Hyperbranched Polyester-Stabilized Nanotitania-Coated Vectran Fibers with Improved UV-Blocking Performance

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An —OH terminated hyperbranched polyester is used to stabilize TiO$_2$ nanomaterials (10 nm) in situ synthesized via a sol–gel method with butyltitanate as precursor. X-ray diffraction (XRD) analyses and thermogravimetric (TGA) analyses illustrate the interactions of the hyperbranched polyester with the TiO$_2$ nanoparticles. The stabilized TiO$_2$ nanocomposites are used in the finishing process of Vectran and a continuous uniform TiO$_2$ coating on the Vectran fiber surface is achieved. The TiO$_2$-treated Vectran filaments exhibit an increased tensile strength compared to the untreated Vectran systems upon exposure to Xenon lamp UV radiation. The coating leads to improved UV-blocking performance.

1. Introduction

Vectran fibers with many unique physicochemical properties including good chemical resistance, high thermal stability, high strength and modulus, excellent fold characteristics, outstanding cut resistance, and high impact resistance are promising materials for deployments in the field of military and aerospace as high performance fibers.[1] For instance, Vectran fibers can be used for load-carrier layer materials in the design of high-altitude airship envelope materials.[2] However, Vectran fiber is susceptible to degradation when exposed to ultraviolet (UV) irradiation, which will deteriorate the strength of the Vectran fibers.[3] Thus, it is necessary to provide effective protection against such damage.

Besides being widely used as an anode material in lithium ion batteries[4] and as photocatalyst for organic pollutant degradation,[5–9] the UV-blocking performance of TiO$_2$ has attracted great interests,[10,11] which is influenced by the particle size and distribution, and the particles with smaller size tend to show better UV-blocking property.[12] However, aggregation of TiO$_2$ nanoparticles in colloid solution or coatings on the fiber surface is especially prone to occur.[13,14] Therefore, synthesis of stable and dispersed nanoparticles with desired UV-blocking performance is becoming crucial for potential applications of high quality end products.

Recently, hyperbranched functional polymers have been studied extensively due to their many functional end groups and surface interactions for potential applications...
The synthesis of nanoparticles with good dispersity can be well controlled by hyperbranched polymers. The presence of plenty of reactive functional end groups of hyperbranched polymers may provide a convenient way for the modification of nanomaterials.

It is well known that the relatively simple low-temperature sol–gel method is an advanced technology to prepare TiO₂ coatings on fiber substrates with poor thermal stability. In a typical sol–gel process, when the hydrolysis reaction of the precursors starts, the hydroxyl groups on the surface of the formed products can interact with the reactive functional end groups of some hyperbranched polymers, and thus nano-TiO₂ with good dispersity and small size can be obtained. Hyperbranched polymers are generally soluble in water and ethanol, such feature is very suitable for in situ sol–gel preparation of hyperbranched polymer-modified TiO₂ coatings on fiber substrates. In situ preparation of titania coatings by using hyperbranched polymers on fibers is of great significance in the finishing process of fibers for attaining UV-blocking, which has not been reported yet.

In this paper, an —OH terminated hyperbranched polyester has been used for modifying in situ sol–gel formed TiO₂ nanomaterials, and the modified materials were used for the finishing process of Vectran fibers, resulting in improved UV-blocking properties. The sol–gel method was used for the preparation of —OH terminated hyperbranched polyester-modified TiO₂ nanoparticles and coatings. The materials obtained were characterized, and the modified nano-TiO₂ fibers have been studied against UV-radiation together with the mechanical properties, while the results were compared with pure Vectran substrates.

2. Experimental Section

2.1. Materials

Vectran fibers (diameter: 22 μm) were supplied by Jinsor-Tech Industrial Corporation (Taiwan). The chemical structure of the fibers were given in our previous study. The fibers were purified by extracting any surface attached impurities with acetone and petroleum ether before finishing. Butyltitanate, absolute ethyl alcohol, glacial acetic acid, and hydrochloric acid were reagent grade. Deionized water was used for hydrolysis of butyltitanate.

The —OH terminated hyperbranched polyester was used for the synthesis of modified nano-TiO₂, which was purchased from Aldrich. The number of —OH functional groups per molecule is 16. M₀ obtained by GPC measurements is 2 860 g·mol⁻¹. The chemical structure of the —OH terminated hyperbranched polyester is shown in Figure 1.

2.2. Sol–Gel Synthesis of Hyperbranched Polyester Modified Titania Nanoparticles

The butyltitanate (17 mL) was mixed with absolute ethyl alcohol (19.5 mL) and glacial acetic acid (3 mL), followed by vigorously stirring for 20 min. A second solution, made up of absolute ethyl alcohol (9.7 mL), deionized water and HCl, was added drop by drop with strong stirring at room temperature. Butyltitanate, water and HCl were maintained in a molar ratio of 1:3:0.8, respectively. The hyperbranched polyester (0.01 g) was dissolved in 20 mL absolute ethyl alcohol as the third solution, which was added dropwise immediately when the dropping of the second solution was finished. The resultant mixture was then heated to 40 °C with strong stirring for 7 h. All the reaction procedures were carried out under ultrasonication. A clear yellow solution of hyperbranched polyester-modified TiO₂ nano-sol was obtained. The nano-sol was stable for 1 d before the preparation of TiO₂ gel and the coating procedure. The sol was dried under vacuum at 50 °C for 24 h, then heated to 150 °C for 20 min, and the modified TiO₂ nanoparticles were obtained, which were used for subsequent X-ray diffraction (XRD) and transmission electron microscopy (TEM) analyses.

2.3. Fiber Treatment with TiO₂ Nano-Sol

The Vectran fibers were dipped in the TiO₂ nano-sol for 5 min and then air dried for 3 min. The dip-coating was performed thrice on
the Vectran substrates. Then the coated Vectran fibers were thermally treated under vacuum at 150 °C for 20 min. The Vectran fibers modified with TiO₂ coatings were used for subsequent analyses.

2.4. Characterization Methods

XRD measurements were carried out using the dry hyperbranched polyester and modified TiO₂ powder samples on a Rigaku D/max-rb using Cu Kα radiation (λ = 0.154 nm) as the X-ray source with a rotating copper anode at 40 kV and 50 mA. The patterns were recorded in the 2θ-angle range of 10–80° at a scanning rate of 5°·min⁻¹.

Thermogravimetric analysis (TGA) measured the initial decomposition temperature of dry hyperbranched polyester powder sample and the titania nanoparticle content in the hyperbranched polyester stabilized titania nanoparticles. TGA was performed with a Q50 thermogravimetric analyzer (TA Instruments, USA). The temperature was programmed to increase at a rate of 20 °C·min⁻¹ up to 800 °C under nitrogen.

The UV transmission of the quartz plate coated with the hyperbranched polyester modified titania modified TiO₂ was measured using a Varian Cary 400 UV spectrophotometer. The sample for UV spectrum was obtained by the same dip-coating procedure as the fiber treatments with TiO₂ nano-sol. The quartz plate (20 × 10 × 1 mm³) was pulled out from the sol with uniform velocity in 30 s.

A small amount of TiO₂ powdered sample in ethanol was dropped to Cu grids after ultrasonication for 20 min, and the grid was then dried in air. TEM studies were carried out at high resolution using Cu Kα radiation (λ = 0.154 nm) as the X-ray source with a rotating copper anode at 40 kV and 50 mA. The patterns were recorded in the 2θ-angle range of 10–80° at a scanning rate of 5°·min⁻¹.

The morphology of the Vectran fiber surface was examined before and after finishing by field emission scanning electron microscopy (SEM) with a Quanta 200 FEG equipped with an energy dispersive X-ray spectroscopy (EDS) to analyze the surface compositions. The samples were gold coated to limit the charging effect for a better imaging quality.

The UV-blocking behaviors of the TiO₂ coated Vectran fibers were investigated by exposing the specimens to UV radiation using a Xenon lamp (Atlas Ci3000 xenon arc weather-ometer with an intensity of 0.75 W·m⁻²) for 24, 96, and 336 h, respectively. The patterns were recorded in the 2θ-angle range of 10–80° at a scanning rate of 5°·min⁻¹.

3. Results and Discussion

3.1. Preparation of Nano-Sol and TiO₂ Coating

The hyperbranched polyester was used in the synthesis of modified TiO₂ nano-sol. In the preparation process of TiO₂ sol, the hyperbranched polyester was dissolved in absolute ethyl alcohol in advance. The resulting solution was added dropwise immediately when the hydrolysis of precursor butyltitanate just began. The described treatment allows the interaction between the —OH groups on the surface of the hydrolyzed titania products and the reactive —OH functional end groups of the hyperbranched polyester before the formation of final TiO₂ network.

XRD measurements were performed to disclose the crystallinity of the in situ synthesized hyperbranched polyester stabilized TiO₂ and hyperbranched polyester. Figure 2 shows the XRD patterns of pure hyperbranched polyester and hyperbranched polyester modified TiO₂ nanoparticles. The hyperbranched polyester modified TiO₂ nanoparticles sample exhibits broad peaks at 25.28°, corresponding to the distinctive anatase crystal plane of (101), Figure 2b, indicating the formation of small content of anatase crystallites. The diffraction peak at 17.48° of hyperbranched polyester in Figure 2a cannot be observed in the XRD pattern of hyperbranched polyester modified TiO₂ nanoparticles, indicating that the crystallinity of the hyperbranched polyester is possibly damaged through the interactions with the —OH groups of the TiO₂ hydrolysis products. However, another possible reason for the disappearance of the diffraction peak of hyperbranched polyester is that the drying temperature of experimental procedure is higher than the decomposition temperature of hyperbranched polyester. Therefore, TGA analysis of hyperbranched polyester was performed to determine its decomposition temperature. As shown in Figure 3a, the initial decomposition temperature of the hyperbranched polyester is about 250 °C, while the drying temperature of the modified TiO₂ gel is only 150 °C. Thus, the influence of drying temperature can be eliminated. The TGA curve for modified TiO₂ nanoparticles is shown in Figure 3b, which is similar to the trends that are reported in other papers for pure nanocrystalline anatase TiO₂ powders prepared via the sol–gel method. The gradual weight loss is mainly attributed to the loss of residual organics and absorption water. The loading of TiO₂ on the Vectran fibers was determined from TGA, Figure 3c. The gradual weight loss is
largely caused by the decomposition of hyperbranched polyester and Vectran polymer fibers. The curve is gradually stable after 700 °C. The residual composition is mainly for TiO₂, and the content is approximate 47 wt.%.

The interaction mechanism between the —OH groups of the TiO₂ hydrolysis products and the hyperbranched polyester is presented in Figure 4. The covalent bonds might be formed, and also the physical interactions might be present between the two active —OH groups. The steric hindrance effect contributes to the stable dispersion of TiO₂ hydrolysis products to avoid aggregation of TiO₂ nanoparticles.

Figure 5 shows the UV transmission profile of the modified TiO₂ coating on quartz substrate. The figure shows that the transmission of the treated quartz plate is completely blocked in the spectral region between 250 and 320 nm, which is attributable to the UV absorption of TiO₂ coating, indicating a good UV-blocking performance of hyperbranched polyester-modified TiO₂.

3.2. Morphology Characterization

Figure 6 shows the TEM microstructures of the hyperbranched polyester modified TiO₂ nanoparticles. Nanocrystallites of smaller than 10 nm are identified, Figure 6a, indicating that the hyperbranched polyester has effectively prevented the aggregation of TiO₂ nanoparticles. The measured lattice spacing from the electron diffraction pattern shown in the insert of Figure 6a indicates that the TiO₂ nanocrystallite is the anatase phase. The high-resolution image in Figure 6b shows the lattice fringes of 0.353 nm, which corresponds to the anatase crystal plane of (1 0 1). This is in good agreement with the XRD observations.

Figure 7 shows the SEM surface morphology of the untreated and TiO₂ treated Vectran fiber samples. The surface structure appears to have clear ridges and striations in the longitudinal direction of Vectran fiber, Figure 7a. After treatment with TiO₂ sol, the surface of Vectran is observed to be smoother and does not display any ridges and striations of Vectran fiber, Figure 7b. This suggests that the TiO₂ nanoparticles have formed a uniform continuous layer on the fiber surface. The high-resolution SEM image shows that the sizes of TiO₂ nanoparticles on the surface of Vectran fiber are only a few nanometers. The obtained microstructure of the coating surface is very dense. The performance of small size effect can be well exerted to achieve good UV-blocking property. Figure 7d shows the EDS image of Vectran sample finished with hyperbranched polyester-modified TiO₂. For coated Vectran fiber, carbon, oxygen, chlorine, and titanium were the detected elements. It is clear that, the EDS image confirms that the TiO₂ was loaded on the fiber substrate. The carbon element may be attributed to the hyperbranched polyester and the
Vectran fiber. In addition, the chlorine element appears due to the HCl used in the preparation of TiO₂ nano-sol.

### 3.3. Tensile Mechanical Properties

In order to evaluate the effect of TiO₂ coating on the UV-blocking performance, the tensile property change with irradiation time was analyzed. The tensile tests of the untreated and TiO₂ treated Vectran filaments were carried out after 0, 24, 96, and 336 h. Figure 8 shows the comparison of the tensile strength values of the two samples. As expected, the tensile strength of the treated sample is observed to increase apparently in the presence of Xenon lamp irradiation, reflecting the positive role of the nano-scaled TiO₂ coating on improving the UV-blocking performance of Vectran fiber. However, it is also found that the loss of tensile strength is still high for long radiation exposure time. This is attributed to the fact that an unwanted high transmission of TiO₂ coating in the UV region above 320 nm cannot be avoided, Figure 5. Some organic UV absorbers that allow good UV absorption in wavelengths above 320 nm may be beneficial for the significant enhancement of the tensile strength upon irradiation. Further studies on the combination of organic UV absorbers and TiO₂ in one coating appear to be necessary.
fibration have shown positive effects of the nano-scaled TiO₂ coatings; UV-blocking layers; Vectran fibers

4. Conclusion

In this study, —OH terminated hyperbranched polyester modified TiO₂ nanomaterials were used in the Vectran finishing process for attaining good UV-blocking properties. In situ sol–gel reaction has been successfully used to prepare —OH terminated hyperbranched polyester modified TiO₂ nanoparticles with an average size smaller than 10 nm. The treated fibers exhibit a uniform, continuous layer with a grain size of a few nanometers. EDS images confirm that TiO₂ was loaded on the fiber sample. Tensile strength tests for the untreated and TiO₂ treated Vectran fibers have shown positive effects of the nano-scaled TiO₂ coating on the UV-blocking performance of Vectran fibers, as reflected by the sensible increase of tensile strength of the treated sample over the as-received Vectran fiber upon exposure to Xenon lamp irradiation. Although the UV-blocking behavior of the Vectran fibers is sensibly improved by TiO₂ coating, the loss of tensile strength is still high for long radiation exposure.

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