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ARTICLE

Facile preparation of aramid nanofibers from Twaron fibers by a downsizing process

Cite this: DOI: 10.1039/x0xx00000x

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Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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We introduce a simple preparation procedure for aramid nanofibers from Twaron fibers by using a downsizing process. Alkaline hydrolysis pretreatment brings ionic charges on the fiber surface, allowing facile disintegration of Twaron into nanofibers by virtue of the electrostatic repulsive force. Since the nanofibers can be dispersed homogeneously in water, the processability and formability of the polymer were improved. The resulting aramid nanofibers, having a high degree of physical performance, a uniform nanosized morphology, and a high surface-to-volume ratio, will expand the range of novel applications of aramid fibers.

1. Introduction

Since nanofibers have an extremely high surface-to-volume ratio, and form a highly porous mesh, their properties are different from those of microsized fibers.^{1,2} Their unique dimensional, optical, mechanical, and other characteristics make the preparation of nanofibers an important subject.

Recently, we prepared chitin nanofibers from dried chitin powder extracted from crab shell.^{3,4} Since chitin powder is made up of an aggregate of nanofibers,⁵ it was disintegrated into nanofibers by a simple mechanical treatment. An acidic condition is the key to disintegrating chitin powder.^{6,7} A small number of amino groups in the chitin are cationized by the addition of an acid, which promotes the disintegration of chitin into nanofibers by electrostatic repulsion.

Twaron is a sort of aramid fiber commercially produced by Teijin Aramid and has a simple structure of poly(*p*-phenylene terephthalamide) (PpPTA) (Fig. 1a). Twaron is obtained by a wet-spinning process from the polymer solution dissolved in sulfuric acid. PpPTA shows liquid crystal behavior in sulfuric acid, exhibiting anisotropic properties thanks to the orientational ordering of the rigid molecules.⁸ Therefore, aramid fibers are of high strength and high Young's modulus, with good thermal stability and high impact resistance; they are used in automotive, construction, sporting, aerospace, and military applications.⁹ These characteristics are the result of a 100% paracrystalline structure with molecular chains preferentially oriented along the fiber axis caused by the process of spinning lyotropic liquid crystal.¹⁰ Nanofibers from

Twaron would offer useful application as a novel high-performance material. The electro-spinning process enables the artificial production of nanofibers from a wide range of polymer solutions.¹¹ However, electro-spinning of aramid polymer is impossible due to its low solubility in common solvents. As well as chitin powder, since Twaron fiber consists of microcrystals, aramid nanofibers could be obtained by downsizing the structure of Twaron fiber. Yang et al. reported preparation of aramid nanofibers by so-called top-down approach.¹² Homogeneous aramid nanofiber dispersion was obtained by stirring in KOH/DMSO solvents. However, the reaction took one week, chemical structure was different from original aramid by removal of H atom from amide group (CO-N-H), and considerable amount of un-fibrillated residue remained. Inspired by the previous work, we have studied for the first time the facile mechanical disintegration of commercially available Twaron fiber into nanofibers by a downsizing process.

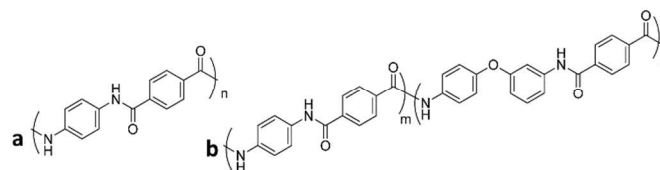


Figure 1. Chemical structures of aramid fibers. (a) Twaron, and (b) Technora.

2. Experimental

2.1. Nanofiber Preparation

Chopped Twaron fibers 0.25 mm long obtained from Teijin Aramid were treated with 10 wt.% NaOH for 3 hours under reflux for partial hydrolysis of amide bondings. After washing with distilled water, the obtained sample was dispersed in water at 1 wt.% and was passed through 30 cycles of a high-pressure water jet atomization treatment (Star Burst Mini, HJP-25001S, Sugino Machine).¹³ The atomization system was equipped with a ball-collision chamber. The slurry was ejected from a small nozzle with a diameter of 100 μm under high pressure of 200 MPa (Fig. 2a and 2b).

2.2. Nanofiber sheet

Forty gram of aramid nanofiber slurry with 0.5 wt.% was dehydrated by filtration. The sample was then hot-pressed under 20 MPa for 20 min at 100 °C. The density of the resulting sample was about 0.9 g/cm³.

2.3. Characterization

Infrared spectra of the samples were recorded with an FTIR spectrophotometer (Spectrum 65, Perkin-Elmer Japan Co., Ltd.) equipped with an ATR attachment. For field emission scanning electron microscopic (FE-SEM) observation, the sample was coated with platinum by an ion sputter coater and observed by FE-SEM (JSM-6700F; JEOL, Ltd.) operating at 2.0 kV. X-ray diffraction profiles of the nanofibers were obtained with Ni-filtered CuK α from an X-ray generator (Ultima IV, Rigaku) operating at 40 kV and 30 mA. The tensile strength and Young's modulus were measured by a universal testing instrument (AG-X, Shimadzu) for samples 40 mm long and 10 mm wide at a cross head speed of 1 mm min⁻¹ with a gage length of 15 mm. For data accuracy, six specimens were used for testing.

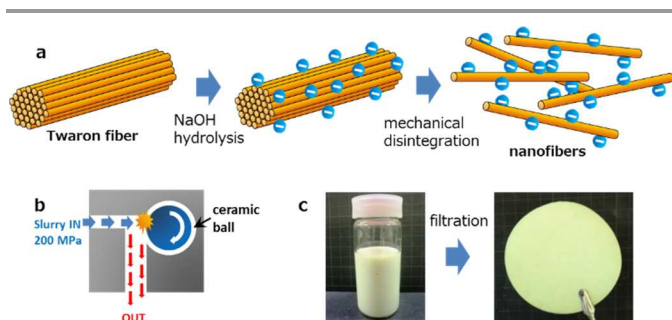


Figure 2. (a) Overview of aramid nanofiber fabrication. (b) Structure of ball-collision chamber of high pressure water jet system. (c) Aramid nanofibers dispersed in water with 1.0 wt.% concentration and the nanofiber sheet fabricated by filtration.

3. Results and Discussion

Fig. 3a shows an SEM image of Twaron fiber, which is made up of aggregate of aramid microcrystals with a crystallite size of approximately a dozen nanometers.⁹ To atomize the aggregates, the Twaron was passed through high-pressure water jet atomization equipment with 1 wt.% concentration. After 30 cycles of mechanical treatments, the Twaron fiber was not disintegrated at all even though the system applied a super-

high-pressure water jet of 200 MPa (Fig. 2b). However, a nano-texture was visible on the surface after mechanical treatment (Fig. 3b). This lack of atomization is due to strong hydrogen bond interactions between carbonyl groups and N-H centers on the surface of aramid microcrystals. Additional interaction is derived from π - π aromatic stacking interactions, thus making it difficult to atomize Twaron. To enhance atomizing efficiency, Twaron fiber was pre-treated with 10 wt.% NaOH under reflux before disintegration. The dispersion was separable into supernatant and precipitate by centrifugation. The ratio by weight of the supernatant fraction was 40% and the residue was 60%. The fractions were divided according to the size of aramid fibers. Interestingly, the supernatant fraction dispersed homogeneously and stably with a light yellow color for more than 3 months in water, although aramid nanofiber, reported by Yang et al. formed dark red solution.¹² This may come from the difference of nanofiber morphology and chemical structure. SEM images of the supernatant show that the aramid fiber successfully disintegrated into nanofibers (Fig. 3c and 3d). The sample had a homogeneous nanofiber network and a high aspect ratio in a broad area. The fiber width showed a narrow distribution in the 14-33 nm range, with an average width of 20 nm. The successful disintegration is due to the main-chain scission of aramid polymer by alkaline treatment, as described below. Indeed, after the alkaline treatment, the yield of aramid fiber was 85%, which indicates some extent of degradation. On the other hand, in the precipitate fraction, the widths of the fibers were distributed across a wide range of 10-200 nm (Fig. 3e).

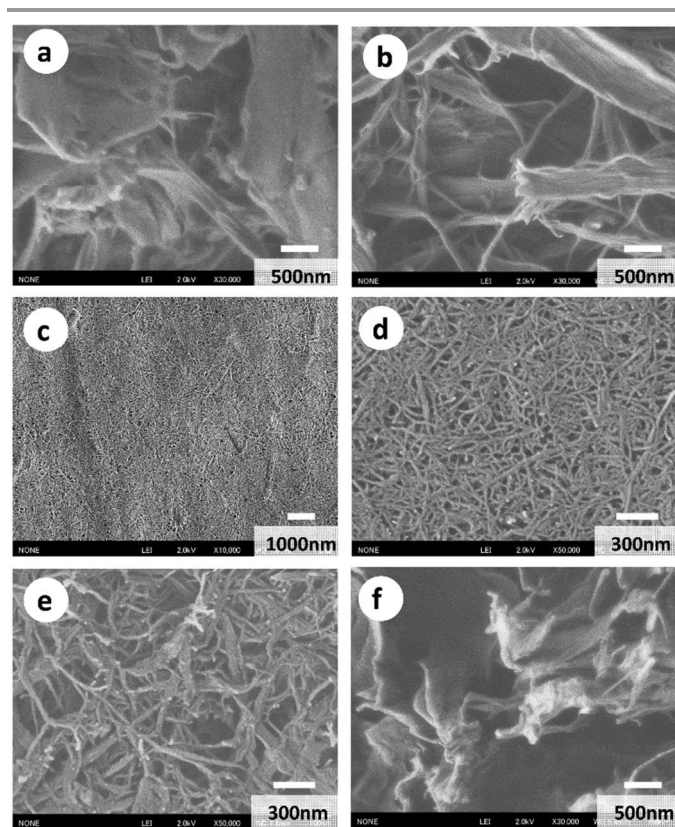


Figure 3. FE-SEM images of (a) Twaron, (b) after mechanical treatment, after alkaline hydrolysis pretreatment followed by mechanical treatment of (c and d) supernatant fraction and (e) precipitate fraction, and (f) Technora after alkaline hydrolysis pretreatment followed by mechanical treatment.

To examine chemical structure changes after NaOH treatment, FT-IR spectra of aramid fibers subjected to alkaline and mechanical treatments were examined (Fig. 4). Although the two spectra were basically similar, in the alkaline-treated sample, a C=O stretching vibration band corresponding to carboxylic acid and a C-N stretching vibration band corresponding to primary amine were observed at 1714 cm^{-1} and 1185 cm^{-1} as small shoulder peaks, respectively (Fig. 4b), indicating that alkaline hydrolysis of amide bonding occurred slightly. We have reported that the cationization caused by amino groups on the chitin fiber facilitates disintegration into nanofibers by electrostatic repulsion.⁷ Therefore, ionic functional groups on the Twaron fiber surface also allowed effective atomization of nanofiber aggregate and homogeneous dispersion in water by electrostatic repulsion (Fig. 2a). However, anionic charge density was too small to estimate the specific value using electro conductivity titration method. Conventional Twaron is insoluble in most solvents and is difficult to form. On the other hand, nanofibers can disperse homogeneously in water (Fig. 2c). Moreover, they can stably disperse in aprotic polar solvents such as dimethyl sulfoxide by solvent replacement too. Hence, they were easy to handle and shape into the desired forms by drying processes such as filtration or freeze drying (Fig. 2c). Their surfaces can also be modified depending on their application. This characteristic will expand the commercial application of Twaron as a novel nanomaterial. Table 1 show average of the Young's modulus, tensile strength, and strain of aramid nanofiber sheet fabricated by filtration followed by hot-pressing at $100\text{ }^{\circ}\text{C}$. Young's modulus, tensile strength, and strain were considerably high of 2.0 GPa, 26.8 MPa, and 1.5%, respectively. These mechanical properties are strongly affected by fabrication process.

The crystalline structure of aramid nanofibers was studied by XRD profiles (Fig. 5). Diffraction pattern of aramid nanofiber coincided closely with that of fiber without alkaline treatment. The diffraction peaks of the nanofibers observed at $2\theta = 20.6^{\circ}$, 22.9° , 28.4° corresponded to 110, 200, and 004 planes, respectively. They were typical crystal patterns of Twaron fiber. Therefore, original crystalline structure was maintained after alkaline hydrolysis and following mechanical treatment. The downsizing process is not applicable to other synthetic polymers that are not made up of nanosized substances. For example, Technora is also a commercial aramid fiber consisting of poly(*p*-phenylene terephthalamide-co-3,4'-oxydiphenylene terephthalamide) (Fig. 1b). Since Technora co-polymer is not a liquid crystalline polymer, it is not downsized into microcrystalline structures even after alkaline hydrolysis and subsequent mechanical treatments (Fig. 3f).

Table 1. Average mechanical properties of aramid nanofiber sheet

Young's Modulus (GPa)	Tensile Strength (MPa)	Fracture Strain (%)
2.0 (0.2)	26.8 (2.1)	1.5 (0.3)

standard deviations are given in parentheses

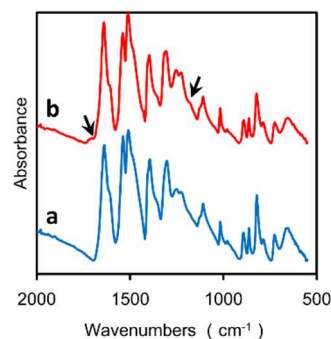


Figure 4. FT-IR spectra of (a) Twaron, and (b) the nanofibers obtained by alkaline hydrolysis and mechanical treatments.

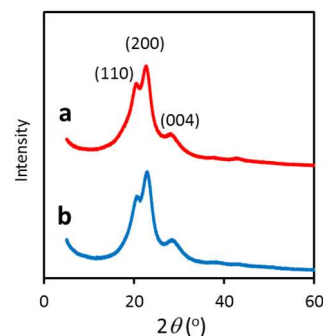


Figure 5. XRD profiles of mechanically treated Twaron fibers (a) without and (b) with alkaline hydrolysis treatment.

4. Conclusions

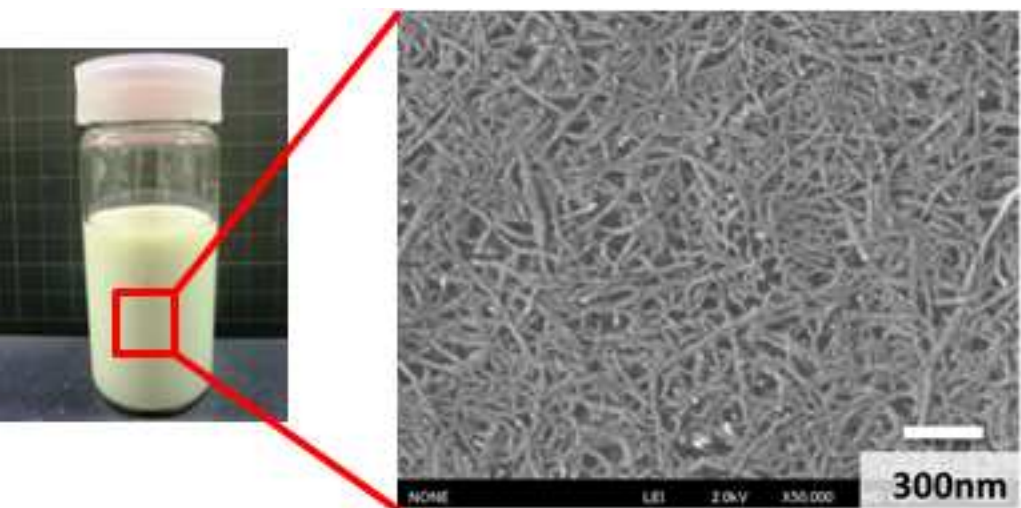
We prepared aramid nanofibers consisted of paracrystallite, by a mechanical treatment of Twaron. It was easily disintegrated into nanofibers with the help of electrostatic repulsive force. This top-down approach will be applicable to other synthetic fibers fabricated from liquid crystalline polymers, such as Kevlar. Aramid nanofibers with high thermal resistance, efficient mechanical properties, uniform widths, and very high surface-to-volume ratios will open the door to novel applications of aramid polymers, such as reinforcement filler to provide high-performance nanocomposites.

Notes and references

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Aramid nanofiber

- Facile preparation
- Homogeneous dispersion in
- 20 nm Thick
- High formability