

Surface Characterization of Helium Plasma Treated Nano-SiO₂ Sol-gel Coated UHMWPE Filaments by Contact Angle Experiments and ATR-FTIR

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Abstract: Ultrahigh molecular weight polyethylene (UHMWPE) Filaments has a low surface free energy and therefore modification of their surface properties before any use is often needed. Atmospheric pressure plasmas treatment is a convenient and environment friendly way to obtain these modifications by introducing new chemical groups at the surface without affecting the bulk properties. This paper studies the influence of nano-SiO₂ Sol-gel coated pretreatment on atmospheric pressure jet (APPJ) treatment of UHMWPE fibers with helium used as the treatment gas. The surface properties of the plasma-treated UHMWPE Filaments are characterized using contact angle measurements and ATR-FTIR spectroscopy. The UHMWPE Filaments show a remarkable increase in surface free energy after plasma treatment. ATR-FTIR spectroscopy of the plasma-treated UHMWPE Filaments reveals that plasma treatment introduces oxygen-containing functionalities, such as ketones, aldehydes, alcohols and carboxylic acids on the UHMWPE Filaments surface leading to the increase of surface free energy.

Keywords: Plasma jets, UHMWPE, contact angle, fourier transform infrared spectroscopy.

1. Introduction

Ultra-high molecular weight polyethylene (UHMWPE) filaments with outstanding characteristics such as high tensile strength, high Young's modulus, low density etc. has been widely used in various fields ranging from civil to military applications [1]. Nevertheless, surface treatments of the UHMWPE filaments have received great interests with a view to improving its shortcomings such as low surface energy and chemically inert surface as a result of the poor interfacial adhesion between the UHMWPE filaments and matrix in the recent decades [2].

Therefore, extensive researches focusing on surface treatments of the UHMWPE have been carried out including flame-oxidation; chemical etching and ultraviolet initiated grafting by introducing chemically active groups onto the surface of the UHMWPE filaments with an aim of improving interfacial adhesion of UHMWPE-reinforced composites [3]. For instance, Moon et al. reported that oxygen plasma treatment introduces micro pitting on the UHMPE filament surface, which not only improved

interfacial adhesion and flexural properties, but also decreased impact properties of UHMWPE filament/epoxy composites and UHMWPE filament/vinylester composites through mechanical interlocking [4]. Then, Cho et al. reported that the interfacial bonding strength between UHMWPE and PMMA bone cement considerably improved by c-ray irradiation method [5]. Osterom et al. showed that the adhesion properties of UHMWPE improved to various degrees after the surface treatments including UV/Ozone, corona, abrasion, glow discharge and a combination of abrasion and glow discharge treatment [6]. Yet, till now, there are limited papers related to coating technology applied to the UHMWPE surface modification. Yet pretreatment of nano-particles is an essential procedure for the purpose of achieving the relatively specific dispersion of the nano-particles on the fiber surface, otherwise the advantages of nanoparticles do not exhibit since nano-particles have a strong tendency to agglomerate induced by its high surface energy [7]. In our previous work, a series of commercialized nano-fillers including nano-SiO₂, nano-TiO₂, nano-ZnO particles, carbon

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nano-tube and montmorillonite have been successfully modified and activated with the aim of achieving uniform dispersion of nano-fillers in the polypropylene/ polylactic acid (PP/PLA) matrix and increasing the cohesive affinity of the matrix by using atmospheric pressure plasma jet [8-11].

The attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy has been used successfully to obtain structural information of plasma-treated polymer surfaces [12,13]. In this article, it will be shown that by choosing the appropriate ATR accessory, ATR-FTIR spectroscopy is able to detect structural alteration upon plasma surface treatment nano-SiO₂ coating UHMWPE filaments. This work focuses on ATR-FTIR analysis of plasma-modified nano-SiO₂ coating UHMWPE filaments. The plasma treatment was performed using APPJ. The surface properties of the plasma-treated nano-SiO₂ coating UHMWPE filaments are characterized using contact angle measurements, surface free energy calculations and ATR-FTIR.

2. Experimental

2.1. Materials

Nano Silicon dioxide (nano-SiO₂) obtained from Hong Sheng Materials Technology Co., Ltd. The UHMWPE fiber with an average single fiber diameter of 28 μ m supplied from Ningbo Dacheng Chemical Fibers Company (Zhejiang, China).

2.2. Plasma treatment

The surface of UHMWPE filaments by sol-gel dip-coating technique was deposited with Nano-SiO₂ particles. Nano-SiO₂ sol-gel with a primary size of 14 nm in acetone was employed. After the diluted solution was filtered, it was coated on the surface of UHMWPE filaments by dip coating. By changing the concentration of nano-SiO₂ sol-gel and the speed of dip coating, the coverage of nano-SiO₂ particles on UHMWPE filaments can be tuned. In this paper, the

concentration of nano-SiO₂ colloid was about 0.5 wt %, and the speed of dip-coating was 0.13 mm/s.

After coating, these filaments were treated by an APPJ (Atomflo-R, Surfex Company, USA) with 100% Helium gas. The APPJ was a small plasma jet with a length of around 15cm, consisting of two concentric electrodes with a 1.6mm gap through which the working Helium gas flows. The gas discharge was ignited by applying a low 13.56MHz radio frequency power, which enabled the jet to produce a stable discharge and to avoid the arc transition.

The distance between the nozzle and the top of the nano-SiO₂ coating UHMWPE filaments was 5mm. The substrate circumrotated underneath the plasma jet at a speed of 10mm/s. Other plasma treatment parameters were set as follows: flow rate of helium gas was 20L/min, output power was 40W, treatment nozzle temperature was 60°C and sample treatment or stationary time was 3.3s.

2.3. Contact angle measurement

Contact angle measurement was performed to determine the wettability of the fiber surface using sessile drop technique in which the shape of the distilled water droplets attached to the fibers were recorded as digital images taken by the JC2000A Stable contact angle analyzer (Powereach Digital Equipment, Shanghai, China) as described by Carroll [14]. Each contact angle reported was an average of at least 15 different measurements and at least 5 fibers were used. The single fiber specimen fixed by an adhesive tape on a frame with a certain amount of tension and the length of the fiber was about 2.5 cm. The water droplets were sprayed onto the single fiber during the test.

2.4. Fourier transform infrared (FTIR)

Infrared (IR) absorption spectra of the UHMWPE filaments was acquired in attenuated total reflection (ATR) on a Nicolet 5700 FTIR spectrometer (Thermo Nicolet) equipped with a Smart Performance accessory (Thermo Nicolet) with a ZnSe crystal. The spectral region spanned from 4000 to 500 cm^{-1} , with a resolution of 4 cm^{-1} , and 256 acquisitions were gathered.

3. Results and discussions

Siloxane coupling agent implanted into UHMWPE gel fibers during extraction process can then be trapped in the fibers or on the surface of the fibers after subsequent ultra-drawing. From the spectrum of the main peak position and intensity of the contrast, it can be seen that a strong and sharp characteristic absorption of Si-CH₃ appears at 1265.80 cm⁻¹. 860 ~ 760 cm⁻¹ between the strong absorption band, is not a single peak, instead multiple peaks. Figure 1 (PE) shows the reflection spectrum of the untreated UHMWPE filaments. It has two large absorption peaks at 2918.14 and 2849.34 cm⁻¹ because of C-H asymmetric and C-H symmetric stretching vibrations in -CH₂- respectively. The spectrum also shows two smaller absorption peaks at 1466 and 727.17 cm⁻¹. The peak at 1466 cm⁻¹ can be attributed to C-H vibration deformation while the peak at 727.17 cm⁻¹ is due to C-C rocking vibrations in -(CH₂)_n-. The spectrum also shows two stronger absorption peaks at 2363.91 and 819.94 cm⁻¹ of Si-H vibrations.

Helium atoms, Oxygen atoms in the air, radicals, UV photons and ions present in the discharge abstract hydrogen atoms from the SiO₂ and PE polymer chains. The Series of Si groups increase significantly. He-plasma treatment of UHMWPE filaments in air leads to the formation of oxygen containing functionalities, such as alcohols, aldehydes, ketones and carboxylic acids on the surface of UHMWPE filaments. These results agree with the results of Gerenser [15]. He-plasma treatment of PE in air leads to the formation of Si groups containing functionalities on the PE surface [16]. The spectrum normalized at 723 cm⁻¹ assuming that few chain scissions occurs after He-plasma treatment. Figure 1 (PE+HE) clearly shows the peaks at 2920 and 2852 cm⁻¹ significantly decrease after plasma treatment. The He-plasma etching the surface of UHMWPE filaments made many Si group reveal on the surface of UHMWPE filaments within siloxane coupling agent, 3700-3600, 3400-3200, 1030 and 910-830 cm⁻¹ of Si-OH stretching vibrations, peak in 2363.91 cm⁻¹ increases significantly after He-plasma treatment. In the region 1830-1150 cm⁻¹, 1737 cm⁻¹ of CO stretching of ketones, aldehydes and carboxylic acids, 907 cm⁻¹ of carboxylic acids, deformation of aldehydes and vinyl groups (-CHCH₂), 1357 cm⁻¹ of C-H rocking vibrations of aldehydes, 1260-1160 cm⁻¹, 1440 cm⁻¹ of C-O stretching vibrations in alcohols arises after He-plasma treatment.

The spectrum significantly changed at 1125 cm⁻¹ of SiO₂ and 1266 cm⁻¹ of Si-CH₃ assumed that UHMWPE

filaments coated by nano SiO₂. Figure 1 (PE+SI) clearly shows that peaks at 2920 and 2852 cm⁻¹ significantly decrease after coating pretreatment. A large peak at 1725.03 cm⁻¹ of CO stretching of ketones, aldehydes and carboxylic acids decreases after pretreatment. Peaks at 3734.74 and 3565.85 cm⁻¹ of Si-OH stretching vibrations appear as a broadband. The spectrum also shows two stronger absorption peaks at 2363.91 and 819.94 cm⁻¹ of Si-H vibrations. The small peak at 1275 cm⁻¹ of C-H vibrations in Si-CH₃ groups confirms the hybrid character of these coating pretreatment.

Figure 1 (PE+HE+SI) shows the FTIR of the SiO₂ pro-coating UHMWPE filaments after He-plasma treatments. the 3855.26, 3676.32 and 3568.22 cm⁻¹ of Si-OH stretching vibrational absorption peaks, 819.94, 2359.02 cm⁻¹ of Si-H vibrations, 1723.99 cm⁻¹ of CO stretching of ketones, aldehydes and carboxylic acids and 1266.16 cm⁻¹ of Si-CH₃ significantly decrease, but the intensity of 1125.40 cm⁻¹ of SiO₂ related peaks increased. He-Plasma treatment of the SiO₂ pro-coating UHMWPE filaments also leads to form a broad peaks at 847.05, 839.34, 800.53, 827.09, 781.13, 771.16, 757.63, 740.65 cm⁻¹. This peak can be due to Si-CH vibrations and Si-H bending vibrations. There is also a broad peak which appeared in the region of 1260-1160 cm⁻¹ of C-O stretching vibrations in alcohols after treatment.

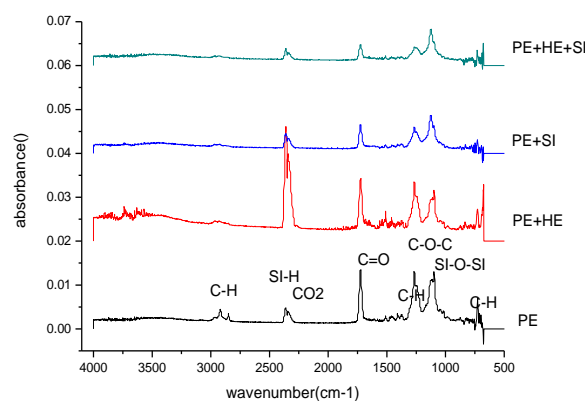


Figure 1 FTIR spectrum of different surface treated UHMWPE filaments.

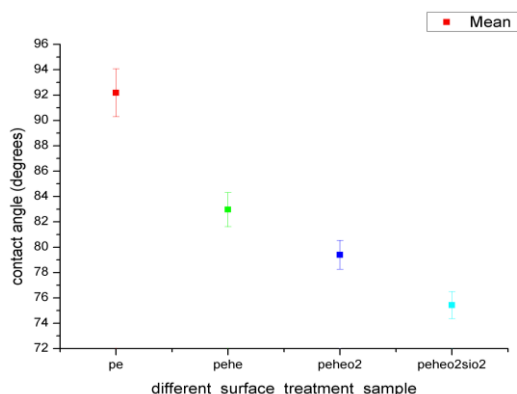


Figure 2 Water contact angle of UHMWPE filaments under different treatments.

The statistical analysis of the water contact angles of the treated UHMWPE filaments is plotted in Figure 2. The mean water contact angle of the control UHMWPE filaments was 92.18256° and it decreased by 10.96% after the nano-SiO₂ coating, 11.11% after the helium plasma treatment and 17.15% after the nano-SiO₂ coating UHMWPE filaments treated by helium plasma, respectively. Moreover, all the standard error of the single contact angles reduced after the different surface treatments. The helium plasma treatment nano-SiO₂ sol-gel coated UHMWPE filaments presented the smallest standard error of the single contact angles and 103.12% lower than that of the control fiber, implying the specific dispersion of the nano-SiO₂ coating of the UHMWPE filaments treated by helium plasma.

4. Conclusion

In this article, it was found that an APPJ treatment in air is an effective tool to decrease the water contact angles of nano-SiO₂ coated UHMWPE filaments; the water contact angles can be decreased from 92 to 78° after only 3.3 s of helium plasma treatment. This large decrease in the water contact angles is due to oxidation of the surface in the helium plasma; a wide range of reactive species is generated in the plasma, which under go consecutive chemical reactions, creating oxygen-containing functionalities on the nano-SiO₂ coated UHMWPE filaments surface. As stated in this article, ATR-FTIR spectroscopy can be used to detect these oxygen-containing groups.

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