TRENDS IN SCIENCES 2022; 19(18): 5816 RESEARCH ARTICLE
https://doi.org/10.48048/tis.2022.5816

The Effects of $CaCl_2$ and Cellulose Concentrations on the Cellulose/PVA/Alginate-Based Filaments Production by Wet Spinning

Illah Sailah[*], **Farah Fahma and Ray Einstein Manuel Sihite**

Department of Agroindustrial Technology, Faculty of Agricultural Technology, IPB University
(Bogor Agricultural University), Jl. Raya Dramaga Kampus IPB Dramaga Bogor,
West Java 16680, Indonesia

([*]Corresponding author's e-mail: illahsailah@apps.ipb.ac.id)

Received: 19 June 2021, Revised: 21 August 2021, Accepted: 29 August 2021

Abstract

Cellulose as an abundantly available natural polymer can be utilized as an environmentally friendly filament material through combination with polyvinyl alcohol (PVA) and alginate. The study on cellulose/PVA/alginate composite as filament material haven not been widely reported and the effects of parameter process on the resulting filament properties still have room to be explored further. Therefore, this study focused on the effect of $CaCl_2$ and cellulose concentration on the cellulose/PVA/alginate filaments' thermal and mechanical properties. In this study, isolated cellulose from Oil Palm Empty Fruit Bunches (OPEFBs) was used as a reinforcement agent in filament production with PVA and alginate as a matrix by wet spinning in a $CaCl_2$ solution as the coagulant solvent. The prepared dopes of cellulose/PVA/alginate at 5, 10 and 15 % cellulose concentration were spun using a syringe pump into 5 and 13 % $CaCl_2$ coagulation bath. Subsequently, the resulting filaments' mechanical and thermal properties were tested. The crystallinity and thermal stability of the filaments coagulated in 13 % $CaCl_2$ were higher than those of in 5 % $CaCl_2$. However, the tensile strength of the filament produced showed just the opposite. Cellulose concentration increase resulted in filament with improved thermal stability and tensile strength, and higher crystallinity. Concisely, higher $CaCl_2$ and cellulose concentration enhanced the filament thermal properties but higher $CaCl_2$ concentration led to filament mechanical property depression contrast to cellulose which higher concentration led to mechanical property increase. Filament has potential application in 3D printing for various application, especially filament with biodegradable, biocompatible, and enhanced mechanical property is potential for particular application such as biomedical applications as a surgical thread or biodegradable scaffold.

Keywords: Cellulose, Filaments, Oil palm empty fruit bunches, Wet spinning

Introduction

Cellulose is a homopolymer of anhydroglucose units-consisted polysaccharide that is abundant and has many advantages. Due to its unique properties in renewability, biodegradability, and excellent properties, cellulose can be widely used to produce various valuable products. The excellent properties provided by cellulose made this material become a great interest of many researchers. Nakagaito *et al.* [1] was looking for the potential of reinforcing polylactic acid instead of a single reinforcement step by mixing cellulose and chitin nanofibers, and Cazón *et al.* [2] developed cellulose-polyvinyl alcohol-glycerol films with a UV protective effect that significant to prevent lipid oxidative oxidation in food packaging. The effect was mainly due to the formation of strong hydrogen bonding in its structure, which resulted in better mechanical and thermal properties [3,4].

One of the promising cellulose sources is OPEFBs, solid waste as a by-product of crude palm oil (CPO) extraction. In 2019, Indonesia produced CPO approximately was 48.4 million tons [5], which resulted in a high amount OPEFBs. About 230 Kg of OPEFBs will be produced during processing 1 ton of fresh palm oil bunches [6]. Generally, OPEFBs contain 43 - 65 % cellulose, followed by hemicellulose (17 - 33 %) and lignin (13 - 37 %) [7]. Because of the high cellulose content with abundant availability, OPEFBs is a great resource to produce cellulose and polymer-based products.

Polymers have been produced in great quantity and variety to make polymer-based product of various field such as film packaging, solid molded form for atuomobile body parts, fiber for clothing and carpets and many more. However, 1 kind of polymer alone might lack in properties suitable for some applications. In order to create a polymer material with characteristics desired for a certain product application, the polymer is reinforced with other component resulting enchanced mechanical performance, and/or new functionalities, which is also known as composites [8]. Two or more component can be combined to form composite through polymer blending.

Polymer blending is a material development method to produce new material with enhanced or modified physicochemical properties by a physical mixture of structurally different polymers or copolymers. The polymers will interact with each other by force with no covalent bonding, such as dipole-dipole forces, hydrogen bonding, and charge-transfer complexes for homopolymer mixtures. The interaction, particularly hydrogen bonding, affect the properties of a material or its molecular characteristic. Among noncovalent bonds, the strength of van der Waals attraction is on the order of 0.2 kcal/mol, whereas hydrogen bond is relatively stronger, lying in the range between 1 to 10 kcal/mol depending on the nature of solvent employed. Hydrogen bond in polymer blends is an interesting subject of many scientists as it usually enhances miscibility of the blend which leads to change in mechanical and thermal properties, particularly the glass transition temperature (T_g), melting temperature, and crystallization behavior. The presence of hydrogen bond in a polymer increases the glass transition temperature, lowers the melting temperature, and suppresses crystallization of a crystalline component [9]. Through polymer blending, such characteristics which are potentially beneficial for many applications can be achieved. Hence, polymer blending has been an attraction in scientific and industrial fields [10].

In this study PVA and sodium alginate were used as matrix and cellulose was used as reinforcing material to produce filaments. PVA and sodium alginate are a widely used semi-crystalline polymer with biodegradability, biocompatibility, good flexibility, and the ability to form fibrous materials [3,10]. Hydroxyl groups of PVA tend to form inter and intramolecular hydrogen bonding with other polymers [11]. Sodium alginate is a linear polymer of 1,4-linked β-D-mannuronate (M) and α-L-guluronate (G) residues arranged in different M/G ratios. Alginate is a non-toxic, biocompatible, and gel-forming polymer. The aqueous alginate solution is immediately converted into gel due to divalent cations, Ca^{2+} from $CaCl_2$ solution. Ca^{2+} cations and G-block regions' binding will form the "egg-box" junction zone [12]. Therefore, as environmentally friendly materials, cellulose/PVA/alginate blend become potential subtitute for commonly used petroleum-based polymers which application has risen environmental problems.

The filament is one of the polymer-based products used widely in various applications, especially in textiles and biomedical productions. There have been numerous studies of PVA/alginate filament, but study on cellulose-reinforced PVA/alginate for filament has not been widely reported. As a composite comprising biocompatible materials, cellulose/PVA/alginate filament possess high potential in biomedical application. Yunus *et al.* [13] reported the biomedical use of filament that was successfully produced from PVA/cellulose-based for surgical thread, utilizing cellulose isolated from OPEFBs.

Various spinning techniques produce the filaments, including dry spinning, wet spinning, dry-wet spinning, and melt spinning. The selection of spinning technique is determined by types of polymer, solidification process (cooling, evaporation of the solvent, or precipitation in anti-solvent) and spinnability. A petroleum-derived polymer, such as polyethylene, polyamide, polyester and polypropylene, is typically melt-spun with high temperature and pressure to produce filaments. Dry spinning was usually conducted for polymers that can be dissolved in a volatile solvent. In dry spinning, the dissolved solution, called dope, will be contacted with the hot stream to evaporate the solvent and solidify it into filaments. Wet spinning is a spinning process in which the spinning dope is immersed and coagulated into the non-solvent solution [14,15].

Wet spinning is used in this study as cellulose/PVA/alginate composite that contain natural polymer is suceptible to thermal degradation if processed with other techniques. This technique typically uses $CaCl_2$ to crosslink alginate thus coagulating the extruded spinning dope into insoluble filament, and cellulose acts as reinforcing material that enhance wet spun of PVA/alginate fibre mechanical and liquid absorption capability [16]. Raus *et al.* [16] reported enchanced tenacity and elongation properties of cellulose/alginate composite produced with wet spinning techniques at 2 % cellulose nanocrystal content, and 5 % $CaCl_2$ coagulation bath [16]. The contribution of $CaCl_2$ and cellulose concentration on composite properties enhancement can be explored further. Therefore, this study investigated the effect of $CaCl_2$ and cellulose concentration on produced filaments' crystallinity index, thermal stability, tensile strength and elongation at break.

Materials and methods

Materials

OPEFBs were sourced from PT Inti Indosawit Subur (palm oil plantation and mills), Riau, Indonesia. PVA (Merck Inc., Germany), NaOH, sodium alginate (HiMedia, India), $CaCl_2$ and H_2O_2 (commercial-grade product) were used as received without any further purification.

Isolation of cellulose from OPEFBs

Isolation of cellulose was conducted as described in a previous study by Arnata *et al*. [17] with modifications. First, 50 g of dried OPEFBs was delignified in 1,000 mL of 10 % NaOH solution for 90 min at ± 95 °C, then washed with distilled water until the pH was neutral. Afterward, delignified fibers were bleached in 30 % H_2O_2 at ± 95 °C for 60 min, followed by washing with distilled water until neutral. The fibers were then bleached in the mixture of alkaline peroxide solution (10 % NaOH and 30 % H_2O_2 solutions in a 1:2 (v/v) ratio) to produce white cellulose. Then, cellulose was diluted using distilled water to a concentration of 2 % and was suspended using a blender for 5 min. Ultrasonication at an amplitude of 80 % for 30 min was used to produce a homogeneous cellulose suspension. The isolated cellulose was reinforced into PVA/alginate matrix for filament production.

Preparation of the spinning dopes

The basis of the sample for the preparation of the spinning dope is 4 g of dry matter consisting of a mixture of cellulose, PVA, and alginate, dissolved in 100 g of distilled water. The formulation of the spinning dope was as follows: PVA and alginate (1:1) and cellulose (0, 5, 10 and 15 wt%). Alginate was added to the cellulose in distilled water and stirred at 1400 rpm until homogeneous. Afterward, PVA was added to the mixture and stirred at 90 °C and 1,500 rpm for 40 min. Homogenous suspensions were degassed by stirring at a low speed of 200 rpm for 5 min to remove the air bubbles produced. Filaments with the addition of cellulose 0, 5, 10 and 15 % were coded as C0, C5, C10 and C15, respectively.

Wet spinning process

The prepared dopes were then wet spun using a 10 mL syringe pump into 5 and 13 % $CaCl_2$ coagulation baths. The spinning rate was set at 0.33 mL/s. The filaments were coagulated for 10 min, followed by washing in distilled water, then were dried at 55 °C for 30 min. Filaments dipped in 5 and 13 % CaCl2 were coded K5 and K13, respectively.

Characterizations

The morphology of filaments was analyzed by scanning electron microscope (SEM) EDX EVO MA10, operating at 20.0 kV. The sample was put on the grid and coated with platinum (Pt) before analysis.

The thermal stability of cellulose/PVA/alginate-based filaments was observed by thermogravimetric analysis (TGA). The TGA thermograms of all samples were recorded using Perkin Elmer TGA4000 at 25 to 500 °C, under a nitrogen atmosphere (20.0 mL/min flow rate).

An X-ray diffractometer (XRD) analysis was conducted to identify the crystallinity index of all samples. The samples were cut into 1 - 2 mm long and placed on the holder. The samples were observed using Shimadzu XRD7000 at a voltage of 40.0 kV and a current of 30 mA. The diffraction patterns were scanned at $2\theta = 10°$ to $80°$. The crystallinity of samples can be found by dividing the area under the crystalline diffraction peaks by the curve's total area.

Mechanical characteristics (including tensile strength and elongation at break) of cellulose/PVA/alginate-based filaments were analyzed by tensile test using Instron 3369 series at room temperature. A single filament was cut into 50 mm long and pre-conditioned for 1 day at room temperature before analysis. The analysis was carried out at a crosshead speed of 5 mm/min for 3 repetitions. The value of tensile strength and elongation at break were determined with following formula (ASTM D2256-80):

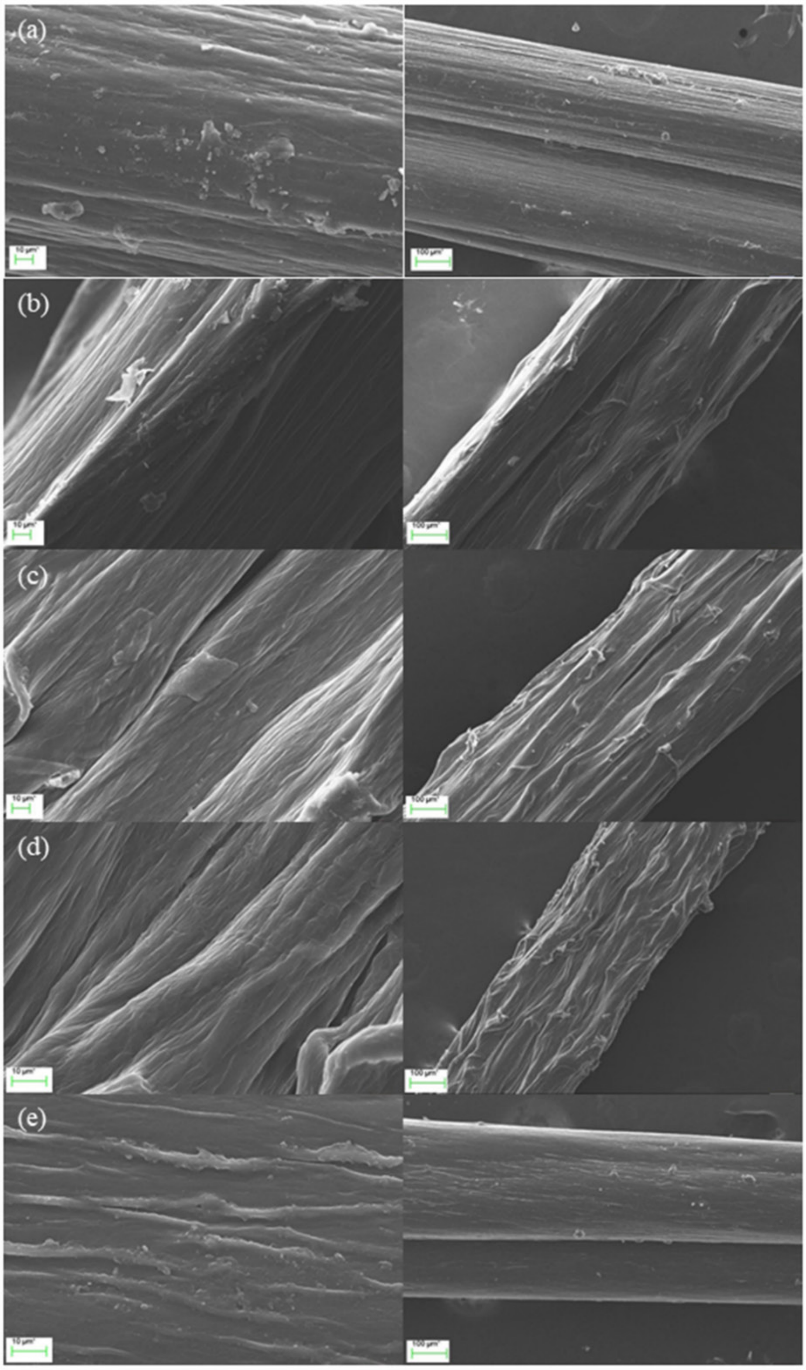
$$\text{Tensile strength (kgf/mm}^2\text{)} = \frac{Maximum\ force\ at\ break\ (kgf)}{Cross\ sectional\ area\ (mm^2)} \tag{1}$$

$$\text{Elongation at break (\%)} = \frac{length\ extended\ at\ breaking\ point - initial\ length}{initial\ length} \times 100 \tag{2}$$

Results and discussion

Morphology of cellulose and cellulose/PVA/alginate-based filaments

The diameter of filaments was 550 ± 71.27 µm. The surface morphology and the real image of cellulose/PVA/alginate-based filaments are presented in **Figures 1** and **2**, respectively. The figures showed that a "mirror" like surface was observed in the filaments with no cellulose addition. Meanwhile, the filaments' surface became rougher and crinkled following the increase of cellulose concentration. The condition might be due to the formation of the filaments' entangled network after incorporating cellulose [18]. However, it was found that the 2 different concentrations of $CaCl_2$ were similar (**Figures 1**(**a**) and **1**(**e**)). Li *et al.* reported that the distribution of calcium elements throughout the matrix was not affected by the concentration of $CaCl_2$ in the crosslinking bath. This might be because Ca^{2+} is much smaller in size than large polymer molecules and can diffuse into the alginate matrix during crosslinking time [19].



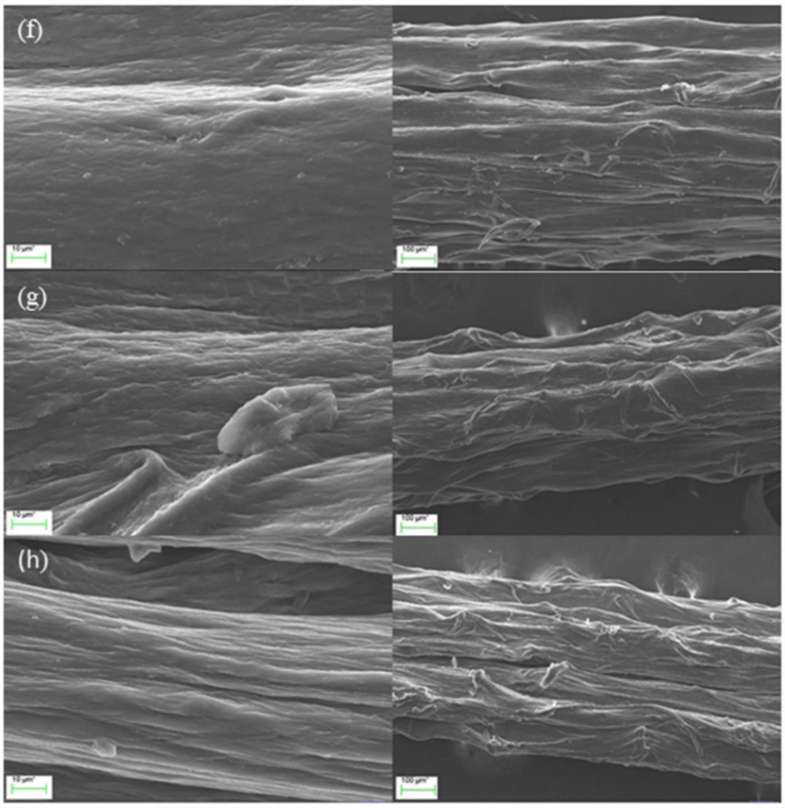


Figure 1 SEM images of cellulose/PVA/alginate filaments' surface with magnification of 1,000× (left) and 100× (right): (a) C0K5, (b) C5K5, (c) C10K5, (d) C15K5, (e) C0K13, (f) C5K13, (g) C10K13 and (h) C15K13.

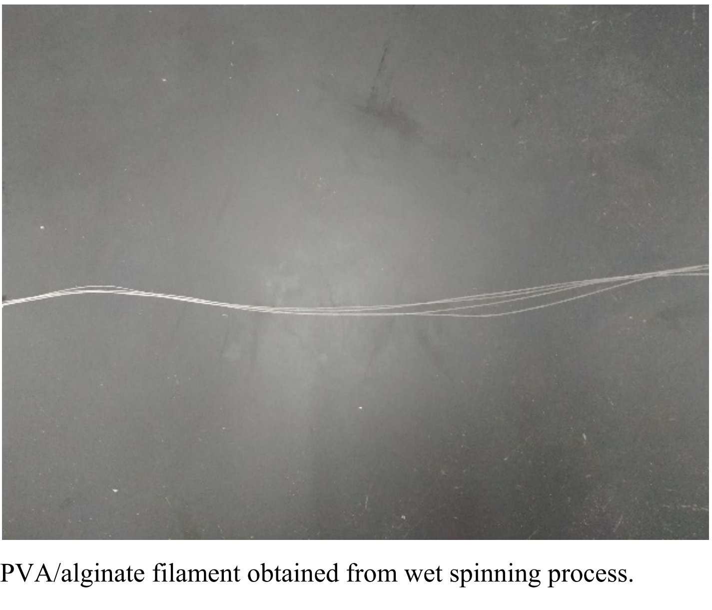


Figure 2 Cellulose/PVA/alginate filament obtained from wet spinning process.

Crystallinity

The XRD diffractograms of cellulose/PVA/alginate-based filaments are illustrated in **Figure 3**. Cellulose had 3 characteristic diffraction peaks, which were detected in 2θ = 15.2°, 16.5° and 22.8°, indicating the characteristic peaks of cellulose type I [20]. PVA exhibited a high-intensity peak at 2θ = 19.5°, which indicated the semi-crystalline structure of PVA due to the high hydrogen bonding of its hydroxyl groups [21]. Another small peak was also detected at 2θ = 41°. Wang *et al.* [22] stated that alginate exhibited 2 crystalline peaks at 2θ = 13.7° and 23.0°.

The characteristic peaks of cellulose at 2θ = 22.7° and PVA at 2θ = 19.6° were detected in the XRD patterns of filaments. The intensity of the characteristic peak of cellulose at 2θ = 22.7° was increased following the increasing cellulose concentration and the filaments' crystallinity index (**Table 2**). This effect was most likely due to strong hydrogen bonds forming between the cellulose and the PVA/alginate matrix, facilitating crystallization of cellulose/PVA/alginate composite [23,24].

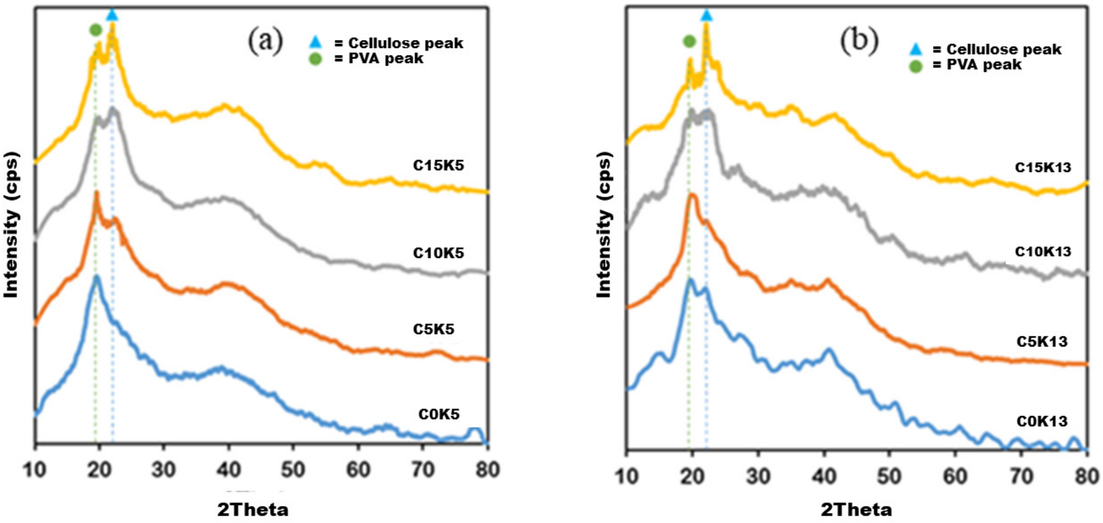


Figure 3 XRD diffractograms of cellulose/PVA/alginate based filaments in (a) 5 % of $CaCl_2$ and (b) 13 % of $CaCl_2$ solutions.

$CaCl_2$ concentrations also influenced the filaments' crystallinity index. It was found that the increase of $CaCl_2$ concentrations led to the increasing filaments' crystallinity (**Table 2**). The interaction between sodium alginate and calcium chloride increased the crystallinity of sodium alginate. Crystallinity increased when the content of Ca+ ions increased [25].

Table 2 The crystallinity index of cellulose/PVA/alginate-based filaments.

Sample	The crystallinity index (%)	
	K5	K13
C0	24.0 ± 1.2	24.3 ± 1.5
C5	33.7 ± 0.9	38.5 ± 1.1
C10	35.3 ± 1.1	39.2 ± 1.3
C15	46.6 ± 1.4	50.3 ± 1.2

Notes: K5 and K13 are the spun samples using a 10 mL syringe pump into 5 and 13 % of $CaCl_2$ coagulation baths, respectively. C0, C5, C10 and C15 denote the sample with the concentration of cellulose 0, 5, 10 and 15 %, respectively.

Thermal properties

Figure 4 shows TGA and its first derivatives (DTG) curves of filaments. As seen from the figures, all samples exhibited 3 stages of weight loss. At below 200 °C (X), the weight loss mainly occurred due to water loss caused by evaporation and partial glycosidic bond destruction. Then, 2nd weight loss occurred at 200 - 400 °C (Y), principally related to the further destruction of the glycosidic bond through dehydration reactions and led to intermediate products' formation. The last stage of weight loss occurred at 400 - 500 °C, which corresponded to the oxidation of formerly intermediate carbonaceous matter [26,27].

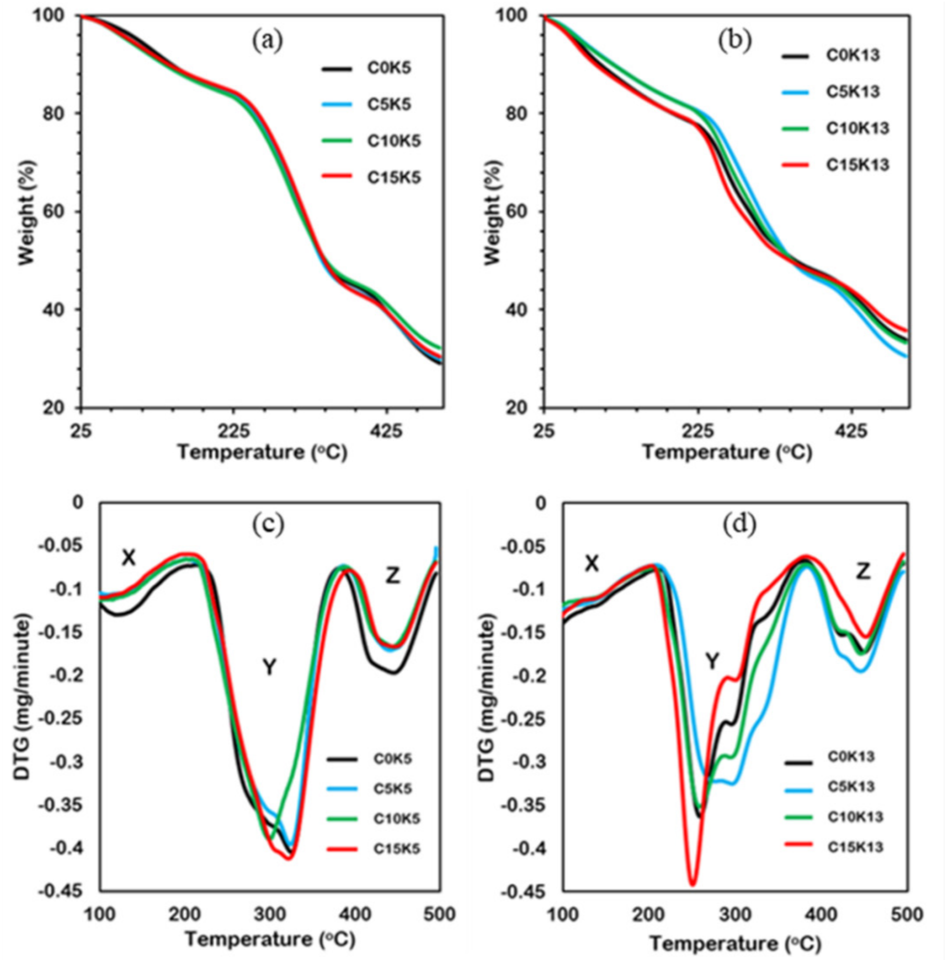


Figure 4 Thermal properties of cellulose/PVA/alginate based filaments: (a and b) TGA and (c and d) DTG curves of filaments in (a and c) 5 % of $CaCl_2$ and (b and d) 13 % of $CaCl_2$ solutions.

After that, the increase of cellulose and $CaCl_2$ concentrations increased char residue at 500 °C (**Table 3**) and increased the filament's thermal stability. The increasing cellulose concentrations resulted in the solid hydrogen bonding of cellulose and PVA/alginate matrix. However, cellulose up to 15 % in C15K5 filament resulted in the decrement of char residues. It might happen because the cellulose was agglomerated and not well dispersed; thus, only a few sides of cellulose fibers were entangled with the matrix [28].

Table 3 Char residue of cellulose/PVA/alginate-based filaments at 500 °C.

Sample	Char residue at 500 °C (%)	T_{max}	Weight lost at T_{max} (%)
C0K5	29.1	330.21	54.19
C5K5	30.0	329.73	53.83
C10K5	32.3	297.12	65.25
C15K5	30.5	323.14	57.50
C0K13	33.9	261.72	68.41
C5K13	30.6	265.63	72.63
C10K13	33.3	261.56	70.87
C15K13	35.8	250.92	69.16

Notes: K5 and K13 are the spun samples using a 10 mL syringe pump into 5 and 13 % of $CaCl_2$ coagulation baths, respectively. C0, C5, C10 and C15 denote the sample with the concentration of cellulose 0, 5, 10 and 15 %, respectively.

Besides, $CaCl_2$ is known as an inorganic compound that is associated with higher ash content. Thus, the increase of $CaCl_2$ concentrations resulted in the increase of char residues at 500 °C. The higher Ca^{2+} ions allowed increasing the total of alginate strands and build thicker "egg-box" junctions, which resulted in a more robust network and excellent thermal stability [29]. However, when $CaCl_2$ concentration increased up to 13 %, the C0 filament had higher char residue than the C5 filament. This condition might be caused by a more saturated $CaCl_2$ solution that led to the deposition of $CaCl_2$ compounds in the filament.

Mechanical properties

As seen from **Figure 5**, the tensile strengths of filaments for both $CaCl_2$ concentrations were gradually increased, following the cellulose content. The addition of cellulose improved the mechanical properties of filaments due to the formation of the rigid network by hydrogen bonding of cellulose and PVA/alginate matrix [26].

Meanwhile, the increase of $CaCl_2$ concentration from 5 to 13 % resulted in decreased filaments' tensile strength. According to Cuadros *et al.* [30], the tensile strength of filaments increased with increasing Ca^{2+} concentration up to a certain point and decreased when it exceeded the point. Based on **Figure 5(a)**, the concentration of 5 % $CaCl_2$ is a point of the maximum tensile strength of filaments. It might indicate achieving the optimum number and size of binding sites in alginate gels. This decrease might occur because the system reversed to dimers' formation with no association between dimers of alginate, which previously had the formation of inter-chain associations.

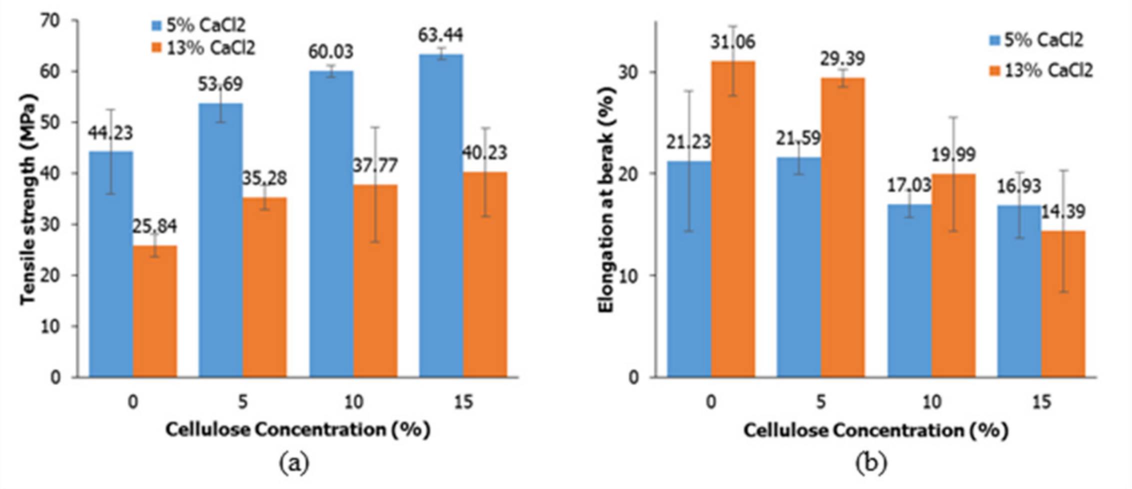


Figure 5 Mechanical properties of cellulose/PVA/alginate based filaments: (a) Tensile strength and (b) Elongation at break.

Furthermore, Ca^{2+} cations will only partially fill the G-blocks. For that reason, the crystallinity and thermal stability increase at a higher concentration of $CaCl_2$ [31]. Mao *et al.* [4] studied the effect of coagulant concentrations on the properties of regenerated cellulose filaments. They stated that decrease of filaments' tensile strength in the higher coagulant concentration might happen because the coagulation process was too fast, thus caused severe condensing and frail [4]. This condition could answer to the decrement of tensile strength in 13 % of $CaCl_2$. It also found that the formation of strong hydrogen bonding is due to the increasing cellulose concentration, which made the filaments stiffer and decremented the filaments' elongation at break (**Figure 5(b)**). Besides, PVA is a polymer with flexibility, so at higher PVA concentration, the filaments were more elastic and had higher elongation at break value [32].

Conclusions

Cellulose was successfully isolated from OPEFBs and reinforced into PVA/alginate matrix. Homogenous suspensions of cellulose, PVA, and alginate were also successfully wet spun into filaments. SEM analysis showed that cellulose's addition caused the filaments' surface to become rougher, which indicated the dispersion of cellulose in the PVA/alginate matrix. Tensile test, XRD and TGA analysis show that cellulose concentration improved tensile strength, crystallinity index, and filaments' thermal stability. These might be due to the strong hydrogen bonding of cellulose and PVA/alginate matrix, which led to a tight network formation.

It also found that the increasing of $CaCl_2$ concentrations led to the increasing of the filaments' crystallinity index and thermal stability. It might be caused by Ca^{2+} cations, which partially filled the G-blocks, so thicker "egg-box" junctions were formed and affected a high crystallinity index and excellent thermal stability. The increasing of Ca^{2+} cations induced junction points in the polymer network and tight crystalline structure. $CaCl_2$ as an inorganic compound also played a role in increasing char residues that were observed at 500 °C. However, the $CaCl_2$ concentration from 5 to 13 % resulted in the decrement of the filaments' tensile strength because it exceeded its saturation point.

Acknowledgements

This work was supported by Riset Kolaborasi Indonesia - WCU (World Class University) 2018 (Contract no. 0760/IT3.11/PN/2018).

References

[1] AN Nakagaito, S Kanzawa and H Takagi. Polylactic acid reinforced with mixed cellulose and chitin nanofibers: Effect of mixture ratio on the mechanical properties of composites. *J. Compos. Sci.* 2018; **2**, 36.

[2] P Cazón, G Velazquez and M Vázquez. Novel composite films from regenerated cellulose-glycerol-polyvinyl alcohol: Mechanical and barrier properties. *Food Hydrocoll.* 2019; **89**, 481-91.

[3] F Fahma, N Hori, S Iwamoto, T Iwata and A Takemura. PVA nanocomposites reinforced with cellulose nanofibers from oil palm empty fruit bunches (OPEFBs). *Emir. J. Food Agr.* 2017; **29**, 323-9.

[4] Y Mao, L Zhang, J Cai, J Zhou and T Kondo. Effects of coagulation conditions on properties of multifilament fibers based on dissolution of cellulose in NaOH/urea aqueous solution. *Ind. Eng. Chem. Res.* 2008; **47**, 8676-83.

[5] Badan Pusat Statistik. *Statistik kelapa sawit Indonesia*. Badan Pusat Statistik, Jakarta, Indonesia, 2019.

[6] N Hidayah and IU Wusko. Characterization and analysis of oil palm empty fruit bunch (OPEFB) waste of PT Kharisma Alam Persada South Borneo. *Trad. Med. J.* 2020; **25**, 152-8.

[7] M Yahya, HV Lee, SK Zain and SBA Hamid. Chemical conversion of palm-based lignocellulosic biomass to nano-cellulose: Review. *Polym. Res. J.* 2015; **9**, 385-406.

[9] SW Kuo. Hydrogen-bonding in polymer blends. *J. Polym. Res.* 2008; **15**, 459-86.

[8] SD Lala, AB Deoghare and S Chatterjee. Effect of reinforcements on polymer matrix bio-composites - an overview. *Sci. Eng. Compos. Mater.* 2018; **25**, 1039-58.

[10] YJ Lee, DS Shin, OW Kwon, WH Park, HG Choi, YR Lee, SS Han, SK Noh and WS Lyoo. Preparation of atactic poly(vinyl alcohol)/sodium alginate blend nanowebs by electrospinning. *J. Appl. Polym. Sci.* 2007; **106**, 1337-42.

[11] F Fahma, Sugiarto, TC Sunarti, SM Indriyani and N Lisdayana. Thermoplastic cassava starch PVA composite films with cellulose nanofibers from oil palm empty fruit bunches as reinforcement agent. *Int. J. Polym. Sci.* 2017; **2017**, 2745721.

[12] D Dechojarassri, S Omote, K Nishida, T Omura, H Yamaguchi, T Furuike and H Tamura. Preparation of alginate fibers coagulated by calcium chloride or sulfuric acid: Application to the adsorption of Sr^{2+}. *J. Hazard. Mater.* 2018; **355**, 154-61.

[13] M Yunus, F Fahma, Z Abidin, D Noviana, RR Mukti and A Kusumaatmaja. Cellulose based surgical threads from oil palm empty fruit bunches in wound healing on male wistar rats. *Indian Vet. J.* 2019; **96**, 21-3.

[14] C Clemons. Nanocellulose in spun continuous fibers: A review and future outlook. *J. Renew. Mater.* 2016; **4**, 327-39.

[15] MJ Lundahl, V Klar, L Wang, M Ago and OJ Rojas. Spinning of cellulose nanofibrils into filaments: A review. *Ind. Eng. Chem. Res.* 2017; **56**, 8-19.

[16] RA Raus, WMFW Nawawi and RR Nasaruddin. Alginate and alginate composites for biomedical applications. *Asian J. Pharm. Sci*. 2021; **16**, 280-306.

[17] IW Arnata, Suprihatin, F Fahma, N Richana and TC Sunarti. Cellulose production from sago frond with alkaline delignification and bleaching on various types of bleach agents. *Orient. J. Chem.* 2019; **35**, 8-19.

[18] J Liu, R Zhang, M Ci, S Sui and P Zhu. Sodium alginate/cellulose nanocrystal fibers with enhanced mechanical strength prepared by wet spinning. *J. Eng. Fibers Fabr.* 2019; **14**, 155892501984755.

[19] J Li, Y Wu, J He and Y Huang. A new insight to the effect of calcium concentration on gelation process and physical properties of alginate films. *J. Mater. Sci.* 2016; **51**, 5791-801.

[20] AP Mathew, A Chakraborty, K Oksman and M Sain. The structure and mechanical properties of cellulose nanocomposites prepared by twin screw extrusion. *ACS Symp. Ser.* 2006; **938**, 114-31.

[21] S Mallakpour and M Dinari. Enhancement in thermal properties of poly(vinyl alcohol) nanocomposites reinforced with Al_2O_3 nanoparticles. *J. Reinf. Plast. Compos.* 2013; **32**, 217-24.

[22] Q Wang, X Hu, Y Du and JF Kennedy. Alginate/starch blend fibers and their properties for drug controlled release. *Carbohydr. Polym.* 2010; **82**, 842-7.

[23] JA Sirviö, A Kolehmainen, H Liimatainen, J Niinimäki and OEO Hormi. Biocomposite cellulose-alginate films: Promising packaging materials. *Food Chem.* 2014; **151**, 343-51.

[24] G Yang, L Zhang, T Peng and W Zhong. Effects of Ca^{2+} bridge cross-linking on structure and pervaporation of cellulose/alginate blend membranes. *J. Membr. Sci.* 2000; **175**, 53-60.

[25] AGSD Laia, EDSC Júnior and HDS Costa. A study of sodium alginate and calcium chloride interaction through films for intervertebral disc regeneration uses. *In*: Proceedings of the 21º CBECIMAT - Congresso Brasileiro de Engenharia e Ciência dos Materiais, Cuiabá, MT, Brazil. 2014, p. 7341-8.

[26] EH Qua, PR Hornsby, HSS Sharma, G Lyons and RD McCall. Preparation and characterization of poly(vinyl alcohol) nanocomposites made from cellulose nanofibers. *Appl. Polym. Sci.* 2009; **113**, 2238-47.

[27] J Zhang, Q Ji, X Shen, Y Xia, L Tan and Q Kong. Pyrolysis products and thermal degradation mechanism of intrinsically flame-retardant calcium alginate fibre. *Polym. Degrad. Stab*. 2011; **96**, 936-42.

[28] YW Chen, TH Tan, HV Lee and SBA Hamid. Easy fabrication of highly thermal-stable cellulose nanocrystals using $Cr(NO_3)_3$ catalytic hydrolysis system: A feasibility study from macro- to nano-dimensions. *Materials* 2017; **10**, 42.

[29] GC Fontes, VMA Calado, AM Rossi and MHMD Rocha-Leão. Characterization of antibiotic-loaded alginate-osa starch microbeads produced by ionotropic pregelation. *BioMed Res. Int.* 2013, **2013**, 472626.

[30] TR Cuadros, O Skurtys and JM Aguilera. Mechanical properties of calcium alginate fibers produced with a microfluidic device. *Carbohydr. Polym.* 2012; **89**, 1198-206.

[31] NE Simpson, CL Stabler, CP Simpson, A Sambanis and I Constantinidis. The role of the $CaCl_2$-guluronic acid interaction on alginate encapsulated βTC3 cells. *Biomaterials* 2004; **25**, 2603-10.

[32] SH Cho, SM Lim, DK Han, S Yuk, GI Lim and JH Lee. Time-dependent alginate/polyvinyl alcohol hydrogels as injectable cell carriers. *J. Biomater. Sci. Polym. Ed.* 2009; **20**, 863-76.