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QILU UNIVERSITY OF TECHNOLOGY

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纤维素来源对高分子复合薄膜稳定性影响

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The influence of cellulose source on the stability of polymer composite film

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Contents

Abstract

Cellulose is one of the most abundant material in the nature. As a renewable and biodegradable material, cellulose has been utilized in many applications such as packaging, biomedical, bio-energy etc. Wood is one of the most common sources for obtaining cellulose. However, other sources are available for the extraction of cellulose as well. The demand of eco-friendly material requires the diversity of sources. Therefore, the comparison of properties between various sources is necessary to explore. Nanocellulose have been widely used as reinforcement in composite. Due to the excellent properties of nanocellulose such as mechanical properties, lightweight, biodegradability, it is one of the promising materials that can be widely used for improving the performance of the composite material and achieve the environmental commitment simultaneously. Furthermore, the utilization of new sources can add value to the raw material which can boost bio-economy as well. This study is going to discover the different performance among flax, jute cellulose nanocrystals in the composite. By using the same treatment and combined with PVA matrix, these two sources can be compared through different analysis to determine their various performance in the composite.

Keywords: flax, jute, cellulose nanocrystal, composite material

摘　要

纤维素是自然界中最丰富的物质之一。作为可再生和可生物降解的材料，纤维素已用于许多应用中，例如包装，生物医学，生物能源等。木材是获得纤维素的最常见来源之一。但是，其他来源也可用于提取纤维素。对环保材料的使用需求的增加要求纤维素来源的多样性。因此，有必要探索纤维素来源之间的差异。纳米纤维素已被广泛用作复合材料的增强材料。由于纳米纤维素的优异性能，如机械性能，轻质，可生物降解性，它是可广泛用于改善复合材料性能并同时实现环保承诺的有前途的材料之一。此外，利用新资源可以为原材料增加价值，也可以促进生物经济。这项研究将研究亚麻和黄麻纤维素纳米晶体在复合材料中的不同性能。通过使用相同的处理方法并与 PVA 基质结合，可以通过不同的分析方法（包括 FITR，X 射线衍射，UV-vis，热重分析和扫描电子显微镜）比较这两种来源，以发现它们在复合材料中的各种性能。

关键词：亚麻　黄麻　纤维素纳米晶体　复合材料

Chapter 1 Introduction

1.1 Cellulose

The interest for discovering sustainable material is more and more demanding since the raising awareness of environmental protection. Cellulose as a natural resource has drawn attention in the material research. Besides, cellulose displays many advantages including good mechanical properties, biodegradable properties etc. However, there are some drawbacks existing when using nanocellulose such as poor moisture resistance and the incompatibility with hydrophobic matrix. There are several sources which can extract cellulose such as from bast, fruit, wood, animal or mineral fibers. Nevertheless, natural fibers show more potential from the perspectives to optimize the polymer composite's tensile strength, stiffness and thermal stability. In the natural fiber, it composes cellulose, hemicellulose, lignin and extractives. Cellulose accounts for 35-50 wt% while, hemicellulose and lignin's content are 20-35 and 10-20% respectively[1] There are two different forms of cellulose. One is triclinic Iα and the other is monoclinic Iβ. However, there are still much unknown detail about the structure of cellulose such as the biological cellulose synthesis complex and the bond between the cellulose crystallization.[2]

1.2 Nanocellulose

Nanocellulose can be obtained through different treatment such as mechanical treatment, chemical treatment, biological or hybrid treatment from cellulose. Nanocellulose can be classified into cellulose nanocrystals, cellulose nanofibers and bacterial nanocellulose.[3] Compared with cellulose, nanocellulose displays better mechanical strength, surface area, crystallinity which can be utilized in many industries such as food packaging, medicine etc. The nanocellulose is a good reinforcement in nanocomposite which can improve material's mechanical properties. Furthermore, the nanocellulose which is extracted from non-wood plant displays a better barrier property.[4] The source can affect the dimension of the fiber.[5]

Figure 1.1． Different cellulose sources[5]

1.2.1 Cellulose Nanofibers

There are crystalline and amorphous regions in cellulose nanofibers. Cellulose nanofibers' dimension is various. There are different treatments producing cellulose nanofibers such as mechanical methods which displays an energy consumption problem. Various pretreatment can mitigate this problem, for example, alkaline treatment, enzymatic treatment, chemical and radiation treatment. Tempo (2,2,6,6, -tetramethylpiperidin-1-yl) oxidation is a common way to obtain cellulose nanofibers when in the pretreatment. [1]

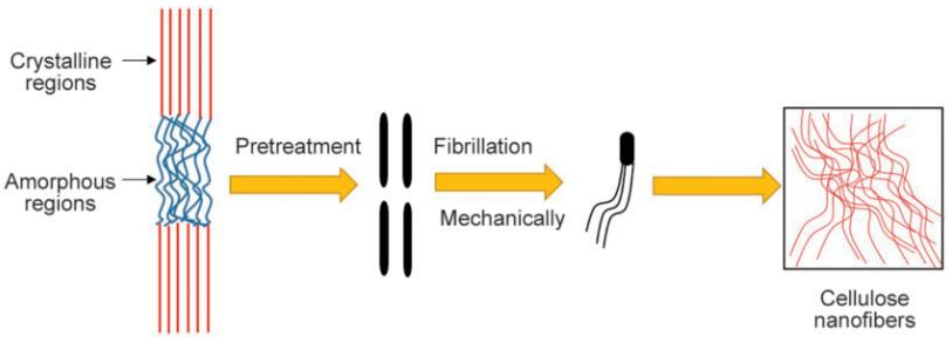


Figure 1.2. Cellulose nanofibers extraction[1]

The product of cellulose nanofibers is gel-like and it possesses excellent tensile

strength, lower oxygen transmission rate, little thermal expansion etc. Therefore, it can be utilized in pharmaceutical, food packaging, printing industry and electronic device when processing into film. Nevertheless, poor compatibility with hydrophobic material and slow dewatering are two drawbacks of cellulose nanofibers.[6]

1.2.2 Cellulose nanocrystals

Cellulose nanocrystals are whisker-shaped. There is a fundamental technique producing cellulose nanocrystals, acid hydrolysis. The principle of acid hydrolysis is to keep crystalline regions in the cellulose while remove the region where contains much amorphous substances. There are two acids commonly used in acid hydrolysis which are hydrochloric acid and sulphuric acid. Cellulose nanocrystals show excellent mechanical strength, remarkable optical properties and it is a quite stable material. Various applications such as drug delivery, films which displays good barrier function, antimicrobial film, hybrid films etc. [7]

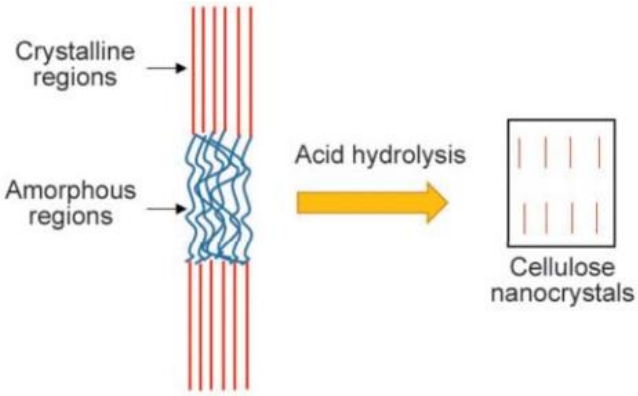


Figure 1.3. Cellulose nanocrystals extraction[1]

1.2.3 The applications of nanocellulose

1.2.3.1 Biomedical Science

Nanocellulose shows great potential in the application of biomedical science. The advantage of nanocellulose is the biocompatibility, low risk of toxicity, distinct geometry, surface modification, self-assembly function and rheology etc. The

application in the biomedical is quite diverse including flexible optoelectronics to scaffold for tissue regeneration. [8]

1.2.3.2 Drug Delivery

Nanocellulose is one of the promising materials in the future since its excellent properties such as recyclability, low toxicity, biocompatibility and easy modification of the surface. Nanocellulose is usually extracted from plant cells where the walls compose of cellulose, hemicellulose and lignin. In terms of the mechanical treatment, this method is the way that uses the mechanical forces to defibrillate the cellulose. About the chemical treatment, different chemical is used such as HCl, H_2SO_4, HBr, metals salts, ionic liquid and oxidation (TEMPO-mediated) of which the acid hydrolysis's function is to keep the crystalline while remove the amorphous region. The third way to extract nanocellulose is biological method, the principle of this technique is to use biological reactions to degrade the cellulose. Nevertheless, in real situation, the combination of these two methods is used to improve the whole process and adjust the properties of the final product. Meanwhile, the diversity of the nanocellulose forms is able to enhance its advantages such as recyclable properties, biocompatibility and the surface modification. In drug delivery, the nanocellulose are widely utilized for preparing particles both in nano and micro scales, tablets, aerogels, hydrogels etc. In the drug delivery, the nanocellulose as a carrier can not only control the release of the drug but also spot the local drug delivery to eliminate the consumption effectively. In addition, the ratio between the surface and volume brings better cellular binding. Besides, the low toxicity is another advantage when using in drug delivery.[9]

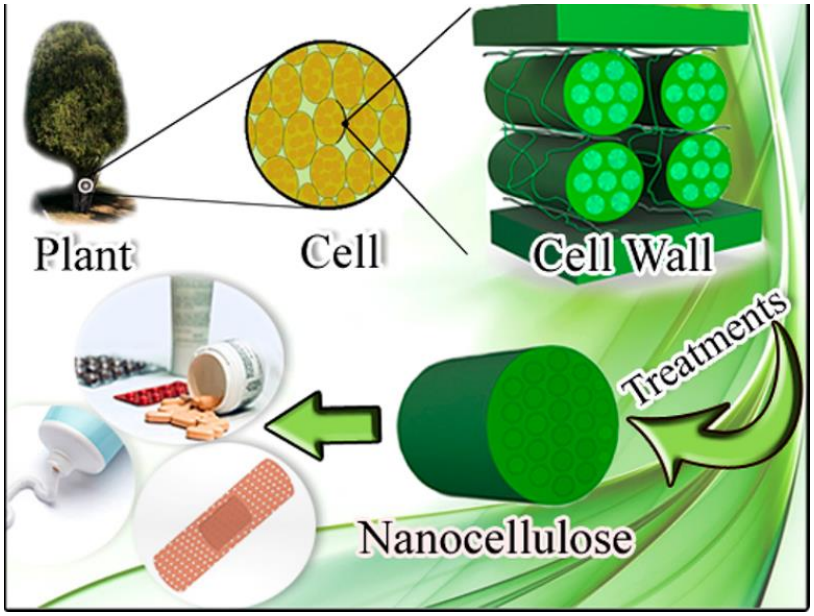


Figure 1.4. Drug delivery applications[6]

1.2.3.3 Food packaging

The requirement of packaging is more and more demanding. Customers are requiring more safe, eco-friendly and high-quality product.[2] In real life, the material which used in food packaging is usually derived from fossil fuels which is not renewable and biodegradable posting a threat to the environment. The bio-based material is a good replacement of fossil fuels in food packaging material. Although, the nanocellulose is usually used as reinforcement, it can be used also as matrices. In the application where nanocellulose is used as matrices, bacterial cellulose is the best choice in this case since its specific properties. The bacterial cellulose is free from hemicellulose and lignin which can eliminate the cost of purifying and the damage of the environment.[10] Decrease of size of the particle shows increase of the risk of toxicity.[11]

1.2.3.4 Pollutant purifying

Water pollution has been posted a huge threat to the environment and human life. Dyes affluent and textile industries waste water are main pollutant. For example, most organic dyes have risk of toxicity and are not biodegradable which will affect human health. Therefore, it is necessary to remove this toxic substance from water. In the

processing of removing, various methods could be applied such as chemical precipitation, filtration of membrane, adsorption, oxidation or reduction, bio-methods and ion exchange. Among all these ways, adsorption methods have many advantages, for instance, easy handling, more economic and high capacity etc. The capacity and rate are importance in the removal of pollutant, the activated carbon is a very common adsorbent but it is high cost. So, economic and eco-friendly adsorbent is quite demanding. The cellulose-based adsorbent displays good ability of adsorption and high efficiency.[12]

1.2.3.5 Textiles

Nanomaterial can help textile to improve its performance. Nanomaterial can be combined with polymers or coated on the surface. Low cost, lightweight, eco-friendly, conductivity, high resistance and self-clean are the advantages that nanocellulose could bring to the textile industry. Furthermore, the products can protect some hazardous substances combined smart-textile and nanotechnology which can be applied in hospitals, rescue services and military services providing the function of monitoring of body. [13]

1.3 Nanocrystal extraction

1.3.1 Acid hydrolysis

Acid hydrolysis is a common and easy way to extract cellulose nanocrystals from fibers. The amorphous region can be removed through acid hydrolysis. Meanwhile, the crystalline contacts can be damaged at high concentration acid hydrolysis where mechanical is applied afterwards as well. However, this process can be detrimental to the environment since the wastewater producing from the acid hydrolysis.[14] The principle of hydrolysis is to make hydrolytic cleavage of glycosidic bond between two units of anhydro-glucose resulting in the removing of amorphous region while keeping the crystalline part. Usually, the mechanical method is needed to disintegrate the structure.[15] The process should consider the environmental impact, process time and the homogeneousness etc.[16]

1.4 Characterization of nanocellulose

There are various analytical methods to evaluate the nanocellulose including its morphology which displays the surface of nanocellulose, liquid crystallinity, mechanical characteristics etc. Different source and treatment can lead to various dimension and morphology of nanocellulose. In terms of the ways to discover the morphology of it, scanning electron microscopy, atomic force microcopy and transmission electron microscopy which SEM is a quick examination that require the minimal preparation of samples while it is not very detailed. In addition, the crystallinity of nanocellulose can be analyzed by X-ray scattering and nuclear magnetic resonance. Furthermore, the thermal stability can be determined by thermogravimetric analysis. [1] [17]

1.5 Polymer composite

Nanocellulose can be utilized as reinforcement in polymer matrix. Polyvinyl alcohol belongs to thermoplastic. It is derived from petroleum and has good film forming and properties of emulsifying. More important, it is biodegradable. Nevertheless, it is not hydrophobic and its strength is not good as well as thermal stability. Usually, to improve the drawbacks of the PVA, nanocellulose can be integrated with PVA material to enhance its performance such as mechanical properties, barrier properties, thermal stability moreover, the composite material is eco-friendly. Among all additives, cellulose nanocrystals are good candidate when selecting the reinforcement for PVA matrix.[18] Polyvinyl alcohol can be dissolved in water and utilized in coating, adhesives, composites both for packaging and agriculture fields. Besides, Polyvinyl is biodegradable so, it could be combined with other biodegradable material to make a eco-friendly composite.[19] Comparing with other polymers , polyvinyl alcohol is a competitive candidate because it is economic, biodegradable, good stability and good optical properties.[20] Therefore, PVA was selected as matrix to combined with cellulose to discover their properties.

Chapter 2 Experimental Section

2.1 Reagents and apparatus

2.1.1 Reagents

Table 1. Reagents used in this experiment.

Reagents	Purity	Manufacturer
NaOH	AR	Damao Chemical Reagent Factory
$NaClO_2$	AR	Aladdin
H_2SO_4	98%	Yantai Far Eastern Fine Chemical
NaCl		
PVA	Mw 31,000-50,000, 98-99% hydrolyzed	Sigma-Aldrich
Glacial acetic acid	AR	Fuyu Chemical
Jute	AR	Sheng Cun Ren
Flax	AR	Xiyifang

2.1.2 Apparatus

Table 2. Instruments used in this experiment.

Name	Model	Manufacturer
Transmission Electron Microscope (TEM)	JSM-6480INCA-EBSDEDS	JEOL
UV-visible Spectrophotometer	UV2600	Shimadzu
FITR	IRPrestige-21	Shimadzu
XRD	XRD-6100	Shimadzu
TGA	SDT-Q600	TA

2.2 Cellulose nanocrystals extraction

2.2.1 Washing of the fibers

The fibers are washed by distilled water 2times at 60℃ for 1h under mechanical stirring.

2.2.2 Pre-treatment

The fibers were cut into small pieces and put into NaOH solution 2 times at 80℃ for 2h. Meanwhile, mechanical stirring is undertaken. Then bleaching solution was prepared. Bleaching composes two different solution. One of them consist of 13.5g NaOH and 37.5ml glacial acetic acid which was diluted to 1 L distilled water. The other part is 1.7 wt% $NaClO_2$ solution. The bleaching solution composes equal volume of these two parts. Then the alkali-treated fibers are put into bleaching solution at 80℃ for 2h and the step was repeated 3 times.

2.2.3 Cellulose nanocrystals extraction

These two fibers are put into 64 wt.% HSO_4 solution for 30mins at 50℃. Under the mechanical stirring (250rpm). Afterward sonication method is applied to the mixture for 15 mins at 28% amplitude which is undertaken under ice bath.

2.2.4 Composite films

The nanocellulose which are extracted from these two materials are incorporated in PVA matrix. Firstly, PVA should be put into distilled water for 1h at 95℃. At the same time, mechanical stirring is undertaken. The suspensions which contain 7.5wt.% of nanocellulose crystal are mixed with PVA solution after the suspensions are ultrasonicated for 5 mins. The mechanical stirring is undertaken when mixing PVA solution and the suspensions. At last, the mixture is stored in petri dish and placed in laboratory hood to evaporate the water contained.

Chapter 3 Results and Discussion

3.1 Lignin and hemicellulose removal

There are several pretreatments before the extraction process such as washing, alkali-treatment, bleaching with mechnical treantment as well. The hydrolysis is used to extract cellulose nanocrystals and the hydrolysis time is 30mins both for the jute and flax. During the acid hydrolysis, the amorphous region is dissolved keeping the crystalline part left. From the picture, there is a significant change from the color because the color shows the removal of the lignin step by step. During the chemical treatment, mechnical methods such as ultrasonification are used to break the fibers into smaller scale and homogenize the fibers as well.

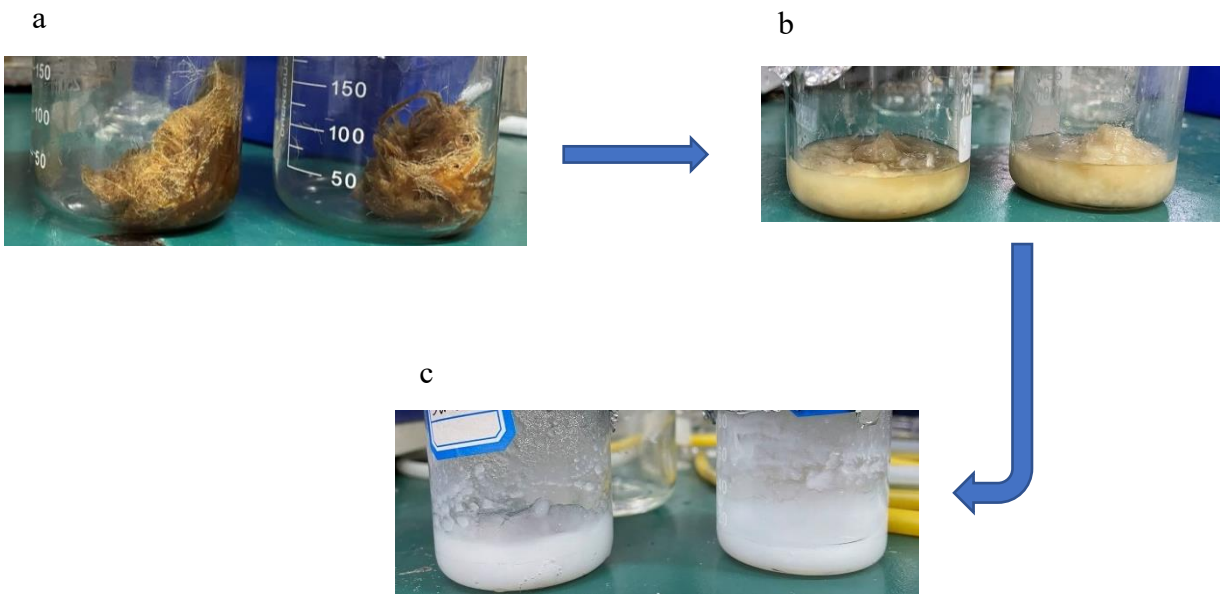


Figure 3.1. a) Raw fiber b) Alkali-treated fiber c) bleached fiber

3.2 Characterization

3.2.1 Infrared spectroscopy

Jute, flax, PVA, jute-PVA and flax-PVA were investigated by FITR. Raw flax and raw jute fibers showed that cellulose characteristic peaks at 2853 cm-1 and 3323cm-1 which

displays that stretching vibration of hydrogen-bonded hydroxyl groups (-OH) and the symmetrical stretching of CH- respectively.[21] In terms of the FITR spectra of composite films, the broad band of 3289 cm-1 were observed representing the hydrogen-bonded hydroxyl groups (-OH) stretching.[22,23] In addition, at 2932 cm-1 the band shows that the asymmetric stretching of CH_2 group of PVA polymer structure. [24,25]In the figure of PVA film, the band displaying at 2915 cm-1 representing the stretching of CH. Meanwhile, the H-O-H deformation are showed at 1655 cm-. While, at 1573 cm-1 the band is attributed to the C=C stretching within PVA polymer acetate groups. [26]Furthermore, peaks at 1387 cm-1 and 1066 cm-1 shows that the rocking of the CH group and the peaks at 1353 and 972 cm-1 are attributed to the CH_2 symmetric bending mode. [25]The C-O stretching of secondary alcohols of PVA is displayed by the peak at 1271cm-1 approximately. Two peaks at 1066cm-1 and 1397cm-1 characterized the stretching of C-O-C mode. [27]Comparing the figure of cellulose nanocrystals integrated with PVA, they did not show huge changes in PVA jute-PVA and flax-PVA composites which reveals that PVA's chemical properties are not affected so much by flax and jute cellulose nanocrystals. However, there are some changes observed such as the 1066 cm-1 band was separated into 1045 and 1024 cm-1which suggest that after integrating, the cellulose asymmetric ring breathing mode and the C-OH bending vibrations of the alcoholic cellulose groups have impact on PVA's chemical properties.[28]

FITR confirmed that PVA film chemical structure remains almost the same and the interaction between cellulose nanocrystals of flax and jute in the interface.

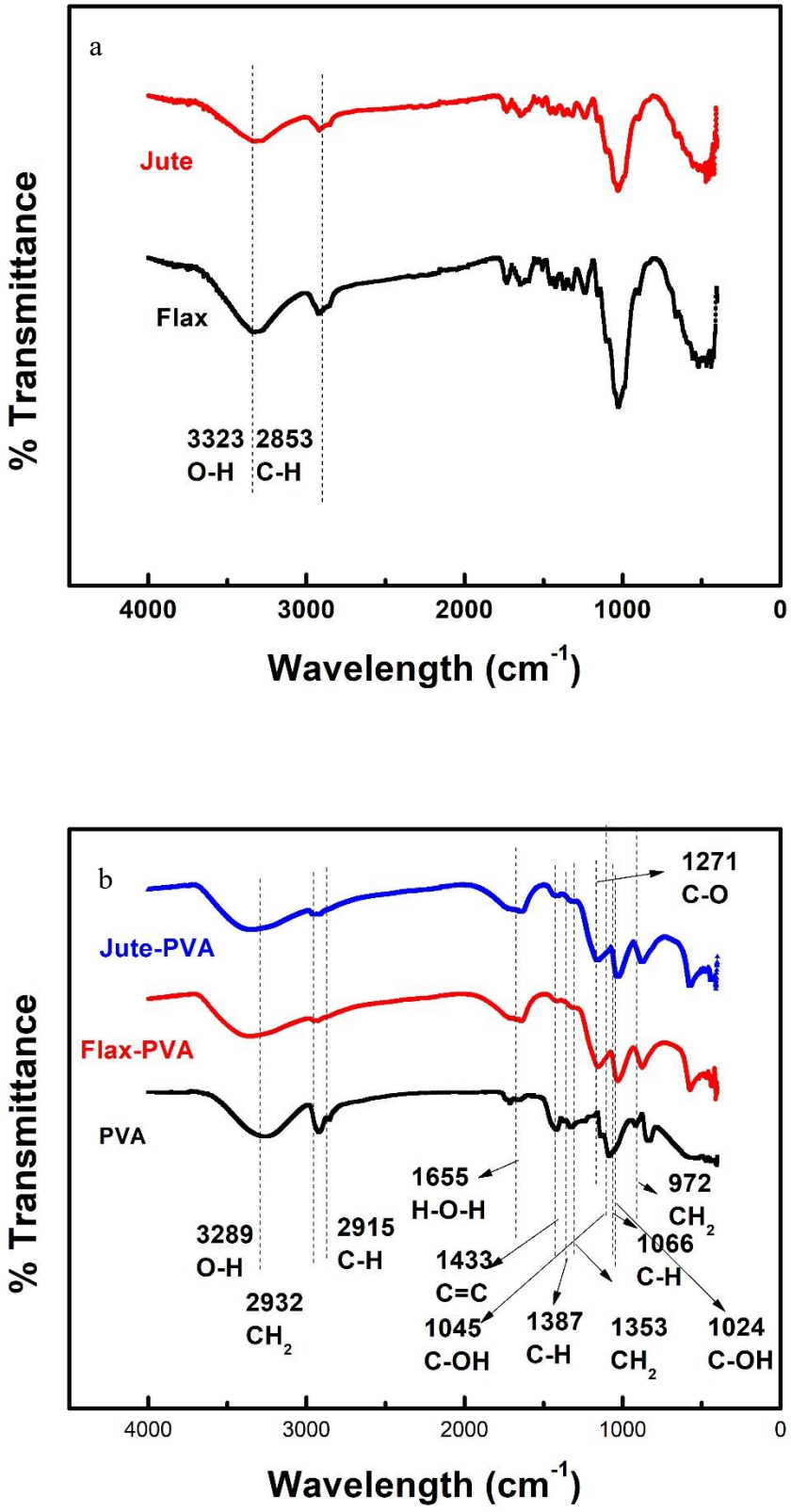


Figure 3.2. a) FITR spectra of flax and jute fiber b) FITR spectra of PVA, flax-PVA and jute-PVA

3.2.2 Morphology

The morphology of jute and flax raw fibers and the fibers after treatment were displayed by SEM. The figure shows a huge change after treatment of the fibers. The raw fibers showed very rough surface and strong bonded fibers while in the treated fibers figure, the bundle of fibers is broken into individual smaller scale fibers. Furthermore, it shows a clean and much smoother surface than untreated. It suggests that the hemicellulose and lignin are removed from the cellulose.

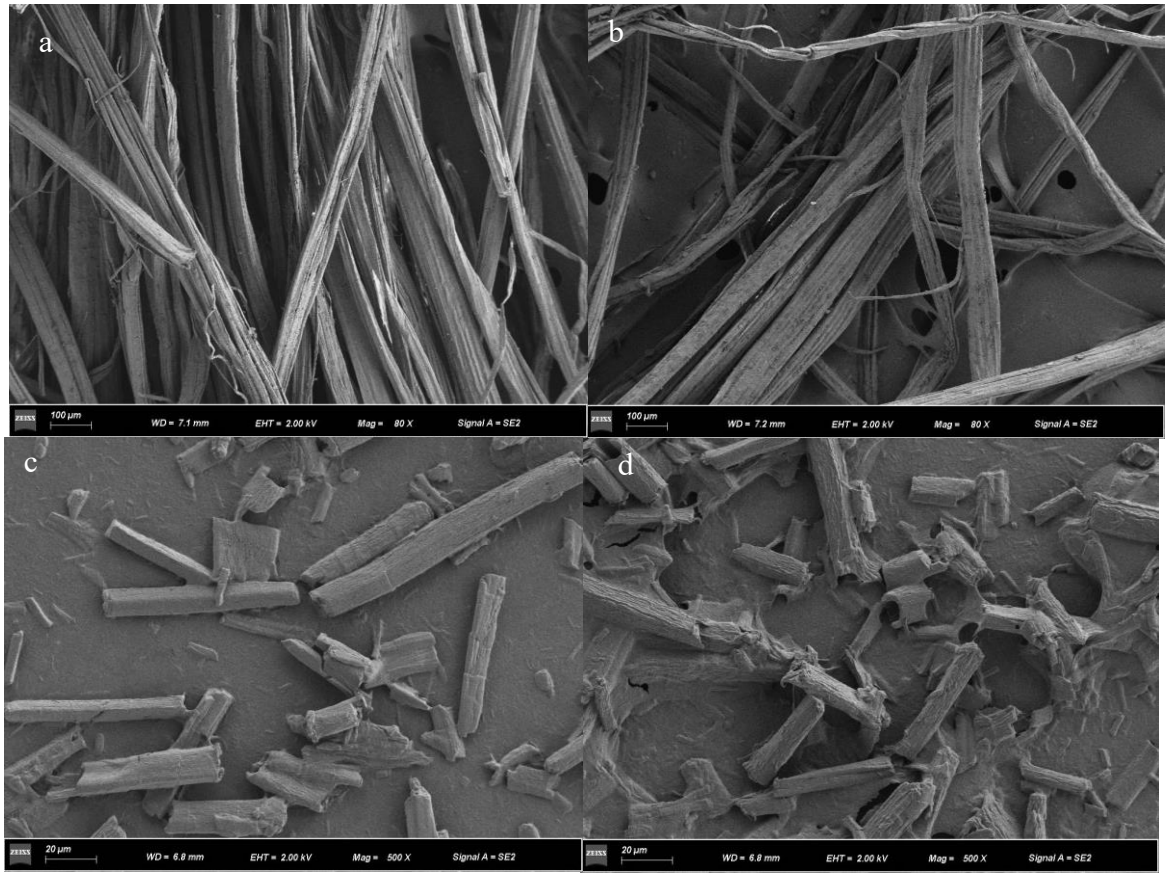


Figure 3.3. SEM of a) flax fiber b) jute fiber c)flax fiber after treatment d) jute fiber after treatment

3.2.3 UV-vis

The optical properties can be analyzed by UV-vis transmittance spectra. According to the figure, PVA film exhibits the highest transmittance among all samples in the visible

light area (90% transmittance). The film integrated with jute ranks the second and shows good transparency as well in the visible light area (79% transmittance) The reason for the decrease may be caused by the agglomeration of the cellulose when combining cellulose nanocrystals and PVA solution.[24,27] In terms of the optical properties of the flax-PVA film, it shows the worst transparency less than 60% transmittance in the visible light area.

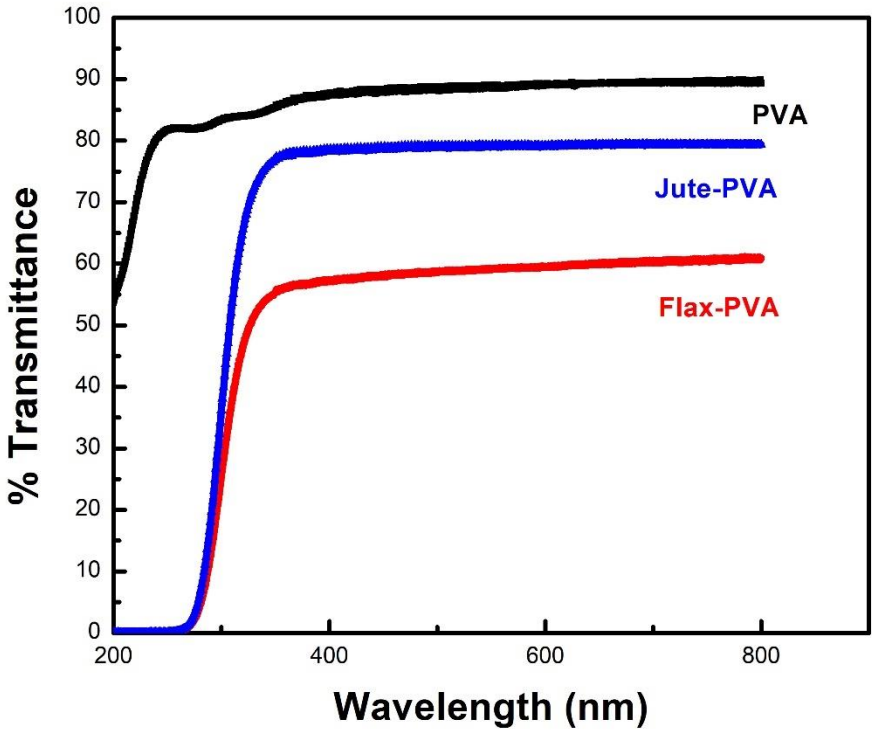
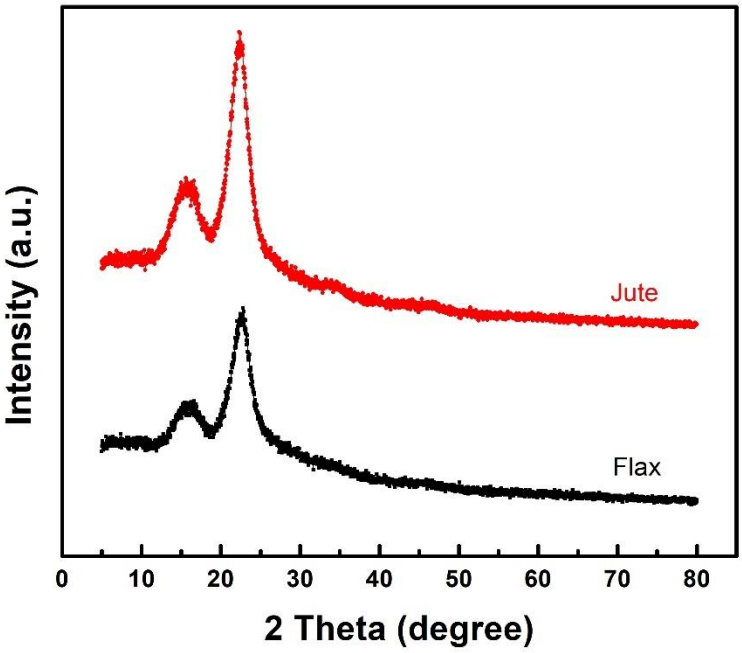


Figure 3.4. UV-vis spectra of PVA, jute-PVA, flax-PVA

3.2.4 XRD

The crystallinity could be observed by XRD analysis. In terms of the raw fibers, they display a semi-crystalline structure by the chains of the cellulose bonded by hydrogen bonds. [29] There are three reflection peaks in a), the peak at 21.6 degree represents the (200) lattice plane of hydrogen-bonded sheets. While the other peak at 14.8 and 16.3 degree is attributed to (110) and ($1\bar{1}0$) lattice plane. Compared with the composite XRD results, the peaks become much smoother than before, representing the influence

of the PVA on the composite's crystallinity. The comparison between the XRD of the cellulose and the composite shows the crystallinity decrease a lot after combining the PVA and the cellulose nanocrystals.



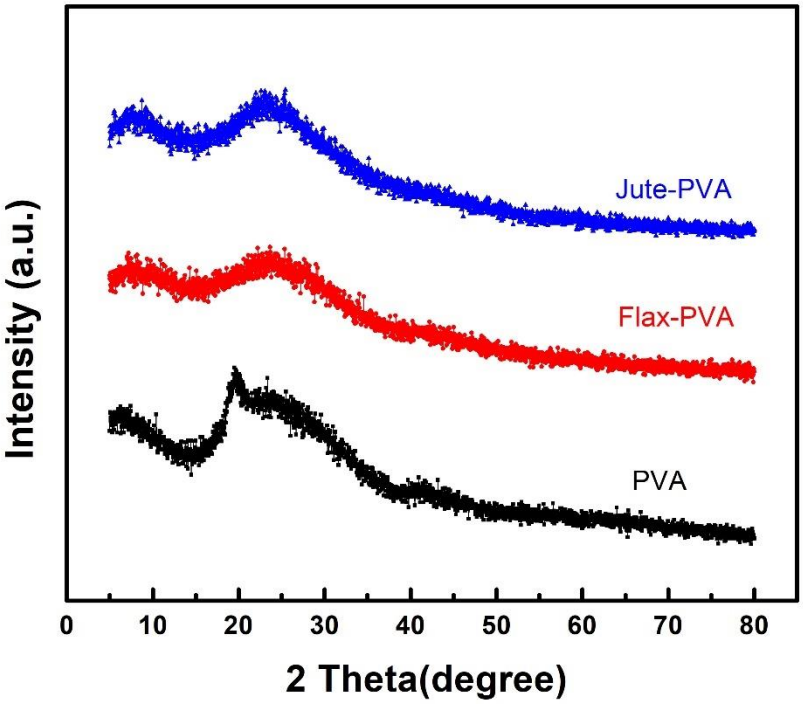


Figure 3.5. a) XRD patterns of flax and jute cellulose b) XRD patterns of PVA, flax-

PVA and jute-PVA

3.2.5 TGA

The result of TGA is depicted in Figure. According to the figure, the degradation temperature of the jute and flax are much lower than the PVA polymer. The flax and jute low degradation temperature have an effect also on the composite. The T_{onset} of PVA is about 330 ℃ while falx cellulose, jute cellulose, flax-PVA, jute-PVA's T_{onset} is about 50 ℃ due to the degradation of lignin and hemicellulose. [30]Apparent, the thermal stability improved after flax and jute cellulose were integrated with PVA. The composite of flax-PVA and jute-PVA could stand the higher temperature than the PVA films. The reason of the lower thermal stability of the cellulose nanocrystals might be the existence of the sulfate and carboxylic groups.[27,31]

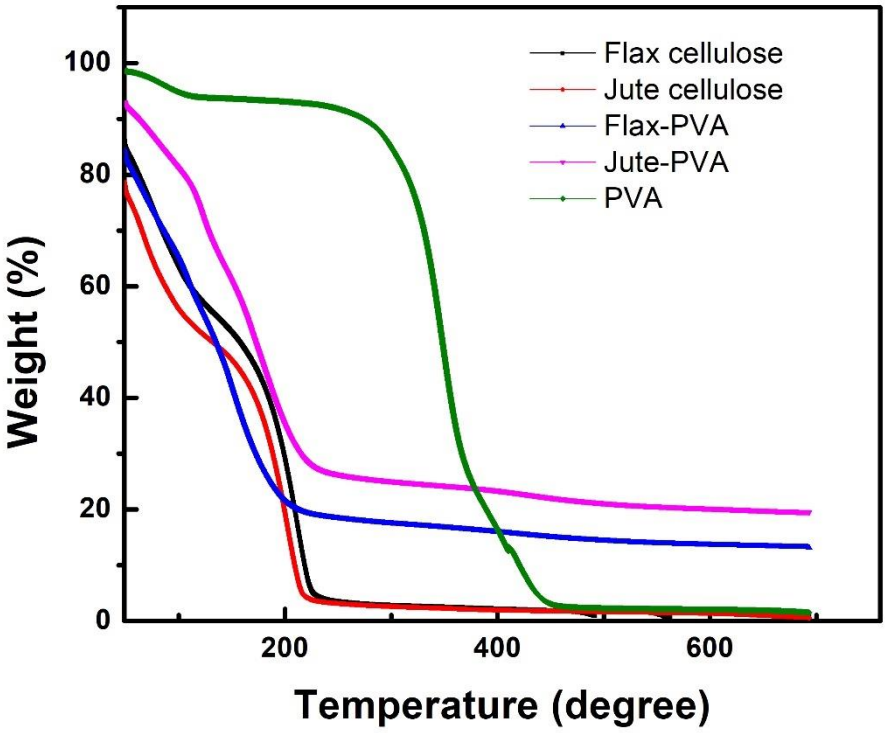


Figure 3.6. TGA of flax cellulose, jute cellulose, flax-PVA, jute-PVA and PVA

Chapter 4 Conclusion

According to the results showing above, flax and jute are available material to extract the cellulose nanocrystals and able to integrate with polymer as reinforcement. However, the source of the cellulose has impact on the performance on composite. For instance, the cellulose nanocrystals which was extracted from jute has better optical properties. However, the cellulose nanocrystals decrease the PVA's transparency. In terms of the thermal stability, the cellulose nanocrystal has a negative impact on the PVA films but jute performed better than flax in the analysis of TGA. Furthermore, the combination of PVA and cellulose nanocrystals affect the crystallinity of the composites. Above all, the cellulose nanocrystals show the difficulty when integrated with polymers which influencing the properties of the material such as crystallinity, thermal stability, transparency etc. The experiment confirms that the source of cellulose has impact on the composites' properties.

The selection of cellulose source is an important factor to optimize material's properties and the integration process is another aspect should be considered when applying when combining the cellulose and the polymers.

References

[1] Kumar, R, Rai B, Gahlyan S, Kumar G. A Comprehensive Review on Production, Surface Modification and Characterization of Nanocellulose Derived from Biomass and Its Commercial Applications[J]. Express Polymer Letters. 2021,15, 104-120.

[2] Leppanen K, Andersson S, Tokkeli M, Knaapila M, Kotelnikova N, Serimaa R. Structure of Cellulose and Microcrystalline Cellulose from Various Wood Species, Cotton and FLax Studied by X-Ray Scattering[J]. Cellulose 2009, 16, 999-1015.

[3] Tayeb A H, Amini E, Ghasemi S, Tajvidi M. Cellulose Nanomaterials—Binding Properties and Applications: A Review[J]. 2018, 23, 2684.

[4] CHEN Q, Liu Y, Chen, G. A Comparative Study on the Starch-Based Biocomposite Films Reinforced by Nanocellulose Prepared from Different Non-Wood Fibers[J]. molecules. 2019, 26, 2425-2435.

[5] Jonoobi M, Oladi R, Davoudpour Y, Oksman K, Dufresne A, Hzmzeh Y, Davoodi R. Different Preparation Methods and Properties of Nanostructured Cellulose from Various Natural Resources and Residues: A Review[J]. Cellulose. 2015, 22, 935-969.

[6] Salimi S, Sotudeh-Gharebagh R, Zarghami R, Chan S Y, Yuen K. Production of Nanocellulose and Its Applications in Drug Delivery: A Critical Review[J]. ACS: Sustainable Chemistry & Engineering. 2019, 7, 15800-15827.

[7] Habibi Y, Lucia L A, Rojas O J. Cellulose Nanocrystals: Chemistry, Self-Assembly, and Applications[J]. Chemical Reviews, 2010, 110(6): 3479–3500.

[8] Abitbol T, Rivkin A, Cao Y, Nevo Y, Abraham E, Ben-Shalom T, Lapidot S, Shoseyov O. Nanocellulose, a Tiny Fiber with Huge Applications[J]. Current Opinion in Biotechnology, 2016, 39, 76-88.

[9] Voisin H, Bergström L, Liu P, Mathew A P. Nanocellulose-Based Materials for Water Purification[J]. nanomaterial. 2017, 7, 57.

[10] Azeredo H M C, Rosa M F, Mattoso L H C. Nanocellulose in Bio-Based Food Packaging Applications[J]. Industrial Crops and Products, 2017, 97, 664-671.

[11] Fröhlich E, Roblegg E. Models for Oral Uptake of Nanoparticles in Consumer Products[J]. Toxicology. 2012, 291, 10-17.

[12] Liu L, Gao Z Y, Su X P, Chen X, Jiang L, Yao J M. Adsorption Removal of Dyes from Single and Binary Solutions Using a Cellulose-Based Bioadsorbent[J]. ACS Sustainable Chemistry & Engineering, 2015, 3, 432–442.

[13] Salah S M. Application of Nano-Cellulose in Textile[J]. Textile Science & Engineering. 2013, 3:3.

[14] Jahan M S, Saeed A, He Z, Ni Y H. Jute as Raw Material for the Preparation of Microcrystalline Cellulose[J]. Cellulose. 2011, 18, 451–459.

[15] Abraham E, Deepa B, Pothan L A, Jacob M, Thomas S, Cvelbar U, Anandjiwala R. Extraction of Nanocellulose Fibrils from Lignocellulosic Fibres: A Novel Approach[J]. Carbohydrate Polymers, 2011, 86, 1468-1475.

[16] Moran J I, Alvarez V A, Cyras V P, Vazquez A. Extraction of Cellulose and Preparation of Nanocellulose from Sisal Fibers[J]. Cellulose. 2008, 15,149-159.

[17] Krishnamachari P, Hashaikeh R, Tiner M. Modified Cellulose Morphologies and Its Composites; SEM and TEM Analysis[J]. Micron. 2011, 42, 751-761.

[18] Aloui H, Khwaldia K, Hamdi M, Fortunati E, Kenny J M, Buonocore G G, Lavorgna M. Synergistic Effect of Halloysite and Cellulose Nanocrystals on the

Functional Properties of PVA Based Nanocomposites[J]. ACS Sustainable Chemistry & Engineering, 2016, 4, 794–800.
[19] Hu X P, Mamoto R, Shimomura Y, Kimbara K, Kawai F. Cell surface structure enhancing uptake of polyvinyl alcohol(PVA) is induced by PVA in the PVA-utilizing Sphingopyxis sp. strain 113P3[J]. Arch Microbiol. 2017, 188, 235-241.
[20] Alipoori S, Torkzadeh M M. Mazinani S, Aboutalebi S H, Sharif F. Performance-tuning of PVA-based gel electrolytes by acid_PVA ratio and PVA molecular weight [J]. SN Applied Sciences. 2021, 3, 310.
[21] Zhao Y, Moser C, Lindstörm M E, Henriksson G, Li jiebing. Cellulose Nanofibers from Softwood, Hardwood, and Tunicate: Preparation–Structure–Film Performance Interrelation[J]. ACS Applied Materials & Interfaces. 2017, 9, 13508-13519.
[22] Kassab Z, El Achaby M, Tamraoui Y, Sehaqui H, Bouhfid R, Qaiss A E K. Sunflower Oil Cake-Derived Cellulose Nanocrystals: Extraction, Physico-Chemical Characteristics and Potential Application[J]. International Journal of Biological Macromolecules. 2019. 136: 241–252.
[23] Kassab Z, Boujemaoui A, Ben Youcef H, Hajlane A, Hannache H, El Achaby M. Production of Cellulose Nanofibrils from Alfa Fibers and Its Nanoreinforcement Potential in Polymer Nanocomposites[J]. Cellulose. 2019. 26, 9567–9581.
[24] Solikhin A, Murayama K. Enhanced Properties of Poly(Vinyl Alcohol) Composite Films Filled with Microfibrillated Cellulose Isolated from Continuous Steam Explosion[J]. International Journal of Plastics Technology. 2018. 22, 122–136.
[25] Bian H, Wei L, Lin C, Ma Q, Dai H, Zhu J Y. Lignin-Containing Cellulose Nanofibril-Reinforced Polyvinyl Alcohol Hydrogels[J]. ACS Sustainable Chemistry & Engineering. 2018, 6, 4821–4828.
[26] Jahan Z, Niazi M B K, Gregersen Ø W. Mechanical, Thermal and Swelling Properties of Cellulose Nanocrystals/PVA Nanocomposites Membranes[J]. Journal of Industrial and Engineering Chemistry. 2018, 57, 113–124.
[27] Kassab Z, Mansouri S, Tamraoui Y, Sehaqui H, Hannache H, Qaiss A E K, El A M. Identifying Juncus Plant as Viable Source for the Production of Micro- and Nano-Cellulose Fibers: Application for PVA Composite Materials Development[J]. Industrial Crops and Products. 2020, 144, 112035.
[28] Fortunati E, Puglia D, Luzi F, Sanruli C, Kenny J M, Torre L. Binary PVA Bio-Nanocomposites Containing Cellulose Nanocrystals Extracted from Different Natural Sources: Part I[J]. Carbohydrate Polymers. 2013, 97, 825–836.
[29] Luzi F, Fortunati E, Puglia D, Lavorgna M, Santuli C, Kenny J M, Torre L. Optimized Extraction of Cellulose Nanocrystals from Pristine and Carded Hemp Fibres[J]. Industrial Crops and Products. 2014, 56, 175–186.
[30] El Achaby M, Kassab Z, Barakat A, Aboulkas A. Alfa Fibers as Viable Sustainable Source for Cellulose Nanocrystals Extraction: Application for Improving the Tensile Properties of Biopolymer Nanocomposite Films[J]. Industrial Crops and Products. 2018, 112, 499–510.
[31] Kassab Z, Kassem I, Hannache H, Bouhfid R, Qaiss, A E K, El Achaby M. Tomato Plant Residue as New Renewable Source for Cellulose Production: Extraction of Cellulose Nanocrystals with Different Surface Functionalities[J]. Cellulose. 2020, 27(8): 4287–4303.

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