Materials Research Express

PAPER

Fabrication and characterization of co-electrospun cellulose/poly (4-methyl-1-pentene) nanofibers with improved tensile properties

Abdul Rahim Narejo, Raja Fahad Qureshi, Rabia Almas, Sanam Irum Memon, Faraz Khan Mahar ©, Noureen Syed, Farooq Ahmed ©, and Zeeshan Khatri ©
Department of Textile Engineering, Mehran University of Engineering & Technology, Jamshoro, 76020, Sindh, Pakistan
E-mail: zeeshan.khatri@faculty.muet.edu.pk

Keywords: CA, cellulose nanofibers, tensile strength, co-electrospinning

Abstract

In this study, cellulose acetate and poly (4-methyl-1-pentene) (CA/PMP) nanofibers were co-electrospun with a blending ratio of 1:1 and followed by deacetylation treatment to produce cellulose/PMP nanofibers. The physical morphology of nanofibers was characterized by SEM which reveals even and bead-less morphology of nanofibers with an average diameter of 650 nm. FTIR study confirmed the removal of acetyl groups after deacetylation, and x-ray diffraction analysis was performed to analyze the crystalline nature of nanofibers. The calculated crystallinity and crystal size of CA/PMP nanofibers are 82% and 34 Å. The tensile strength study revealed that the combination of both CA and PMP nanofibers with the blending ratio of 1:1 has improved the tensile strength of composite nanofibers. Further, the deacetylation process has also increased the tensile strength. The obtained tensile strength and Young’s modulus are 6.9 MPa and 195 MPa for cellulose/PMP nanofibers which could be a value addition in cellulose-based membranes.

1. Introduction

Nanofibers are unique in nature because of their fine diameter with superior nanofibers connection and high surface area to volume ratio. Therefore nanofibers have achieved great importance in different fields, for instance, filtration, adsorption, biomedical and electronic devices [1–6]. In nanofibers, cellulose is considered amongst one of the most abundantly found natural biopolymers which include chitosan, pullulan, and zein. Cellulose nanofibers possess some outstanding properties such as excellent thermal stability, chemical resistance, and biodegradability which in turn have increased their usage in a variety of potential applications like biosensors drug delivery, tissue engineering, separation technology, and food packaging [7–10]. Though there are numerous ways for extracting cellulose nanofibers from various sources which include plants and different marine filamentous algae using both physical as well as chemical methods, however, the production and yield of these methods are still not sufficient. Fabrication of cellulose nanofibers using electrospinning technique, on the other hand, has gained significant attention due to its easy operation and high production [11, 12]. It has also significant advantages over the other spinning techniques and has also the ability to produce fibers from submicron to nanoscale diameter [13]. Direct electrospinning of cellulose using N-methyl morpholine-N-oxide (NMMO) hydrate is the most frequent method reported for the production of cellulose nanofibers [14, 15]. In the said reported method, Cellulose/NMMO hydrate solutions can be co-electrospun at an elevated temperature of 80–130 °C. Apart from the advantage of comparatively high processing temperature, the said method faces some serious drawbacks. Nanofibers with inferior homogeneity, an intensive washing step to remove the residual solvent completely and significant energy usage are a few of the limitations of the above-said process [16]. On the other hand, Cellulose nanofibers can also be efficiently made from Cellulose acetate (CA) by the deacetylation process. Initially, cellulose acetate is electrospun directly with easily accessible solvents like Acetone and Dimethylformamide (DMF) [17]. The CA nanofibers are subsequently deacetylated, converting them into cellulose nanofibers. This method produces cellulose nanofibers with superior morphologies and production rates [18, 19].
For some potential applications such as filtration, adsorption, biomedical and electronic devices, nanofibers require high mechanical properties. Individually cellulose nanofibers cannot provide such mechanical strength. Therefore, to improve the mechanical strength of cellulose nanofibers, producing composite nanofibers by co-electrospinning technique is a simple and easy process. The properties of nanofibers can be enhanced by combining them with different nanofibers [10, 20].

Recently, Farooq et al produced cellulose nanofibers blended with polycaprolactone nanofibers to enhance the wicking behavior of cellulose nanofibers [20]. Gao Kezheng produced highly flexible and conductive CA nanofibers by mixing graphene, which enhanced the physical characteristics of cellulose nanofibers [21]. In a study by Chang Ma, electrospun polycrylonitrile/cellulose nanofibers were fabricated to produce electrode carbon materials, which improved mechanical strength compared to a neat polycrylonitrile membrane-based carbon material [22].

In a study reported by Zhang Yirong, CA/polystyrene nanofibers were produced by electrospinning technique for the collection of water fog. The properties of both polymers improved the surface roughness and hydrophobicity of materials [23]. Phan D, fabricated chitosan/cellulose nanofibers with enhanced mechanical properties having inherent adsorption characteristics [24].

Poly(4-methyl-1-pentene) (PMP) is a polymorphic polyolefin polymer that possesses excellent dielectric properties, high chemical resistance, permeability to gases, and high tensile strength [25]. In research reported by Wahab Jatoi, PMP nanofibers were produced by the electrospinning technique, which showed better mechanical strength [26].

In this study, CA and PMP co-electrospun nanofibers have been produced by the electrospinning technique and followed by a deacetylation process. The nanofibers membranes were prepared at different blending ratios CA and PMP such as 1:0, 1:1, 1:2, 2:1, and 0:1. The co-electrospun nanofibers membranes were characterized by FTIR, SEM, and XRD investigation. The effect of deacetylation and the content of PMP nanofibers on the tensile properties of CA/PMP nanofibers were observed.

2. Experimental

2.1. Materials & methods
Cellulose acetate, (39% acetyl content, Mw = 30 kDa) with a DS of 2.45, Poly (4-methyl-1-pentene) (PMP), N-N Dimethyl Formamide (DMF), and Acetone were purchased from Sigma-Aldrich, Japan. NaOH for deacetylation was purchased from Merck, Germany. The chemicals were directly used without any additional purification.

2.2. Preparation of cellulose acetate and PMP nanofibers
The nanofibers were produced by the electrospinning technique following the previously reported works [11, 12]. The polymeric solution of cellulose acetate was prepared by dissolving 17% cellulose acetate polymer in DMF and acetone with a blending ratio of 2:1 and stirred for 24 h until a homogeneous solution was ready. Simultaneously, the PMP polymeric solution was prepared by dissolving 12% PMP polymer in DMF solvent and stirred for 24 h until a homogeneous solution was ready. Both the solutions CA and PMP were filled in two different plastic syringes with a tip diameter of 0.8 mm and fixed to two different feed pumps. A piece of aluminum foil was raped on a rotating metallic collector. The distance from the tip to the collector was set at 15 cm for both types of nanofibers. The rate flow of CA and PMP polymers was set at 1.2 ml h⁻¹, and 1.1 ml h⁻¹, respectively. A high voltage of 15 kV was applied to the CA solution and 17 kV to the PMP polymer. The nanofibers CA and PMP were electrospun with different ratios of 1:0, 1:1, 1:2, 2:1, and 0:1. The co-electrospun nanofibers membranes were peeled off from the aluminum foil and were kept for drying at room temperature for 24 h.

2.3. Deacetylation of cellulose acetate nanofibers
The prepared nanofibers membranes were deacetylated in order to convert cellulose acetate nanofibers into cellulose nanofibers. Following the previously published work, the deacetylation process was carried out [10]. Briefly, 1 g of NaOH was added to 500 ml of deionized water to make 0.05 M solution. The nanofiber membrane was cut into 12 inches (length) by 8 inches (width) and placed into a glass dish containing an aqueous solution of 0.05 M NaOH. The deacetylation process continued at room temperature for 48 h. The nanofibers membrane was thoroughly rinsed-off in distilled water until their pH reached neutral, and then nanofibers were dried at room temperature. All the nanofibers membranes with different blending ratios were treated.
3. Characterization

The nanofibers were characterized by scanning electron microscopy (SEM, JEOL model JSM 6010 LA). Nanofibers were sputtered coated with Pd-Pt before the examination. ImageJ software was used to calculate the diameter of nanofibers and Origin Pro 9.0 was used for the graphical representation of data. Fourier Transform Infrared (FTIR, Shimadzu, 8900-FT-IR spectrometer Tokyo Japan) was used to analyze surface functional groups and their interaction. The wide-angle x-ray diffraction (WAXID) (Rotaflex RTP300, Rigaku. Co., Japan) was used to investigate the crystalline nature of nanofibers with 40 kV, 150 mA at the scanning speed of \(2\theta = 2^\circ\ min^{-1}\). The Scherrer equation (1) was used to calculate the crystallite size of nanofibers from XRD data [27].

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]  

Where ‘K’ is the shape factor with a value of 0.89 for spherical samples and it has been used in the literature [28], ‘\(\lambda\)’ is the x-ray wavelength of 1.54 for CuK\(\alpha\) x-ray source, ‘\(\beta\)’ is the line broadening width at half maximum intensity in radians, ‘\(\theta\)’ is the Bragg angle and ‘D’ is the crystallite size (Å).

The mechanical test was performed using universal Tensile Tester Machine (Titan Tensile universal Tester, Company Ltd). The test was performed in accordance with ASTM standard D5034-95. The samples were cut in Dog-bone-shape with the dimension of 22 mm (length) by 5 mm (width) using the rotary cutter. The applied load cell was set at 120 N, and the stretching speed was set at 5 mm min\(^{-1}\). The test was performed at room temperature of 24 ± 1 °C and relative humidity of 45 ± 5%. The obtained stress-strain curves were used to calculate tensile strength, elongation %, and young’s modulus. The thickness of the nanofibers membranes was measured by the Digital Micrometer Screw Gauge. The average thickness of the specimen ranged from 0.05 mm to 0.06 mm.

4. Results & discussion

4.1. Physical morphology of nanofibers

The SEM images of nanofibers as shown in figure 1 (a)–(e) indicate that the nanofibers are smooth and bead-free at all blending ratios before and after deacetylation. From the SEM images in figure 1(a)–(c), the diameter of nanofibers was calculated using ImageJ software, and the histogram of diameter was made using Gaussian Fitting (Origin Pro 9). As shown in figure 2(a)–(e) the diameter of CA nanofibers is in the range between 100 nm and 500 nm with an average diameter of 389 nm, and after deacetylation, the range of diameter is almost the same, but the average diameter is reduced to 300 nm. The diameter range of pure PMP nanofibers is between 500 nm to 3000 nm, and the average diameter is 1250 nm which is significantly higher than CA nanofibers. When PMP and CA nanofibers were co-electro spun with the blended ratio of 1:1, the average diameter is reduced to 960 nm, and the range is between 200 nm and 1600 nm. Similarly, after the deacetylation process, the fiber diameter is further reduced to 650 nm. Because during the deacetylation process, the acetyl groups were removed, therefore, the diameter was reduced to some extent.

4.2. Chemical study of nanofibers

The FTIR spectra of pure CA nanofibers as shown in figure 3 reveals some major peaks at 3400 cm\(^{-1}\), 1800 cm\(^{-1}\), 1345 cm\(^{-1}\), and 1240 cm\(^{-1}\) corresponding to the OH stretching, C-O stretching, C-CH\(_3\) bending, and C-O-O...
vibrational stretching [20]. The adsorption peaks at 1800 cm\(^{-1}\), and 1345 cm\(^{-1}\) corresponding to acetyl groups in CA nanofibers disappeared after deacetylation indicating the removal of acetyl group. The peak at 3400 cm\(^{-1}\) corresponding to the OH band increased significantly, indicating the excessive OH groups on the surface of cellulose nanofibers [10]. Pure PMP nanofibers showed a major absorption peak at 2950 cm\(^{-1}\), and a minor peak at 1540 cm\(^{-1}\) corresponding to C–C bending and C=O stretching respectively. The spectra of CA/PMP nanofibers showed an additional peak at 3400 cm\(^{-1}\), 1800 cm\(^{-1}\), and 1345 cm\(^{-1}\) corresponding to O–H stretching, C–O bending, and C–CH\(_3\) stretching. Similarly, after the deacetylation of CA/PMP nanofibers, the peak at 1800 cm\(^{-1}\) and 1345 cm\(^{-1}\) disappeared and indicated the removal of the acetyl group, and it confirmed the deacetylation process. The results indicated that cellulose acetate nanofibers were converted into cellulose nanofibers.

4.3. XRD analysis of nanofibers
The XRD diffraction of the prepared samples was obtained. In figure 4 the CA nanofibers showed diffraction peaks centered at 9° and 22.5° indicating the semi-crystallinity of acetyl groups in cellulose acetate. After deacetylation, nanofibers displayed more intensive peaks corresponding to characteristics of cellulose II structure and indicating the better crystallinity of cellulose nanofibers than cellulose acetate nanofibers [29]. The calculated degree of crystallinity from XRD data as summarized in table 1 is 77% for CA nanofibers, however, after treatment, it increased to 85%. Similarly, the crystallite size calculated using the Scherrer equation also increased from 21.1 Å to 36.1 Å. The diffraction pattern of pure PMP nanofibers showed a sharp peak at 2θ = 9.2°, indicating the crystalline nature of PMP nanofibers [26]. The crystalline size and degree of
crystallinity of PMP nanofibers are found to be 23.6 Å and 85%, respectively. After combining CA and PMP nanofibers by co-electrospinning, the spectra showed a wide peak at $2\theta = 11^\circ$, and the obtained crystalline size and degree of crystallinity are found to be 37.6 Å and 80.9%, a minor decline in the crystallinity may be due to the combined characteristics of CA and PMP nanofibers. Similarly, after deacetylation of CA/PMP samples, the obtained spectra showed two bands at $2\theta = 10^\circ$ and $2\theta = 22^\circ$, this could be attributed to cellulose II structure with more crystalline nature [30]. In addition, the improvement in crystallite size of 37.2 Å and degree of crystallinity of 82% has also confirmed the successful deacetylation of nanofibers, which could lead to enhanced tensile strength.

4.4. Tensile strength of nanofibers
Mechanical properties of nanofibers such as membrane thickness, tensile strength, elongation % and young’s modulus were also observed and summarized in table 2. Figure 5 shows typical stress-strain curves of blended CA and PMP nanofibers with blending ratios of 1:0, 1:1, 1:2, 2:1, and 0:1 before and after treatment. The results show that after the treatment of nanofibers, the tensile strength for all samples has significantly increased. In figure 5 the CA nanofibers exhibited a tensile strength of 1.8 MPa with a young’s modulus of 57 MPa and an elongation of 3.8%. After deacetylation, the tensile strength increased from 1.8 MPa to 2.2 MPa and the young’s modulus increased to 85 MPa, which could be attributed to excessive hydroxyl groups holding the chains more firmly which gives cellulose nanofibers higher tensile strength than CA nanofibers [24]. The stress-strain curve of pure PMP nanofibers exhibited a tensile strength of 6.5 MPa with a young’s modulus of 172 MPa and an elongation of 2.9%. We also observed the effect of deacetylation on tensile properties of PMP nanofibers, the results show that after treatment of PMP nanofibers, it has a minor effect on tensile properties, and the young’s modulus of PMP nanofibers has decreased to 169 MPa. The combination of CA and PMP nanofibers with a blending ratio of 1:1 exhibited a tensile strength of 5.5 MPa with an elongation of 3.4% and a young’s modulus of 123 MPa, the enhancement in tensile properties of CA/PMP is due to the high mechanical characteristics of PMP nanofibers [26]. The tensile strength of CA/PMP nanofibers after the deacetylation process increased to 6.9 MPa with an elongation of 3.5% and a young’s modulus reached to 195 MPa. It is obvious that after the
deacetylation, the tensile strength of CA nanofibers increases resulting in an enhancement in the tensile strength of CA/PMP nanofibers. The combination of CA/PMP with a blending ratio of 1:2 exhibited a tensile strength of 6.2 MPa which is lower than the blending ratio of 1:1. Similarly, after the deacetylation, the enhanced tensile of the blending ratio of 1:2 is 6.5 MPa that is also lower than the blending ratio of 1:1 after its deacetylation. When the blending ratio was changed to 2:1, the samples exhibited a tensile strength of 3.5 MPa before deacetylation and 4.5 MPa after deacetylation, which is significantly lower than the blending ratio of 1:2 before and after its deacetylation. The obtained results at the blending ratio of 1:1 are better than the rest of the samples.

5. Conclusion

In the present study, co-electrospun cellulose/PMP nanofibers with different blending ratios were fabricated by electrospinning technique and followed by deacetylation. The SEM images showed smooth and bead-free morphology of nanofibers. The blending of CA and PMP with 1:1 showed an average diameter of 960 nm. When the CA/PMP nanofibers were deacetylated, the average diameter decreased to 650 nm. The FTIR study confirmed the successful conversion of CA nanofibers into cellulose nanofibers by removing the acetyl group from cellulose acetate. The XRD analysis showed improved crystallinity of cellulose nanofibers. The degree of crystallinity for CA/PMP with a blending ratio of 1:1 after deacetylation was found to be 82%. The tensile strength and young’s modulus of the composite nanofiber membrane with the blending ratio of 1:1 were 6.9 MPa and 195 MPa, respectively, which were higher than the other samples. The obtained nanofibers membrane with improved mechanical strength could be a value addition in cellulose-based membranes.

| Sample | Treatment | Thickness/μm | Young’s Modulus/MPa | Ultimate Strength/MPa | Elongation/% |
|--------|-----------|--------------|---------------------|-----------------------|-------------|
| CA:PMP 1:0 | Before | 58 ± 5.2 | 57.2 ± 2.8 | 2.4 ± 0.19 | 3.6 ± 0.14 |
| | After | 48 ± 3.5 | 85.1 ± 3.6 | 2.7 ± 0.21 | 3.3 ± 0.11 |
| CA:PMP 1:1 | Before | 66 ± 8.4 | 123.8 ± 11.7 | 5.4 ± 0.38 | 3.3 ± 0.12 |
| | After | 58 ± 7.8 | 195.4 ± 21.4 | 6.8 ± 0.43 | 3.0 ± 0.11 |
| CA:PMP 1:2 | Before | 66 ± 9.1 | 162.4 ± 18.1 | 6.2 ± 0.39 | 2.9 ± 0.1 |
| | After | 60 ± 8.4 | 175.2 ± 20.6 | 6.5 ± 0.41 | 3.1 ± 0.12 |
| CA:PMP 2:1 | Before | 66 ± 5.6 | 75.9 ± 5.0 | 3.5 ± 0.25 | 3.5 ± 0.18 |
| | After | 57 ± 6.2 | 120.6 ± 12.2 | 4.5 ± 0.27 | 3.2 ± 0.17 |
| CA:PMP 0:1 | Before | 58 ± 6.3 | 172.4 ± 15.1 | 6.01 ± 0.37 | 3.0 ± 0.12 |
| | After | 56 ± 5.5 | 169.9 ± 15.0 | 5.9 ± 0.31 | 3.1 ± 0.13 |

Figure 5. Strain stress curves of CA, D-CA, PMP, CA/PMP, & D-CA/PMP nanofibers.
Acknowledgments

The work was supported by the Department of Textile Engineering, Mehran University of Engineering & Technology, Jamshoro, Pakistan.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Faraz Khan Mahar https://orcid.org/0000-0002-4417-3339
Farooq Ahmed https://orcid.org/0000-0002-8444-2038
Zeeshan Khatri https://orcid.org/0000-0001-8779-3805

References

[1] Lee H, Kim M, Sohn D, Kim S H, Oh S G, Im S S and Kim I S 2017 Electrospray tungsten trioxide nanofibers decorated with palladium oxide nanoparticles exhibiting enhanced photocatalytic activity RSC Adv. 7 6108–13
[2] Khatri Z, Jatoi A W, Ahmed F and Kim I S 2016 Cell adhesion behavior of poly(ε-caprolactone)/poly(L-lactic acid) nanofibers scaffold Mater. Lett. 171 178–81
[3] Gopiraman M, Jatoi A W, Hironmichi S, Yamaguchi K, Jeon H Y, Chung I M and Soo K I 2016 Silver coated anionic cellulose nanofibers composites for an efficient antimicrobial activity Carbohydrate Polym. 149 51–9
[4] Mitchell R R, Gallant B M, Thompson C V and Shao–Horn Y 2011 All-carbon-nanofiber electrodes for high-energy rechargeable Li–O 2 batteries Energy Environ. Sci. 4 2952–8
[5] Sambaer W, Zatloukal M and Kimmer D 2011 3D modeling of filtration process via polyurethane nanofiber-based nonwoven filters prepared by electrosprining process Chem. Eng. Sci. 66 613–23
[6] Lee H, Nagahishi T, Phan D N, Kim M, Zhang K Q, Wei K and Kim I S 2017 Effect of graphene incorporation in carbon nanofiber decorated with TiO2 for photocatalytic applications RSC Adv. 7 6574–82
[7] Zhang W X, Wang Y Z and Sun C F 2007 Characterization on oxidative stabilization of polyacrylonitrile nanofibers prepared by electrosprining J. Polym. Res. 14 467–74
[8] Saligheh O, Forouharshad M, Arasteh R, Eslami-Farsani R, Khajavi R and Yadollah Roudbari B 2013 The effect of multi-walled carbon nanotubes on morphology, crystallinity and mechanical properties of PBT/MWCNT composite nanofibers J. Polym. Res. 20 1–6
[9] He B, Tian L, Li J and Pan Z 2013 Effect of hot-stretching on morphology and mechanical properties of electropun PMIA nanofibers Fibers Polym. 14 405–8
[10] Khatri Z, Wei K, Kim B S and Kim I S 2012 Effect of deacetylation on wicking behavior of co-electrosprun cellulose acetate/polyvinyl alcohol nanofibers blend Carbohydrate Polym. 87 2183–8
[11] Khatri Z, Mayakrishnan G, Hirata Y, Wei K and Kim I S 2013 Cationic-cellulose nanofibers: preparation and dyeability with anionic reactive dyes for apparel application Carbohydrate Polym. 91 434–43
[12] Khatri Z, Ahmed F, Khatri A, Khatri M, Qureshi U A and Kim I S 2017 Screen-printed electrosprun cellulose nanofibers using reactive dyes Cellulose 24 4561–8
[13] Li N and Bai R 2005 Copper adsorption on chitosan–cellulose hydrogel beads: behaviors and mechanisms Sep. Purif. Technol. 42 237–47
[14] Han S O, Youk J H, Min K D, Kang Y O and Park W H 2008 Electrosprinning of cellulose acetate nanofibers using a mixed solvent of acetic acid/water: effects of solvent composition on the fiber diameter Mater. Lett. 62 759–62
[15] Fischer S, Thümmler K, Volkert B, Hettrich K, Schmidt I and Fischer K 2008 Properties and applications of cellulose acetate In Macromolecular Symposia 262 (Weinheim: Wiley) 89–96 (January)
[16] Onoobi M, Harun J, Mathew A P, Hussein M Z B and Oksman K 2010 Preparation of cellulose nanofibers with hydrophobic surface characteristics Cellulose 17 299–307
[17] Son W K, Youk J H, Lee T S and Park W H 2004 Electrosprinning of ultrafine cellulose acetate fibers: studies of a new solvent system and deacetylation of ultrafine cellulose acetate fibers J. Polym. Sci., Part B: Polym. Phys. 42 5–11
[18] Liu H and Hsieh Y L 2002 Ultrafine fibrous cellulose membranes from electrosprinning of cellulose acetate J. Polym. Sci., Part B: Polym. Phys. 40 2119–29
[19] Son W K, Youk J H and Park W H 2004 Preparation of ultrafine oxidized cellulose mats via electrosprinning Biomacromolecules 5 197–201
[20] Ahmed F, Saleemi S, Khatri Z, Abro M I and Kim I S 2015 Co-electrosprun poly(ε-caprolactone)/cellulose nanofibers-fabrication and characterization Carbohydrate Polym. 115 388–93
[21] Gao K, Shao Z, Wu X, Wang X, Li J, Zhang Y and Wang F 2013 Cellulose nanofibers/reduced graphene oxide flexible transparent conductive paper Carbohydrate Polymers 97 243–51
[22] Ma C, Chen J, Fan Q, Guo J, Liu W, Cao E and Song Y 2018 Preparation and one-step activation of nanoporous ultrafine carbon fibers derived from polycrylonitrile/cellulose blend for used as supercapacitor electrode J. Mater. Sci. 53 4527–39
[23] Zhang Y, Zhang C and Wang Y 2021 Recent progress in cellulose-based electrosprun nanofibers as multifunctional materials Nanoscale Advances 3 06040–47
[24] Phan D N, Lee H, Huang B, Mukai Y and Kim I S 2019 Fabrication of electrosprun chitosan/cellulose nanofibers having adsorption property with enhanced mechanical property Cellulose 26 1781–93
[25] Griffith J H and Ránby B G 1960 Dilatometric measurements on poly (4-methyl-1-pentene) glass and melt transition temperatures, crystallization rates, and unusual density behavior J. Polym. Sci. 44 369–81
[26] Wahab J A, Lee H, Wei K, Nagaishi T, Khatri Z, Behera B K and Kim I S 2017 Post-electrospinning thermal treatments on poly (4-methyl-1-pentene) nanofiber membranes for improved mechanical properties Polym. Bull. 74 5221–30

[27] Lee H, Yamaguchi K, Nagaishi T, Murai M, Kim M, Wei K and Kim I S 2017 Enhancement of mechanical properties of polymeric nanofibers by controlling crystallization behavior using a simple freezing/thawing process RSC Adv. 7 43994–4000

[28] Sivakumar P, Ramesh R, Ramanand A, Ponnusamy S and Muthamizchelvan C. 2011 Synthesis and characterization of nickel ferrite magnetic nanoparticles Mater. Res. Bull. 46 2208–11

[29] Phan D N, Dorjjugder N, Khan M Q, Saito Y, Taguchi G, Lee H and Kim I S 2019 Synthesis and attachment of silver and copper nanoparticles on cellulose nanofibers and comparative antibacterial study Cellulose 26 6629–40

[30] French A D and Santiago Cintrón M 2013 Cellulose polymorphy, crystallite size, and the segal crystallinity index Cellulose 20 583–8