Journal of Applied Science and Engineering Innovation, Vol.5, No.4, 2018, pp. 109-112
ISSN (Print): 2331-9062
ISSN (Online): 2331-9070

Preparation and Properties Investigation of agar/TiO_2 Fibers

Tengfei Li[1,2], Cunzhen Geng[2], Zhixin Xue[1,2], Yanzhi Xia[2]

[1] *College of Chemistry and Chemical Engineering, Qingdao University, Qingdao 266071, China*
[2] *State Key Laboratory of Bio-fibers and Eco-textiles, Institute of Marine Biobased Material, Collaborative Innovation Center of Shandong Marine Biobased Fibers and Ecological textiles, Qingdao University, Qingdao 266071, China*

Abstract: A novel kind of agar fiber containing nano-TiO_2 (agar/TiO_2 fiber) was prepared through wet spinning. The nano-TiO_2 powders were homodispered in the dimethyl sulfoxide (DMSO) and then the agar powders were dissolved in DMSO/TiO_2 solution to obtain the dope. Then the dope went through a spinneret and coagulation bath to obtain agar/TiO_2 fiber. The fibers were characterized by SEM, tensile strength, water absorption and barrier properties of UV light. The result showed that the agar/TiO_2 fibers had better softness. The tensile strength, water absorption and UV barrier properties of agar/TiO_2 fibers were improved when compared to those of traditional agar fibers. Compared with traditional agar fibers, the novel fibers will gain some special properties such as high water absorption and UV shielding for the material.

Keywords: Agar/TiO_2 fiber, Nano-TiO_2, Wet spinning

INTRODUCTION

Fiber have been widely used in life and production and become an irreplaceable part. The emergence of seaweed fiber greatly compensates for the shortage of raw materials. The seaweed has attracted global attention and because of their innocuity, biodegradability and renewability [Bhutiya, et. al., 2018]. Seaweed polysaccharides was extracted from natural algal, which is environmentally friendly and rich.

Agar extracted from red algae such as Gracilaria is a natural polysaccharide [Freile-Pelegrín, et. al., 2005]. It consists of agarose and agaropectin [Bao, et. al., 2010]. Agarose is a linear polymer, which is an uncharged neutral. It dissolves in water above 90℃, but has good gel properties at room temperature [Ellis, et. al., 2017]. This feature of agar has unique applications in biological and medical research [Teng, et. al., 2009]. Agaropectin is a derivative of agarose. Monosaccharide residues are replaced by sulfate, and pyruvic acid [Rocha, et. al., 2014]. The content of the sulfate group affects the mechanical properties of the agar gel. In this study, the agar fiber was prepared by wet spinning. This method is simple when compared to that of other spinning methods. Then the raw liquid is extruded from the spinneret to form a trickle. Trickle through a coagulating bath to form the nascent fiber [Claudia, et. al., 2018].

Nano-TiO_2 has good chemical stability. There are also many characteristics that are superior to other materials, such as high photocatalytic efficiency and non-toxicity [Li, et. al., 2018]. Ultraviolet light causes damage to the human body. Thus, it is necessary to prepare the functional fibers containing anti-ultraviolet properties. As a functional additive, the addition of nano-TiO_2 improves UV shielding properties and water absorption of materials [Zhao, et. al., 2018]. In this work, the nano-TiO_2 was added into the agar/DMSO system to modify agar fibers.

EXPERIMENTAL

Materials

The agar (Gel strength ≥1200g/cm2 at 1.5%) was purchased from Lanji technology development Co., LTD (Shanghai, China) and used without further process. Dimethyl sulfoxide and barium chloride were purchased from Sinopharm Chemical Reagent Co., LTD (shanghai, China).

Nano-TiO_2 with anatase and rutile phase, ranged from 20 to 25 nm were purchased from Evonik Degussa (Shanghai, China). Distilled water was prepared by our laboratory with a equipment (JII-0.5, China).

Preparation of spinning dopes

Nano-TiO_2 (0, 3g, 6g) was added to 1000 mL DMSO, and the mixture was vigorously stirred at 85℃ for 30 min in water bath. Afterward AG powder (136 g) was dissolved in DMSO/ DMSO-TiO_2 dispersion at 97℃ for 2 h under 600 rpm magnetic stirring to obtain homogeneous spinning dope named Dope-1, Dope-2, Dope-3. Then the spinning dopes were placed at room temperature for eliminating the bubbles.

Wet-spinning of agar/TiO_2 fibers

Agar/TiO_2 fibers was preparated by the wet spinning process according to the spinning method of agar fiber provided by Jingjing Liu with minor modification [Liu, et. al., 2018]. The prepared

spinning dopes were poured into a 1.5L dope storage cylinder and extruded under a pressure of 0.1 MPa. The speed of the metering pump was 36 rpm through a spinneret with 30 holes into the first coagulation bath containing 7% barium chloride in 30% ethanol solution, and the stretch bath 3% barium chloride in 25% ethanol solution. The obtained fibers were drawn at a draw rate of 1.2 between two sets of rollers. The fibers were collected in the second rollers. The fibers produced from dope-1, Dope-2 and Dope-3 were referred as Fiber-1, Fiber-2, Fiber-3, respectively. A schematic of the wet spinning machine is shown in figure 1.

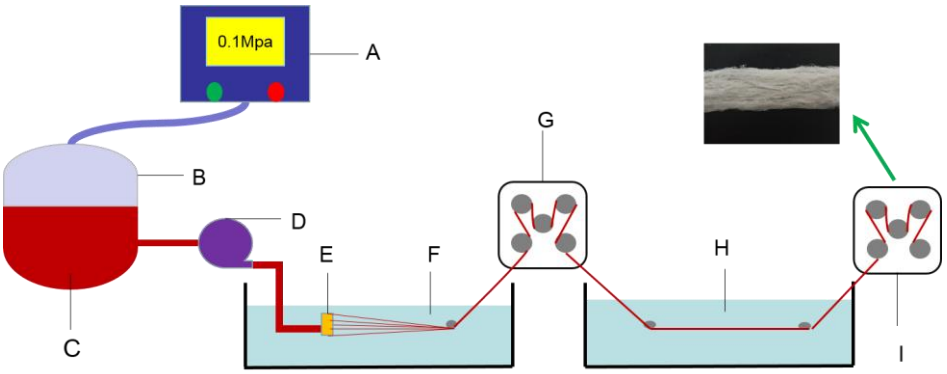

Figure 1 Process diagram showing the custom-made device used for spinning
(A. air compressor; B. dope storage cylinder; C. spinning dope; D. metering pump; E. spinneret; F. coagulation bath; G. roller (I); H. stretch bath; I. roller (II).)

Characterization of agar fibers

The appearance and macroscopic shape of the agar/TiO_2 fibers were recorded by a digital camera. The surface and cross section morphology of the agar/TiO_2 fibers was observed by a scanning electron microscope (SEM) (Hitachi TM-3000, Japan) at 15 kV after sputtering with gold. XRD patterns of nano-TiO_2 powder and fibers were measured using DX2700 X-ray diffraction at a scanning of 2 °/min, angles range was 2θ = 5° to 90 °. XRD test were provided with an accelerating voltage of 40 kV and an applied current of 30 mA under Cu-Xα radiation [Liu, et. al., 2018].

An amount of agar/TiO_2 fibers was wrapped in tin foil and placed under a tableting machine to form a sheet (40 mm × 40 mm), the pressure was 20MPa and time for 20min. The fiber measurements were picked out by T9 double beam spectrophotometer UV-visible (Beijing General instrument, China). Scanning wavelength from 200nm to 600nm. The strength of the agar/TiO_2 fibers was measured by an LLY-27 fiber fineness analyzer instrument (Lai zhou Electronic Instruments, China). Fibers were measured at the certain temperature and humidity of 24 ±0.5℃; 35 ± 5%, where the gauge was 10 mm and the stretching speed was 10 mm/min. The measurements were repeated at least 30 times. The swelling degrees of agar/TiO_2 fibers were evaluated according to the method reported by Xiubin Hou et al [Hou, et. al., 2018]. About 1g samples of Fiber-1, Fiber-2 and Fiber-3 were desiccated in vacuum at 100℃ for 12 h. And then they were weighed to evaluate the weight of dry mass. The weighed samples were then immersed in 300 mL distilled water. After 12 h, the fibers were removed from water and the remaining water surface was quickly absorbed by an absorbent paper. The soaked samples were then weighed to determine their masses. The measurement of each fiber was repeated at least three times, and the swelling degree (SD) was calculated with eq. (4):

$$SD(\%) = \frac{w_2 - w_1}{w_1} \times 100 \quad (4)$$

Where w_1 and w_2 are the weight of the film samples before and after soaking in the water.

RESULTS AND DISCUSSION

Analysis of morphological and XRD

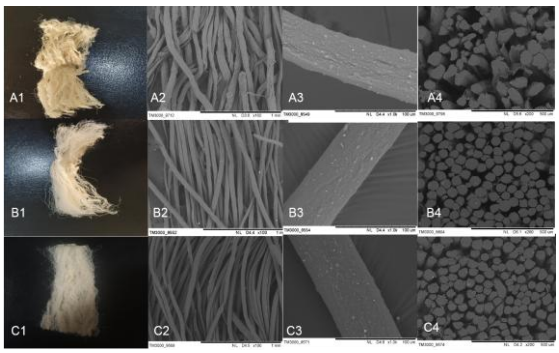

Figure 2 Digital photo and electron micrograph of fibers
(1: digital photo; 2:SEM of ×100; 3:SEM of ×1000; 4: SEM of ×200; 2,3: the surface; 4: the cross-section. A. Fiber-1; B. Fiber-2; C. Fiber-3.)

The digital photos and SEM of fibers are shown in figure 2. After adding nano-TiO_2, the color of the agar fiber is changed from light yellow (Figure 2A1) to white (Figure 2B1, 2C1). There are still uneven gullies on the surface of the Fiber-1, but the surface of Fiber-3 is smoother. Nano-TiO_2 might improve fiber structure. For the cross-section SEM of Fiber-1

(Figure 2A4) has irregular, tiny interstices and rough cross-section. All fibers are solid structures without visible voids. The fiber was prepared by phase-separation of spinning dopes. The nano-TiO_2 contents may affect fast phase inversion of polymer solution for the within structure of fibers [Khorasani, et. al., 2010]. The agar/TiO_2 fiber shows dense structure, cross-section of the fiber has nearly circular morphology (Figure 2C4).

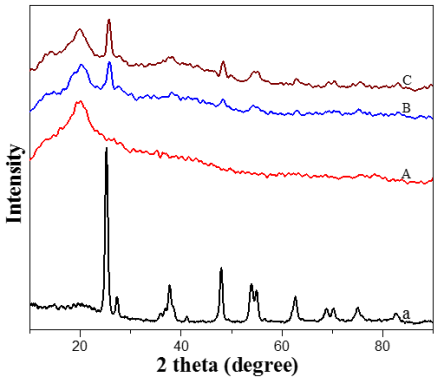

Figure 3 X-ray diffraction spectra.
(a. nano-TiO_2 powder; A. Fiber-1; B. Fiber-2; C. Fiber-3.)

The XRD spectra of nano-TiO_2 powder and fibers are shown in figure 3. The XRD pattern of nano-TiO_2 shows several different diffraction peak at 2θ of 26, 38, 48, 54, 63, 69 and 75 ° (Figure 3a), there is a strong and distinct diffraction peak at 2θ of 26 °. The diffraction peak of agar appears in all fibers, which shows a typical amorphous peak at 2θ of 18.4 °. Characteristic diffraction peak of nano-TiO2 appears in the XRD spectra of agar/TiO_2 fibers at 2θ of 26 ° (Figure 3B, 3C), indicating that nano-TiO_2 participates in the process of fiber forming. Compared with Fiber-2, the intensity of characteristic diffraction peak at 2θ of 26 °increases in Fiber-3 with the increasing of the content of nano-TiO_2. Nano-TiO_2 has the same effect in the preparation of film [Hou, et. al., 2018].

UV analysis

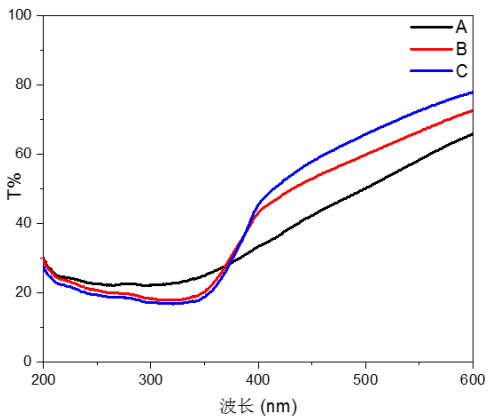

Figure 4 UV-transmittance curve.
(A. Fiber-1; B. Fiber-2; C. Fiber-3.)

Ultraviolet light is a wavelength ranging from 10 nm to 400 nm in the electromagnetic spectrum. The ultraviolet region is divided into UVA (400-315nm)、UVB (315-280nm) and UVC (280-190nm). UVA and UVB is harmful to human body. Figure 4 showed the change in transmittance of three kinds of fibers in the ultraviolet and visible regions. The transmittance of agar/TiO_2 fibers in the ultraviolet region has a significant decrease trend, but Fiber-1 is not obvious. The fiber with nano-TiO_2 has a lower transmittance in the ultraviolet region than Fiber-1 (Figure 4B, 4C), showing good UV shielding and absorption. The reason might be that the energy of ultraviolet light can be converted into heat or other low energy situation. At the visible light range, the visible light transmittance increased gradually and the visible light is harmless to the human body. The figure shows that along with the content of nano-TiO_2 in the fiber increases, the absorption of ultraviolet light is enhanced.

Tensile strength analysis

Table 1 The mechanical properties of fiber: (A. Fiber-1; B. Fiber-2; C. Fiber-3)

sample	Breaking force (cN)	Linear density (dtex)	Linear intensity (cN/dtex)
A	13.0	52.4	0.248
B	13.5	49.3	0.274
C	14.2	52.7	0.269

Table 1 shows the mechanical properties of fibers. As can be seen, the adding of nano-TiO_2 enhanced breaking force and linear intensity of fiber. The linear intensity increased from 0.248 cN/dtex to 0.269 cN/dtex and breaking force increased from 13.0cN to 14.2cN. The reason might be that the surface of the nano-TiO_2 contained active groups such as hydroxyl group. Moreover, the nanoparticles of TiO_2 had high chemical reactivity and reacted with the active sites on the molecular chains of fibers [Li, et. al., 2010]. The linear density of several fibers differs little.

Water absorption analysis

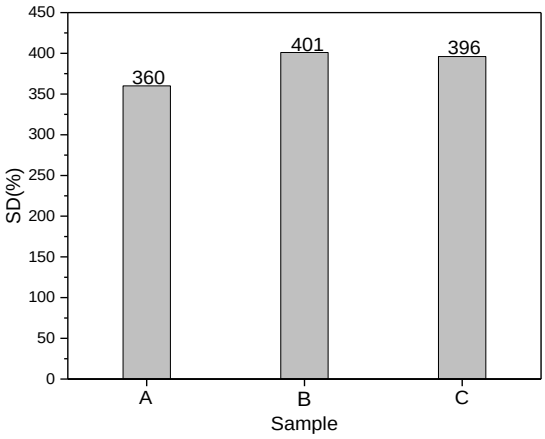

Figure 5. Water absorption ratio of the fiber.
(A. Fiber-1; B. Fiber-2; C. Fiber-3.)

Agar fiber had a large amount of hydroxyl groups on the surface, which led to the strong hydration ability. It maybe used as a good medical material or a highly absorbent fiber. Figure 5 shows the water absorption capacity of all the three fibers. The

agar/TiO_2 fibers have a significant improvement in water absorption compared with Fiber-1 (Figure 5B, 5C). The absorption ratio of Fiber-1 was 360%. At the same time, agar/TiO_2 fibers could reach about 400%. However, as the content of nano-TiO_2 increased from 0.3% to 0.6%, the water absorption properties of prepared fibers did not enhanced, which might be that nano-TiO_2 has super-hydrophilic surface. Under the light condition, electrons migrated and the structure of nano-TiO_2 was changed, forming hydroxyl group in nano-TiO_2 surface.

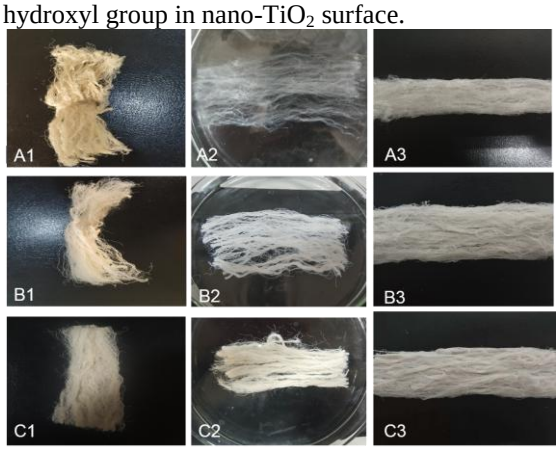

Figure 6 Appearance change of the fiber.
(1: normal fiber; 2: fiber in water; 3: dried fiber. A. Fiber-1; B. Fiber-2; C. Fiber-3.)

All fibers were undissolved and had good stability in water. Figure 6 showed that the Fiber-1 had a transparent and slightly white appearance. Agar/TiO_2 fibers was white and opaque. After soaking in water for 24 h, the Fiber-2 did not decolorize and the water remained colorless and transparent. The phenomenon indicated that nano-TiO_2 does not come out of the fiber after soaking, which further explained that nano-TiO_2 was not only adsorbed on the surface of the fiber, but also involved in the fiber forming process.

CONCLUSION

The novel functional fibers were prepared by wet spinning. Through the combination of nano-TiO_2, the morphology of the fibers are more smoother. XRD spectra shows that nano-TiO_2 was involved in the agar/TiO_2 fibers. Agar/TiO_2 fibers has the function of preventing ultraviolet radiation, which can reduce the damage of ultraviolet rays to the human body. The addition of nano-TiO_2 improved the physical strength, compared to that of agar fiber. The water absorption properties of the agar/TiO_2 fibers are further improved because the surface of the nano-TiO_2 is hydrophilic.

REFERENCES

Bhutiya P L, Misra N. Nested seaweed cellulose fiber deposited with cuprous oxide nanorods for antimicrobial activity. International Journal of Biological Macromolecules, 2018, 117: 435-444.

Bao Xuxu, Hayashi K. Novel agarose and agar fibers: Fabrication and characterization. Materials Letters, 2010, 64(22): 2435-2437.

Claudia A. Vega-Cázarez, Jaime López-Cervantes. Preparation and Properties of Chitosan–PVA Fibers Produced by Wet Spinning. Journal of Polymers and the Environment, 2018, 26(3): 946-958.

Ellis A L, Norton A B. Stabilisation of foams by agar gel particles. Food Hydrocolloids, 2017, 73: 222-228.

Freile-Pelegrín Y, Murano E. Agars from three species of Gracilaria (Rhodophyta) from Yucatán Peninsula. Bioresource Technology, 2005, 96(3): 295-302.

Hou Xiubin, Xue Zhixin. Effect of SiO_2 nanoparticle on the physical and chemical properties of eco-friendly agar/sodium alginate nanocomposite film, (2018), https://doi.org/10.1016/j.ijbiomac.2018.09.109.

Khorasani M T, Shorgashti S. Fabrication of microporous thermoplastic polyurethane for use as small-diameter vascular graft material. I. Phase-inversion method. Journal of Biomedical Materials Research Part B Applied Biomaterials, 2010, 76B(1): 41-48.

Li Dongna, Chen Yin. Facile synthesis of Mn/N-doped TiO_2 on wood-based activated carbon fiber as an efficient visible-light-driven photocatalyst. Journal of Materials Science, 2018, 53(16): 11671-11683.

Liu Jingjing, Xue Zhixin. Preparation and properties of wet-spun agar fibers. Carbohydrate Polymers, 2018, 181: 760-767.

Li Ying, Guo Zhaoxia. The influence of silane treatment on nylon 6/nano-SiO_2 in situ polymerization. Journal of Applied Polymer Science, 2010, 84(4): 827-833.

Rocha C M, Souza H K. Rheological and structural characterization of agar/whey proteins insoluble complexes. Carbohydrate Polymers, 2014, 110: 345-353.

Teng Shuhua, Wang Peng. Blend fibers of chitosan–agarose by electrospinning. Materials Letters, 2009, 63(28): 2510-2512.

Zhao Yongsheng, Dang Wanbin. Fabrication of mechanically robust and UV-resistant aramid fiber-based composite paper by adding nano-TiO_2 and nanofibrillated cellulose. Cellulose, 2018, 25: 3913-3925.