure PE fiber ropes and elongation at break was also decreased.

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## 1. Introduction

Ropes, widely used in modern fishery, are most commonly made of synthesized fibers such as polyethylene (PE) fiber, polypropylene (PP) fiber, polyamide (PA) fiber and polyester (PET) fiber (McKenna, Hearle, & O'Hear, 2004; McKenna, 1983, 2006). Among such materials, PE fiber ropes are the most used thermoplastic commodity for fisheries, due to their good mechanical properties, chemical resistance, low density, processability and low cost (Marissen, 2011). Such ropes are widely used in lifting and mooring applications in oceanographic research, offshore oil and gas explorations and commercial fishing (Banfield & Casey, 1998; Da Costa Mattos & Chimisso, 2011). PE fiber ropes in particular, are widely used in industrial applications because of the considerable increase in mechanical performance achieved when appropriate mechanical stretching occurs during manufacturing. The tensile mechanical properties of fishing rope have an effect on the expansion, special offshore work and safety against sea wind (McKenna & Wong, 1979; Vlasblom, Boesten, Leite, & Davies, 2012; Wang, Shi, Chen, & Shi, 2009). With the development of modern fisheries, higher performance of synthetic fiber ropes is needed. The mechanical property of general synthetic fiber ropes can't meet the large scale,

modernization and special offshore operation requirements of modern fishing and aquaculture operations. Hence, PE fishing ropes with high strength are technologically important and have attracted great interest. High molecular weight polyethylene (UHMWPE) rope has been used successfully in fisheries because of its outstanding comprehensive properties (Ma, Guo, & Mao, 2005; Sheng, Jie, Yang, & Cuo, 2003). At present, it has been applied in marine fishing and large aquatic farm fences. UHMWPE fiber mesh has played an important role in improving the resilience of netting against the effects of ocean waves. However, the large-scale application of UHMWPE fiber in the area of fisheries has been limited by its high costs and complicated gel-spinning technique. Therefore, modified PE fiber ropes with reduced production costs and simplified methods of production are critical for the development of fishing ropes.

The properties of ropes are determined by the properties of their fibers and knitting structure. Modified PE fibers have been extensively studied (Fambri, Dabrowska, Ferrara, & Pegoretti, 2016; Kageyama, Tamazawa, & Aida, 1999; Sulong, Park, Azhari, & Jusoff, 2011; Zhao et al., 2015). Pure PE properties can also be improved through the formulation of nanocomposites taking advantage of the synergistic combination of polymer and nanofiller properties (Alonso et al., 2015; Kutlu et al., 2014; La Mantia, Dintcheva, Scaffaro, & Marino, 2008; Rattanawijjan & Amornsakchai, 2012). Alonso et al. (2015) studied the influence of sepiolite content (1, 2, and 3 wt%) and successive drawing steps on the final properties of polyethylene/sepiolite nanocomposite fibers.

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They found that the Young Modulus increased 17 times with drawing in pure PE fibers and was further enhanced 1.5 times when sepiolite was present and a similar effect on strength was also found. Most published studies have reported that rigid fillers in composite systems, including filled polyethylene, improve the mechanical properties of PE fibers (Fouad, Mourad, & Barton, 2005; Tanaka, 2001). The improvement in the mechanical properties of reinforced materials depends on the dispersed states of the nano-fillers and the interactions between polymer and nano-fillers. To facilitate interactions between polymer and nano-fillers, a polymer functionalized with polar groups, such as maleic anhydride or hydroxyl groups has often been employed. Silanes used in the manufacture of crosslinkable polyolefins are mainly vinylalkoxysilane and contain two functional groups in their chemical structures, a C=C group that can be grafted onto polymer and a Si=OR (R: CH<sub>3</sub> or CH<sub>2</sub>CH<sub>3</sub>) that can be coupled with nano-fillers (Azizi, Morshedian, & Barikani, 2009; Fabris, Cardozo, Mauler, & Nachtigall, 2009; Lu, Hu, Li, Chen, & Fan, 2006; Sirisinha, Boonkongkaew, & Kositchaiyong, 2010).

In the present study, the morphology, thermal and mechanical properties of a silane-grafted-polyethylene/SiO<sub>2</sub> (VTMS-g-PE/SiO<sub>2</sub>) hybrid nanocomposite fiber prepared by reactive extrusion in a twin-screw extruder coupled with melt spinning were investigated. The VTMS-g-PE/SiO<sub>2</sub> nanocomposite fiber rope had a diameter of 10 mm and was made via ring twist and strand combine. The morphology and thermal properties of the nanocomposite fiber rope were characterized by scanning electron microscopy (SEM), Fourier transfer infrared (FT-IR) and differential scanning calorimetry analysis (DSC).

## 2. Materials and methods

### 2.1. Materials

High density polyethylene (HDPE 5000S) with an MFI 0.9 g per 10 min and density 950 kg/m<sup>3</sup> was supplied by Sinopec Yangzi Petrochemical Company, China. The initiator dicumyl peroxide (DCP), styrene, and vinyltrimethoxysilane (VTMS) were supplied by Sinopharm Chemical Reagent Company, China. The organically modified SiO<sub>2</sub> was provided from Hangzhou Wanjing New Material Company, China.

### 2.2. Preparation of VTMS-g-PE/SiO<sub>2</sub> nanocomposite fibers

VTMS-g-PE/SiO<sub>2</sub> hybrid was prepared by reactive extrusion in a twin-screw extruder (Jiangsu, China) at 160–220 °C from HDPE (dried at 80 °C for 12 h) with 0.1 phr (part of reagent per hundred parts of HDPE) DCP, 2.0 phr VTMS, 0.1 phr styrene and a pre-determined amount of organically modified SiO<sub>2</sub> (dried at 80 °C for 12 h). The mixing speed was 60 rpm. The extruded strands were pelletized and dried at 80 °C for 24 h to prepare the VTMS-g-PE/SiO<sub>2</sub> hybrid.

The VTMS-g-PE/SiO<sub>2</sub> 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. The drawn ratio was 8.0, and the diameter of VTMS-g-PE/SiO<sub>2</sub> nanocomposite fiber was about 0.2 mm. Crosslinking of the grafted samples was performed by immersing the moulded samples in hot water at 90 °C for 48 h under tension. In the present study, several weight ratios of SiO<sub>2</sub> to VTMS-g-PE/SiO<sub>2</sub> nanocomposite fibers were used, 0.3 wt%, 0.5 wt%, and 1 wt% and named VTMS-g-PE/SiO<sub>2</sub>-0.3, VTMS-g-PE/SiO<sub>2</sub>-0.5 and VTMS-g-PE/SiO<sub>2</sub>-1, respectively.

### 2.3. Preparation of VTMS-g-PE/SiO<sub>2</sub> nanocomposite fiber ropes

A VTMS-g-PE/SiO<sub>2</sub> nanocomposite fiber rope with 3-strand was prepared using a rope twisting machine. The VTMS-g-PE/SiO<sub>2</sub> nanocomposite fiber was first divided and then made into strands. The strands were twisted with VTMS-g-PE/SiO<sub>2</sub> nanocomposite fiber strings and then a number of strands turned around the core to form a twisted rope. The twist was 20 T/m. For comparison purposes, normal 3-strand PE rope and 4-strand twisted PE rope were made as per usual using pure PE fibers.

### 2.4. Characterization

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

FT-IR spectra were measured using a Nicolet spectrometer model 560 (Nicolet Instruments, USA). The samples were scanned 32 times at a resolution of 4 cm<sup>-1</sup>.

Differential scanning calorimetry (DSC) was applied to investigate the melting and crystallisation behaviour of the fibers using a DSC thermal analyser (204F1, Netzsch Instruments, Germany). The samples were scanned at a heating and cooling rate of 10 °C/min in a nitrogen atmosphere. The degree of crystallinity (X<sub>c</sub>) was calculated via the total enthalpy method, using the following equation:

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

where  $\Delta H_f^{obs}$  is the observed heat of fusion values;  $\Delta H_f^0$  is the specific enthalpy of melting for 100% crystalline polymer and  $\Delta H_f^0$  was defined as HDPE 288 J/g.

The tensile properties of VTMS-g-PE/SiO<sub>2</sub> nanocomposite fiber were studied on an Electron Omnipotence Experiment Machine INSTRON-4466 (Instron Instruments, USA) under ambient conditions. The cross-head speed of fibers was 300 mm/min according to SC/T 5005-2014. The cross-head speed of ropes was 100 mm/min according to GB/T 8834-2006. At least five specimens were measured for each of the VTMS-g-PE/SiO<sub>2</sub> (0.3 wt%, 0.5 wt%, and 1 wt%) nanocomposite fiber samples fabricated.

## 3. Results

### 3.1. Grafting analysis from FT-IR and morphology of VTMS-g-PE/SiO<sub>2</sub> nanocomposite fibers

Fig. 1 shows the FTIR spectra of HDPE and VTMS-g-PE. All samples displayed characteristic IR peaks at 720 and 1458 cm<sup>-1</sup> which were assigned to the CH<sub>2</sub> rocking and CH bending vibrations of methyl and methylene groups, respectively. Three additional peaks of methoxysilane (Si–OCH<sub>3</sub>) groups were evident at 802, 1092 and 1192 cm<sup>-1</sup> in the silane-grafted VTMS-g-PE samples (Ahmed, Gilbert, Mainprize, & Rogerson, 2013; Kuan, Kuan, Ma, & Huang, 2005; Lu et al., 2006). The identification of characteristic methoxysilane spectra in all grafted samples confirmed the success of the silane grafting reaction.

Fig. 2 presents the SEM micrographs of VTMS-g-PE/SiO<sub>2</sub>-0.5 nanocomposite fibers (Fig. 2a) and their fracture surface (Fig. 2b). The nanocomposite fiber had a smooth surface and the SEM images of the fracture surface indicated that the SiO<sub>2</sub> nanoparticles were well dispersed throughout the polymeric matrix (see Fig. 2b).

Fig. 3 shows the DSC heating and cooling thermograms of various VTMS-g-PE/SiO<sub>2</sub> nanocomposite fibers. The DSC data are summarized in Table 1 and includes the melting temperature (T<sub>m</sub>),

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