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Helical flow-driven alignment of off-axial silver-functionalized titanium dioxide fibers in polypropylene tube suitable for medical applications

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ABSTRACT

Inspired by Bouligand-type structure in natural materials featured with helically-aligned reinforcing fibers and superior kink-resistance, we demonstrated an analogous architectural configuration in polypropylene (PP) tube by mean of manipulating helical flow and Ag-coated titanium dioxide (TiO_2) fibers. Firstly, the dopamine-assisted immobilization and in situ reduction of Ag ions were completed on the surface of TiO_2 fiber, endowing the latter with antibacterial property. Then, the functionalized fibers were introduced into PP matrix, and extruded longitudinally, simultaneously with mandrel rotation, constructing a unique helical flow. Preferred orientation driven by the applied flow assembled the bio-inspired Bouligand-like structure with helically-aligned functionalized TiO_2 fibers, benefiting torque load bearing and thereby the bulk kink-resistance of polymer tube accompanied by high antibacterial activity. This was exemplified by a substantial increase of 40% in hoop strength with large bacterial inhibition zone in comparison with the pure PP counterpart prepared via convention extrusion. This Bouligand-mimetic alignment strategy can open up a promising possibility of engineering and develop a series of reinforced architectures via simple industrial melt process, satisfying special functionalities and applications unavailable with the other processing technologies.

1. Introduction

Polymeric tube as a medical device is widely used in clinical applications, with which fluid delivery and medical device entry can be achieved with no requirement for large surgical incisions [1]. In the case of most clinical treatment, polymer tube is inserted difficultly to a target site along a tortuous path, so excellent kink-resistance is an important design criterion for the clinical application [2,3]. Due to axial extrusion and orientation in the process, polymer tubes display poor resistance to hoop load and thus are susceptible to kinking occlusion accompanied by ineffective fluid transportation [4,5]. Incorporation of inorganic reinforcing fillers is an effective way to reinforce polymeric devices [6–9]. For example, Wang reported the reinforcement of the electrospun nanofiber on polypropylene [10]. But axial flow in the extrusion causes the axial alignment of the reinforcements, leading to low efficiency on hoop properties [11]. Kink-resistance of polymer tube can't be benefited from the axially-aligned reinforcement.

Nature has very powerful ability to develop hybrid materials, providing instructive design strategy of high-performance and functional materials [12]. Bouligand structure constituted by helically-aligned reinforcing fiber is widely found in natural materials and has been proved to be mechanically advantage against torsional loading [13]. This alignment configuration inspires us to develop a bionic processing technology to organize the reinforcement's helically-alignment. Few attempts are reported to utilize helically-aligned reinforcing fibers for superior kink-resistance in engineering materials, although the other biomimetic materials have been well-demonstrated, such as nacre-mimetic brick-and-mortar architecture, porous gradient architecture from bamboo, and so on [14]. Now, incorporating a helical spring or braiding helically ribbon reinforcement are two main strategies to eliminate the possibility of kinking polymer tube [15,16]. Weak interfacial interaction and complex technical demand hamper widespread use of the technologies. Additionally, helical metal wire and ribbon reinforcements on macroscopic scale will impose an unsurmountable limitation on efforts to decrease wall thickness and form large lumen diameter [17]. Reinforcing fillers

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prefer to align with flow field, so the alignment in the tube can be manipulated by controlling flow pattern. Rotation extrusion holds a great promise as an effective manufacturing technology to precisely control flow pattern of polymer melt by rotating mandrel and die [18,19]. With this, superposition of axial flow caused by extrusion and hoop flow by mandrel and die rotation causes polymer melts flow helically, potentially assembling the bioinspired Bouligand-like structure with helically-alignment of reinforcing fibers to benefit torque load bearing and thereby bulk kink-resistance of polymer tube.

In addition, as most polymers have no capacity of inhibiting microbial attachment, microbes can adhere to polymer tube surface. The device-associated microbial infection can trigger infectious diseases and is a paramount source of nosocomial infections [20]. Introducing antibacterial agents into medical devices can eliminate the implant-associated infections [21]. As a popular antibacterial agent, silver has been used widely in medical device for clinical application, but high cost and soft nature of silver lay down bottleneck for development of kink-resistant antibacterial polymer tube [22]. By mean of compounding with other reinforcing fillers, Ag hybrids exhibited high strength and unique functions [23]. It's demonstrated that Ag can extend light-absorption of titanium dioxide (TiO_2) from UV into visible region via surface plasma resonance so Ag/TiO_2 hybrid exhibit synergetic antibacterial activity, superior to either component [24]. Accordingly, polymer tubes containing Ag/TiO_2 hybrid are expected to improve the kink-resistance and antibacterial activity. Of course, a critical challenge is to control over the off-axial alignment similar to helical spring.

In this paper, we adopted dopamine surface modification technology to achieve self-polymerization of dopamine on TiO_2 fiber surface [25]. With polydopamine (PDA) coating featuring chelation and reduction capacity, Ag ions were anchored to the TiO_2 and reduced into Ag nanoparticles. Then, the functionalized fibers were incorporated into polypropylene (PP) and the alignment configuration was constructed by manipulating helical flow. As a result, the helically-aligned TiO_2 fibers integrated with surface-loaded Ag synchronously boosted the kink-resistance and antibacterial activity of PP tube, permitting the potential in medical application.

2. Experimental

2.1. Materials

Polypropylene random copolymer (R200P) with weighted average molecular weight of 722 kg/mol and ethylene content of 3.8% was provided by Hyosung Co. (Seoul, Korea). TiO_2 fibers with the length and diameter of 4.7 and 0.25 μm were purchased from Ishihara Sangyo Corporation (Japan). Before use, the fibers were washed with acetone to remove β-nucleating agent on the surface. Dopamine hydrochloride was provided by Aoduofuni Biological Technology Co. (Nanjing, China). Silver nitrate ($AgNO_3$) and tris(hydroxymethyl) aminomethane (Tris) were supplied by Chengdu Kelong Chemical Reagent Factory (Chengdu, China).

3. Sample preparation

3.1. Preparation of Ag–functionalized TiO_2 fiber

Based on dopamine surface modification [26,27], TiO_2 fibers were dispersed in 20 mg/ml dopamine hydrochloride solution with Tris-HCl buffer at room temperature. After t_1 hours, the fibers were washed by distilled waters to remove excess dopamine. Then, the obtained PDA-grafted fibers were immersed into 5 mM $AgNO_3$ solution at room temperature under magnetic stirring for 8 h. Finally, the precipitants were washed with deionized water repeatedly to remove residual silver ions and obtain Ag-functionalized TiO_2 fibers. To evaluate the effect of PDA layer on the loading of Ag nanoparticles, t_1 was set as 0 h, 4 h, 6 h and 8 h, respectively.

3.2. Preparation of PP micro-tube

Ag-functionalized TiO_2 fibers and PP in a weight ratio of 5/95, were compounded in a circular conical twin-screw extruder at 190 °C. The obtained granules were extruded into the composite tube via the self-designed rotation extrusion equipment, where polymer melts were extruded longitudinally with mandrel rotation of 40 rpm. In this case, polymer melt went forward in helical pattern and the details on the rotation extrusion were described elsewhere [18]. The prepared tube had an outer diameter of 3 mm with wall thickness of 0.5 mm. As a control, pure PP tube and PP composite tube with 5% pristine TiO_2 fibers were also prepared via convention- and rotation-extrusion.

3.3. Characterization

Scanning Electron Microscope (SEM) with energy dispersive X-ray spectrometry: Surface morphologies of TiO_2, PDA-grafted TiO_2 and Ag-coated TiO_2 were observed with an Inspect F (FEI) SEM instrument at 0.5 Torr and 20 kV, and the element compositions were analyzed by a connected energy dispersive X-ray spectrometry (EDS). In addition, the longitudinal samples were cut along the axial direction of the tubes and etched in a permanganic etchant for 5 h to expose the TiO_2 fiber wrapped by polymer. The alignments in the tube were investigated by SEM.

Transmission electron microscopy: Surface morphology of TiO_2 fiber modified by PDA was observed with FEI Tecnai G2-F20S instrument using an acceleration voltage of 120 kV.

Thermogravimetric Analysis (TGA): TGA measurement of the TiO_2 modified at the different reaction times of dopamine was performed with a thermogravimetric analyzer (model Q500, TA Instrument Co., USA) under nitrogen protection. The temperature ranged from 25 to 700 °C and the heating rate was 2 °C/min. The grafted PDA content was calculated based on the mass loss difference of pristine TiO_2 and the TiO_2 modified by PDA at 600 °C, where PDA was degraded completely.

X-ray Diffraction (XRD) analysis: XRD measurement was carried out with DX-1000 diffractometer (Dandong Fangyuan Instrument Co. Ltd, China). The scanning 2θ ranged from 10° to 40°, with a scanning rate of 1°/s.

Differential scanning calorimetry (DSC) analysis: The melting behaviours of the samples were investigated with a Q20 differential scanning calorimetry apparatus (TA, USA) under nitrogen protection. ~6 mg samples were heated from 40 to 200 °C at a heating rate of 10 °C/min. The crystallinity (Xc) was obtained based on the equation:

$$Xc(\%) = \frac{\Delta H_m}{\Delta H_o} \times 100\%$$

where ΔH_m is the measured fusion enthalpy and ΔH_o is the enthalpy for 100% crystalline PP (209 J/g).

Thermal Shrinkage Experiment: The tube of 20 mm length was cut along the axial direction and put into glycerol at 160 °C for 1 h. After thermal treatment, the lengths were measured and the shrinkage ratio was calculated according to the shrinking size/original size ratio.

Mechanical measurements: The tubes with 40 mm length were cut along the longitudinal direction. During torque testing, the tube was fixed on self-designed torque measurements