Amphiphobic meta-aramid nanofiber mat with improved chemical stability and mechanical properties

Su-Yeol Ryua, Jae Woo Chungb,⁎, Seung-Yeop Kwaka,⁎

a Department of Materials Science and Engineering, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 08826, Republic of Korea
b Department of Organic Materials and Fiber Engineering, Soongsil University, 369 Sangdo-ro, Dongjak-gu, Seoul 06978, Republic of Korea

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ABSTRACT

Electrospun meta-aramid nanofibers are typically extremely vulnerable to dipolar aprotic solvents, such as DMAc, DMSO, and DMF. This low chemical stability has made practical application of such nanofibers difficult. In this work, meta-aramid nanofiber mats with a directional nature were electrospun and sequentially post-treated by salt removal and heat treatment to enhance chemical stability. The salt added to dissolve the meta-aramid in the solvent was completely removed from the meta-aramid nanofibers via repetitive washing. The salt-removed meta-aramid nanofiber mat displayed a glass transition behavior not observed in the pristine nanofiber mat. The crystalline structure of the salt-removed nanofiber mats was regenerated by heat treatment above its glass transition temperature, whereas heat-treated nanofiber mats with salt remained amorphous. The salt between the meta-aramid chains interrupted their rearrangement, indicating that, in the absence of salt, the chains could be arranged during heat treatment. Additionally, the sequential post-treatment induced the reforming of intermolecular hydrogen bonds between the chains; thus, the post-treated nanofiber mat exhibited enhanced mechanical and chemical stabilities, which was confirmed by survival of the meta-aramid nanofiber in DMAc. Furthermore, a surface-modified meta-aramid nanofiber mat showing hydrophobicity and superoleophobicity was fabricated by silanization with trichloro(1H,1H,2H,2H-perfluorooctyl) silane.

1. Introduction

The aromatic polyamides, aramids, are a class of strong, heat-resistant, and chemical stable polymers having repeating units containing phenyl rings linked together by amide bonds. Because phenyl rings prevent polymer chains from rotating and twisting around their chemical bonds and amide groups form intermolecular hydrogen bond networks, aramids have superior properties, such as extremely high strength and high resistance to chemicals, heat, and physical abrasion [1]. The best known aramids are para-aramids, such as poly(p-phenylene terephthalamide), and meta-aramids, such as poly(m-phenylene isophthalamide) [2]. Meta-aramids can be soluble in organic solvents, such as N,N-dimethyl acetamide (DMAc), N,N-dimethyl formamide (DMF), N,N-dimethyl sulfoxide (DMSO), and N-methyl-2-pyrrolidone (NMP), with certain salts such as LiCl and CaCl₂ [3].

Among the various possible nanostructures, nanofibers have received attention for their small diameter, high surface area-to-volume ratio, light weight, and controllable pore structure compared with those of other commercial fibers [4]. Recently, meta-aramids have been fabricated into nanofibers by electrospinning, which has emerged as a novel technique for producing uniform nanofibers owing to its versatility, easy process, simple apparatus, and applicability to various types of polymers in the melt or solution state. These
meta-aramid nanofibers have been intensively studied as filtration media, protective materials, and nanofibrous substrates for various applications. For example, Lin et al. investigated the application of meta-aramid nanofibrous membranes to water purification [5], while Shin et al. reported electrospun meta-aramid nanofibers as a composite filter for water/oil separation [6]. However, compared with commercial meta-aramid fibers, the mechanical properties of electrospun meta-aramid nanofibers have been insufficient because the polymer chains do not have a well-developed molecular orientation.

It is known that as-electrospun meta-aramid nanofibers are typically extremely vulnerable to dipolar aprotic solvents, such as DMAc, DMF, and DMSO, making the fibers difficult to use in practical applications. In terms of developing a crystalline structure of meta-aramid nanofibers that could compete with commercial meta-aramid fibers, but, very few studies aiming to improve the properties of electrospun meta-aramid nanofibers have investigated post-treatments and their effects on the crystalline structure of the nanofibers. Yao et al. annealed electrospun meta-aramid nanofibers at 150, 200, and 250 °C for several days, but the heat treatment did not have an apparent effect [7]. Oh et al. reported that the removal of salts present in as-spun meta-aramid nanofibers exhibited slight increasing of the mechanical strength of the nanofibers, but, the chemical stability of the nanofibers against dipolar aprotic solvents, such as DMAc, DMSO, was not discussed [8]. In addition, Oh et al. showed that the crystalline structure of salt-removed meta-aramid nanofibers can be regenerated by microwave irradiation under wet conditions [9].

Herein, we electrospun aligned meta-aramid nanofiber mats from DMAc/LiCl solution and sequentially treated them with washing and heat treatment to enhance their chemical stability. The removal of residual salt from the nanofibers allowed their original crystalline structure to be regenerated during heat treatment above their glass transition temperature. This structural change was accompanied by a large increase in Young's modulus in the nanofiber mat and an increased chemical stability, as evidenced by its insolubility in DMAc. Furthermore, as an example of the functionalization of the resulting meta-aramid nanofiber mats, amphiphobic meta-aramid nanofiber mats with a water contact angle of 152° and oil contact angle of 123° were also fabricated by surface modification of the post-treated mats with fluoroalkyl silane. These simple treatment processes allow the chemical and mechanical properties of meta-aramid fibers to be greatly improved, opening up new applications including protective layers, filter membranes, and battery separators for this material.

2. Experimental details

2.1. Materials

Poly(meta-phenylene isophthalamide) (meta-Aramid, Nomex®) fiber was purchased from DuPont Plant. N,N-dimethylacetamide (DMAc, anhydrous, 99.8%), lithium chloride (LiCl, ACS reagent, ≥ 99%), trichloro (1H,1H,2H,2H-perfluorooctyl) silane (97%, fluorinated alkyl silane, FAS), toluene (anhydrous, 99.8%), and ethanol (ACS reagent, anhydrous, 99.8%) were purchased from Sigma-Aldrich. The meta-aramid and LiCl were dried at 120 °C for 24 h in a vacuum oven before use to remove moisture absorbed. All other materials were used as received without further purification.

2.2. Electrospun meta-aramid nanofiber mat

To prepare the electrospinning solution, 8.0 g of meta-aramid fiber was dissolved in 50 mL of DMAc solution containing 3.2 g of LiCl as a salt (LiCl:meta-aramid weight ratio of 4:10) at 50 °C for 24 h in an oven shaker (BF-30SI, BioFree, Korea). The hydrogen bonds between meta-aramid chains were weaken by [Li-DMAc] + macrocation complex and Cl− ion, which were formed by DMAc and LiCl, and then meta-aramid fiber was solved into the solution. A pristine meta-aramid nanofiber mat (mANF) was prepared by electrospinning. Briefly, the solution was loaded into a syringe equipped with a stainless steel needle with an internal diameter of 0.33 mm, and then was transferred at a flow rate of 0.2 mL/h for 50 h. The needle tip of the syringe was directly charged to a positive voltage of 20–25 kV. The syringe was placed horizontally and towards an Al-foil covered drum collector rotating at 100 rpm. The collector was charged to −5 kV. The tip-to-collector distance was 15 cm. The electrospinning process was conducted at 23 ± 1 °C and 50 ± 4 RH%.

2.3. Meta-aramid nanofiber mat with improved chemical stability and mechanical properties

To improve the chemical stability and mechanical properties of meta-aramid nanofiber mats, the LiCl salt in the as-prepared mANF was removed by washing treatment. The mANF was fixed in a stainless frame, immersed in deionized water and mildly shaken for 30 min. This procedure was repeated three times. The washed meta-aramid nanofiber mat (W-mANF) was dried under ambient conditions for 12 h and in a vacuum oven for 12 h. The surface morphology of mANF and W-mANF was observed by field emission scanning electron microscopy (FE-SEM; JSM-6335F, JEOL). The removal of the salt in the nanofibers was determined using energy-dispersive X-ray spectroscopy (EDS; XFlash 4000, Bruker AXS). The thermal behavior of mANF and W-mANF was observed using simultaneous differential thermal analysis/thermal gravimetric analysis (DTA/TGA; SDT 2960, TA Instruments, heating rate 10 °C/min, temperature range 40–700 °C, N2 atmosphere) and differential scanning calorimetry (DSC, Q1000; TA Instruments, heating rate 10 °C/min, temperature range 30–375 °C).

The W-mANF was heat-treated at 250 and 300 °C for 10 min in a processing oven (UF 110, Memmert, Germany) to enhance the chemical stability and mechanical properties of the meta-aramid nanofiber mat (HT250-W-mANF and HT300-W-mANF). mANF (an unwashed sample) was also heat-treated at 300 °C for 10 min in the processing oven (HT300-unW-mANF). The chemical structure of the nanofiber mats was observed using attenuated total reflection/Fourier transform infrared spectroscopy (ATR/FT-IR; Nicolet iS5...
with iD5 ZnSe ATR accessory, Thermo Scientific) at room temperature (RT) over a range of 4000–650 cm\(^{-1}\). The crystalline structure of the nanofiber mats was investigated by wide angle X-ray diffractometry (WXRD; New D8 Advance, Bruker) with Cu K\(\alpha\) radiation (\(\lambda = 1.541 \text{ Å}\)) at RT, a voltage of 40 kV, a current of 40 mA, and Bragg angles (2\(\theta\)) of 10–50° with scan rate of 2°/min. The improved chemical stability of the nanofiber mats was confirmed by checking whether the mats survived in DMAC for 24 h. The mechanical properties of the nanofiber mats were measured with a universal testing machine (UTM; Model 5567 INSTRON). Specimens were prepared in the standard dog-bone shape with 3.00 mm width and 0.10–0.20 mm thickness according to ASTM D638 Type V. The specimens were tested in parallel and perpendicular directions to the alignment of the nanofiber mats at a crosshead speed of 1 mm/min.

### 2.4. Amphiphobic meta-aramid nanofiber mat

To produce an amphiphobic meta-aramid nanofiber mat, the HT300-W-mANF, fixed in a stainless frame, was immersed in a glass vessel containing 50 mL anhydrous toluene, and 50 \(\mu\)L of trichloro (1\(H\),1\(H\),2\(H\),2\(H\)-perfluorooctyl) silane (FAS) was added immediately to the solvent to silanize the surface of the nanofiber mat (0.1% V/V FAS/toluene). The glass container, which was closed to the air during the reaction, was slowly shaken at RT for 1 h. After the reaction, the as-silanized nanofiber mat was rinsed three times with toluene to remove physically adsorbed FAS molecules on the nanofiber, and then rinsed three times with ethanol to remove the remaining toluene and FAS on the nanofiber. Next, the nanofiber was stabilized for 10 min at RT under ambient conditions, and then heat-treated for 10 min at 120 °C in the processing oven. This procedure was repeated five times. Static contact angles were measured with a sessile drop of deionized water or hexadecane using a drop shape analysis system (Theta Lite, Attension, KSV Instrument, Finland) with a manually controlled Hamilton syringe. The apparent contact angle of water and simulant drops was measured in air at 25 ± 1 °C. The volume of the droplet formed on the surface of the nanofiber mat was controlled to 3.0 ± 0.2 \(\mu\)l by checking the droplet size. Average WCA and OCA results, from measurements taken at five different positions on each specimen, were reported with standard deviations of ± 2°. It was confirmed that the fluorine atomic concentration of perfluorooctyl side chains on the surface of the silanized nanofiber mat. The side chains on the surface of the silanized nanofiber mat were characterized using attenuated ATR/FT-IR at room temperature (RT) over a range of 4000–650 cm\(^{-1}\). The crystalline structure of the side chain of the nanofiber mat was investigated by WXRD with Cu K\(\alpha\) radiation (\(\lambda = 1.541 \text{ Å}\)) at RT, a voltage of 40 kV, current of 40 mA, and Bragg angles (2\(\theta\)) of 10–50° with scan rate of 2°/min.

### 3. Results and discussion

The meta-aramid solution for electrospinning was prepared using a mixture of DMAC and LiCl solvent system. The DMAC/LiCl is a useful solvent for meta-aramid fiber in several applications. In literature, the maximum values for LiCl concentrations in dry DMAC...
have been reported from 8.46 to 13 wt% [10]. We suggest a mechanism for the dissolution of meta-aramid in DMAc/LiCl solution, as presented in Fig. 1, based on the dissolution mechanism of cellulose in the DMAc/LiCl solvent system [11,12]. In this study, DMAc and LiCl formed [Li-DMAc]+ macrocation complex and Cl\(^-\) ion. Then, the hydrogen bonds between meta-aramid chains were weakened by these macrocation and Cl\(^-\) ion, which interacted with the amide group. As a result, the meta-aramid fiber can be dissolved in the solution. A suitable amount of LiCl for the dissolution of meta-aramid fiber was about 20–40 wt% (LiCl/meta-aramid).

The meta-aramid nanofiber mat (mANF) was efficiently prepared by electrospinning using a drum-type collector. As shown in Fig. 2A, the nanofibers were ca. 200–300 nm in diameter, and had a rough and uneven surface. Additionally, the nanofibers were clearly aligned along the rotational direction of the collector. Analysis of the chemical composition of the nanofibers indicated that there was a considerable amount of Cl element in/on the nanofibers (Fig. 2B). No Li element was detected because the Be window of the EDS detector absorbed the low-energy X-rays of light elements. We were certain that the presence of Cl\(^-\) in the nanofiber mat would have a negative impact on the chemical and physical properties of the nanofibers. Thus, the Cl\(^-\) in the as-spun mANF was removed by repetitive washing with deionized water. Meta-aramid is one of the aromatic polyamide. It has many amide groups, so it can absorb water very well. In addition, lithium chloride (LiCl) is a typical ionic compound, although the small size of the Li\(^+\) ion gives rise to properties not seen for other alkali metal chlorides, such as extraordinary solubility in water (83.05 g in 100 mL of water at 20 °C). Because of these reasons, the embedded salt ions can move off the nanofiber with water molecules during repetitive washing treatment for 90 min (for 30 min of treatment with three times). As shown in Fig. 2C, the washed meta-aramid nanofiber mat, hereafter called W-mANF, retained a smooth surface with fibers of 200–300 nm in diameter. Furthermore, using elemental analysis, we confirmed that the Cl element in the mANF was removed during the repeated washing treatment (Fig. 2D). As mentioned above, the removal of Cl\(^-\) was expected to affect the chemical and physical properties of the nanofibers. Thus, we investigated the thermal properties of the nanofiber mats.

TGA curves obtained during pyrolysis of mANF and W-mANF under N\(_2\) atmosphere at a heating rate of 10 °C/min are shown in Fig. 3A. Two steps of weight loss were observed, at approximately 40–100 °C and 400–650 °C. The first weight loss observed in the curve of W-mANF, which spanned from 40 to about 100 °C, was ascribable to the release of adsorbed moisture. This result is similar to that of a previous study on the thermal degradation of Nomex fibers [13]. However, mANF exhibited a dramatic weight loss near 100 °C, which indicated that a considerable amount of moisture and Cl\(^-\) escaped from the mANF in this temperature range. The second weight loss of both mANF and W-mANF began at approximately 400 °C, corresponding to the amide bonds, which hold the aromatic units together and heterolytically break down between 400 and 550 °C. The heterolytic breaking of the amide bonds occurred until 600–650 °C [14]. Except for the dramatic weight loss at 40–100 °C, mANF showed a similar thermal stability to that of W-mANF.

To confirm the influence of the remaining Cl on the thermal properties of the nanofiber mats, additional thermal analysis was carried out using DSC, as shown in Fig. 3B. In the first scan, endothermic bands were observed at around 106 and 71 °C for mANF and W-mANF, respectively, which suggested that the remaining Cl element and moisture interacting with the Cl absorbed heat. Especially, mANF, containing a considerable amount of Cl element, showed a very large endothermic peak and highest transition temperature. In
the second scan, the transition of the meta-aramid chains in W-mANF was found to occur around 272 °C, which was considered to be the glass transition temperature ($T_g$) of the meta-aramid chains. We conclude that the arrangement of the polymer segments became possible through the dissolution of the meta-aramid in the DMAc/LiCl solution and solidification during electrospinning. In the case of mANF, no glass transition behavior was observed because the presence of Cl between the meta-aramid chains interrupted the rearrangement of the chains during heating. In contrast, segmental motion of the meta-aramid chains in W-mANF became possible owing to the removal of the Cl element by the washing treatment. Later, the selection of the meta-aramid nanofiber mat heat treatment temperature was based on the above DSC results.

To enhance the chemical stability and mechanical properties of the meta-aramid nanofibers, mANF and W-mANF were heat-treated in air at 300 °C for 10 min (HT300-unW-mANF and HT300-W-mANF, respectively). ATR FT-IR spectra were observed to determine the change in the chemical structure of the nanofiber mats. As shown in Fig. 4A, the meta-aramid nanofiber mats (mANF, W-mANF, HT300-unW-mANF, and HT300-W-mANF) exhibited an almost identical chemical structure to that of commercial Nomex® fiber, confirmed by the peaks for N—H stretching at 3307 cm$^{-1}$, aromatic C—H stretching at 3068 cm$^{-1}$, C=O···H stretching (amide I) at 1647 cm$^{-1}$, aromatic C=C skeleton vibration or C=C vibration at 1604 cm$^{-1}$, N—H bending (amide II) at 1528 cm$^{-1}$, and C—N vibration at 1243 cm$^{-1}$ [8,13,15]. These peaks can also be clearly observed in Fig. S1. In the case of mANF, the N—H stretching of meta-aramid and the O—H stretching of water were represented by the overlapping peaks spanning from 2900 to 3700 cm$^{-1}$. However, the peak for water dramatically decreased in intensity in the case of W-mANF, which had no Cl element owing to the washing treatment. Later, the peak became extinct for both samples during heat treatment (HT300-unW-mANF and HT300-W-mANF). Additionally, changes in secondary bonding, such as hydrogen bonding, could be determined by comparing the peak intensity of the C=O···H stretching band (amide I, 1647 cm$^{-1}$) and the aromatic C=C skeleton or C=C vibration band (1604 cm$^{-1}$). The latter should be constant because the aromatic group is stable and would have undergone no chemical change during the electrospinning. The intensity ratios are shown in Fig. 4B. The ratios of the mANF and W-mANF were decreased compared with that of Nomex® fiber. This indicates that hydrogen bonding between amide groups was insufficiently formed when the meta-aramid in DMAc/LiCl solution was electrospun. Heat treatment above $T_g$ (HT300-unW-mANF) only was not enough to regenerate the hydrogen bonds. The Cl remaining between meta-aramid chains interrupted their arrangement and the formation of hydrogen bonding during heating. In contrast, in the case of HT300-W-mANF, sufficient hydrogen bonds were formed, similar to those in Nomex® fiber. It was possible to rearrange the meta-aramid chains in this sample during heat treatment owing to the absence of Cl element between them. When the
enhanced chemical stability, when soaked in DMAc at 50 °C and in DMAc/LiCl at room temperature (see Fig. 6E and F). Also, as maintained its shape despite being soaked in DMAc for 24 h, as shown in Fig. 6D. In addition, the HT300-W-

Fig. 5. WXRD patterns of mANF, W-mANF, HT250-W-mANF, HT300-unW-mANF, and HT300-W-mANF.

of the rotating drum collector to investigate their mechanical properties, such as Young modulus in the longitudinal direction than in the transverse direction. This effect on the mechanical properties of the nano fibers. We conclude that the recrystallization of the meta-aramid nanofibers was closely related to the improvement in their chemical stability.

To confirm the enhanced chemical stability of the nanofiber mats, their survival in DMAc was examined. As shown in Fig. 6B, the mANF, W-mANF, and HT250-W-mANF, which all had a non-recrystallized structure, dissolved in DMAc upon contacting the solvent, whereas the HT300-unW-mANF and HT300-W-mANF held their shape. The HT300-unW-mANF became deformed as time progressed, and finally lost its original form after 24 h. However, the HT300-W-mANF, which had well developed crystalline structure, maintained its shape despite being soaked in DMAc for 24 h, as shown in Fig. 6D. In addition, the HT300-W-mANF exhibited enhanced chemical stability, when soaked in DMAc at 50 °C and in DMAc/LiCl at room temperature (see Fig. 6E and F). Also, as shown in Fig. S3, the HT300-W-mANF showed outstanding chemical stability against organic solvents, acid and base. Interestingly, the HT300-W-mANF, soaked in DMAc/LiCl at 50 °C, became deformed as time progressed. It indicates the reversible recrystallization of the meta-aramid chains by the sequential post-treatment. These results show that the chemical stability of the meta-aramid nanofibers was easily improved by the regrowth of the crystalline structure using the sequential post-treatment.

Tensile tests were carried out on the nanofiber mats along the directions corresponding to the longitudinal and transverse directions of the rotating drum collector to investigate their mechanical properties, such as Young’s modulus. As shown in Fig. 7 and Table S1, all nanofiber mats displayed a higher Young’s modulus in the longitudinal direction than in the transverse direction. This indicates that the directional nature of the nanofibers had a great effect on the mechanical properties of the nanofiber mats. Additionally, the mechanical properties of the nanofiber mats were enhanced in the longitudinal direction by the washing and heat treatments. Especially, the heat treatment of the Cl-removed nanofiber mat (W-mANF) at 300 °C (above Tg) had the greatest influence on the mechanical properties. The mechanical properties of HT300-unW-mANF (Cl-containing nanofiber mat) did greatly increase compared with those of HT300-W-mANF despite the heat treatment above Tg. These results were associated with the regeneration of the crystalline structure (see Fig. 5) bringing about an improvement in chemical stability. The regeneration of the crystalline structure of the meta-aramid was prerequisite for the effective improvement of the mechanical properties of the meta-aramid nanofiber mats.

The improvement of the chemical stability and mechanical properties of the nanofiber mats means an extended applicability under various conditions. Herein, surface modification using trichloro (1H,1H,2H,2H-perfluoroctyl) silane (fluoroalkyl silane, FAS) was carried out to form an amphiphobic surface on the meta-aramid nanofiber mats. The HT300-W-mANF, fixed in a stainless frame, was repeatedly modified with FAS in toluene to endow it with both water- and oil-repellent properties. The resulting amphiphobic surface of the nanofiber mat (A-HT300-W-mANF) was derived from the introduction of fluoroctyl side chains to the nanofiber surface by the silane-modification process. The amphiphobic properties of A-HT300-W-mANF were investigated using water and oil contact angle measurements (Fig. 8A). The mANF, W-mANF (data not shown), and HT300-W-mANF samples were quickly wetted by both water and n-hexadecane, i.e., they originally had an amphiphilic property, whereas A-HT300-W-mANF, which was modified
Fig. 6. Observation of improved chemical stability. (A) mANF, W-mANF, HT250-W-mANF, HT300-unW-mANF, and HT300-W-mANF before being soaked in DMAc. (B, C, and D) mANF, W-mANF, HT250-W-mANF, HT300-unW-mANF, and HT300-W-mANF soaked in DMAc at room temperature for 0, 12, and 24 h, respectively. (E) HT300-W-mANF soaked in DMAc at 50 °C for 168 h. (F) HT300-W-mANF soaked in DMAc/LiCl at room temperature for 168 h. (G) HT300-W-mANF soaked in DMAc/LiCl at 50 °C for 168 h.

Fig. 7. Young’s modulus of mANF, W-mANF, HT250-W-mANF, HT300-unW-mANF, and HT300-W-mANF in the (A) longitudinal and (B) transversal directions.
with a low concentration of FAS (0.1% V/V FAS/toluene), was unwetted by both water and n-hexadecane. As the modification was repeated, the water contact angle (WCA) increased gradually from 138.9° to 156.7°. In contrast, the oil contact angle (OCA) of A-HT300-W-mANF increased to 123.8° after three modifications but decreased to 102.2° after five modifications. Repeated silanization with a low concentration of FAS was more effective than just one silanization with a relatively high concentration of FAS (1.0% V/V FAS/toluene). In terms of surface morphology, the FAS molecules wrapped the surface of the nano fiber bundles of the samples, which were composed of a few nanofibers, as shown in Fig. 8B. The amount of FAS coating the surface of the bundles increased as the silanization was repeated. Correspondingly, the fluorine atomic concentration of the nanofibers observed during elemental analysis increased as the FAS treatment was repeated (8.24, 10.11, 12.78, 14.28, and 21.82 at.%, respectively). Therefore, this surface change was considered to be caused by the increasing content of fluoroalkyl side chains during the repeated modification.

The presence of and variation in the surface modification were confirmed by ATR FT-IR, as shown in Fig. 9A. The peaks at 1236 cm⁻¹ and 780 cm⁻¹ arose from Si–C vibration, while the C–F stretching was observed at 1130–1225 cm⁻¹, indicating the presence of FAS on the nanofiber surface [18]. The peaks associated with network Si–O–Si vibrational motion were observed in the 1100–1000 cm⁻¹ spectral region, indicating the formation of a network structure on the surface of the nanofibers. Other peaks related to Si–O–Si were observed at 760–670 cm⁻¹, which were assignable to the symmetric stretching vibration and the bending vibration of Si–O–Si. These characteristic peaks of FAS increased in intensity as the silane-modification was repeated, indicating an increasing content of fluoroalkyl side chains on the nanofiber mat. Also, this tendency was confirmed by elemental analysis, which showed the increasing contents of fluorine and silicon elements as repeating surface-modification, as shown in Fig. S4. The characteristic crystalline structure, (002) plane, of the fluoroalkyl side chains was confirmed using WXRD (Fig. 9B) [19]. The distance between the side chains (d-spacing, calculated by Bragg’s law) was considerable, and increased from 5.07 Å to 5.20 Å and decreased back to 5.09 Å as the silanization was repeated. The crystalline domain size, obtained from the Scherrer equation, of the side chains increased from 9.80 Å to 14.10 Å as the treatment was repeated. The increases in the content and crystalline domain size of the fluoroalkyl side chains on the nanofiber surface was closely related to the improved water-repellency of the mats, consistent with the findings of previous studies [19–23]. Moreover, the oil-repellency of the samples was also improved after the fluoroalkyl silane treatment.

4. Conclusions

In this study, we fabricated a meta-aramid nanofiber mat with improved chemical stability and mechanical properties using a sequential post-treatment involving the removal of Cl element between the meta-aramid chains, crystallization via heat treatment above Tₘ. Aligned meta-aramid nanofibers containing LiCl (mANF) were prepared using electrospinning with a drum-collector, and the obtained nanofiber mats were post-treated with washing and annealing. The Cl element present between the chains of the as-spun mat was clearly eliminated during washing treatment, and the washed nanofiber mat (W-mANF) showed a glass transition behavior around 272 °C (Tₘ). This indicated that heat treatment above the Tₘ would allow the rearrangement of the meta-aramid chains with no salt, inducing the regeneration of the crystalline structure and inter-molecular hydrogen bonding. Indeed, the meta-aramid nanofiber mat heat-treated at 300 °C for 10 min (HT300-W-mANF) displayed effective improvement of chemical stability, confirmed by its survival in DMAC for 168 h at room temperature, and increasing of 4.6-fold Young’s modulus in the longitudinal direction compared with that of the mANF. These enhancements were attributed to the orientation and crystallization of the salt-removed meta-aramid chains during annealing. Improvement of the chemical stability and mechanical properties of meta-aramid nanofibers is a prerequisite...
for many practical applications requiring high durability, such as protective layers with corrosion resistance, water/gas/particulate filter media, and secondary battery separators. Our results will enable the design and production of enhanced nanofibrous materials based on meta-aramid.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.eurpolymj.2017.03.052.

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318–322.


