



Reinforced bioplastic film at different microcrystalline cellulose concentration

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ABSTRACT

Plastic pollution has led to the development of bioplastic to replace conventional petroleum-based plastic. It has received attention and interest from many researchers due to the global issues of plastic pollution. The formulation to synthesize the bioplastic film has been established throughout the years with the incorporation of renewable sources such as starch, cellulose, plasticizer and several other additives to obtain a high quality bioplastic film. This study formulated a biocomposite using carrageenan, microcrystalline cellulose (MCC), polyethylene glycol (PEG), glyoxylic acid and hydroxypropyl methylcellulose (HPMC) to produce bioplastic films reinforced from a renewable resource. The percentage of MCC was manipulated through the study to observe the strength of the film obtained with the increasing percentage of MCC. The film was cast onto the stainless steel plate and left to dry for 3 h at 60 °C. The results demonstrated that the highest value of tensile strength is 20.74 MPa at 1% of MCC addition. Besides that, the value of moisture content increased with the increasing percentage of MCC which is 16.72% at 3.5% of MCC concentration. Results showed that the increasing concentration of MCC increased the moisture content in the film hence influenced the strength of the bioplastic film obtained.

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1. Introduction

Bioplastic is an alternative to the conventional petroleum-based plastic [1] to resolve the environmental pollution. Bioplastic are a form of plastic that derived from renewable biological resources such as plants, bacterial and algal sources [2]. Bioplastic has been applied in numerous types of fields including food packaging, medical care, agricultures and electronics. Although significant improvements have been achieved such as non-brittle film, there are still some restrictions to be overcome to obtain low-cost bioplastic with the same mechanical properties which are comparable to the conventional plastic material [3]. Some characteristics of the bioplastic such as poor heat seal ability, thermal instability, high

water vapour, brittleness and low melt strength which needs to be improved. Coating, blending and addition of cellulose are some of the methods proposed to overcome the limitations of these bioplastics [4,5] such as high water vapour and thermal instability.

A review on carrageenan structure [6,7] which is a natural polysaccharide contains 3,6-anhydro group. The carrageenan structure is held by inter- and intra-molecular forces, such as hydrogen bonds, hydrophobic and Van der Waals forces [7,8]. The establishment of physical crosslink or hydrogen bond interaction between kappa carrageenan and crosslinker in the biocomposite application affects the carrageenan matrix arrangement to change the swelling property. The biocomposite improved the disintegration time in water which is an important criterion to develop biodegradable plastic to combat the environmental pollution. Meanwhile, cellulose is one of the natural fibres and it is abundant polymer on earth. It contains β -1,4 linked glucopyranose units with polymer chains associated by hydrogen bonds. Cellulose

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can be biosynthesized by a number of living organisms from lower to higher living plants, sea animals, bacteria and fungi [9,10,11]. Cellulose is in high demand for biocompatible and environmental friendly products since it is renewable by nature in relatively short period of time and abundant. Out of many, microcrystalline cellulose (MCC) is widely used in variety of applications such as pharmaceutical, cosmetic, food and polymer industries. MCC was utilized as a stabilizer, water retainer and emulsifier in different types of colloidal form of pastes and creams [12]. Special features such as lightness, strength, non-toxicity, water insolubility, biodegradability and renewability provides MCC a more attractive to be used in diverse industrial applications [13,14,15].

In this study, bioplastic film was produced by incorporated carrageenan and different concentration of microcrystalline cellulose (MCC) with polyethylene glycol (PEG), glyoxylic acid and hydroxypropyl methylcellulose (HPMC) as plasticizer, crosslinker and thickener, respectively. This study was purposed to investigate the effect of the different percentage of cellulose (MCC) on the strength of the bioplastic film obtained.

2. Materials and methods

2.1. Materials

Refined carrageenan was purchased from TACARA, Sabah, Malaysia. Glyoxylic acid ($C_2H_2O_3$, MW: 74.04 g/mol); hydroxypropyl methylcellulose (HPMC) ($C_{56}H_{108}O_{30}$) and microcrystalline cellulose (MCC) were purchased from Sigma-Aldrich, USA. Meanwhile polyethylene glycol (PEG) was purchased from Merck, Germany.

2.2. Preparation of carrageenan-cellulose biofilm

The 3 g of carrageenan was dissolved in 200 mL of deionized water at 60 °C for 1 h. At the same time, 1 g (0.5%) of MCC and 1 g of HPMC was dissolved in 50 mL of deionized water, separately. All of the solution was continuously stirred until a homogenous solution was obtained.

After that, MCC and carrageenan solution were mixed together and continuously stirred for 30 min. PEG and HPMC were added into the carrageenan-MCC solution and stirred for another 30 min. Finally, 0.2 mL of glyoxylic acid as the crosslinker was added into the mixture with continuously stirring for 30 min. Then 200 mL of the sample solution were poured onto 43 cm × 29 cm × 1.8 cm stainless steel trays. The thicknesses of each film were measured using electronic vernier caliper after 3 h drying in the oven at 60 °C. The process was repeated with different percentage of MCC (1, 1.5, 2, 2.5, 3, and 3.5%) concentration.

2.3. Biofilm characterizations

2.3.1. Moisture content

The moisture content of the biofilm was determined using moisture analyzer (AND MS-70, Japan). Approximately 0.1 g of biofilm sample was placed on the heating pan and the sample was heated with continuous heating. The analysis was stopped automatically when constant value of moisture content were obtained [16].

2.3.2. Viscosity and strength analysis

The viscosity analysis of the formulation solution were measured using Viscometer (Brookfield, Rheo 3000, USA) equipped with LCT 25. Approximately 16.5 mL solution was programmed at the speed of 300 rpm with 100 MPoints at a constant temperature (40 °C).

Meanwhile the elongation at break (EAB) and tensile strength of the biofilm were carried out using textile analyzer testing machine (CT3-Texture Analyzer, Brookfield, USA) equipped with TexturePro CT V1-8 Build 3.1. The biofilm was cut into the dumb-bell shape (2 cm × 10 cm) and fixed to the tensile machine at both end prior to the mechanical testing with 50 kg load cell. The method was sets accordance to ASTM D882-12 and a crosshead speed of 50 mm min⁻¹ was employed [16,17]. Elongation at break (EAB) and tensile strength was calculated from the data obtained from the textile analyzer testing machine by using the equations as followed [18,19]:

$$\text{tensile strength (MPa)} = (\text{load at break}) / (\text{original width}) \times (\text{original thickness}) \quad (1)$$

$$\text{elongation at break (\%)} = (\text{elongation at rupture} / \text{initial gage length}) \times 100 \quad (2)$$

where the load at break and the elongation at rupture can be collected from the data from texture analyzer and initial gage length was depend on the crosshead speed used during the testing.

2.3.3. FTIR functional group determination

For the determination of the functional group presence in the biofilm, a Perkin Elmer ATR-FTIR spectrometer (Frontier, USA) was used. The sample was analyzed in the range of 400 to 4000 cm⁻¹. A total of 32 scans were acquired with spectra resolution of 6 cm⁻¹. Then the spectra were analyzed using OMNIC software.

3. Results and discussion

3.1. Moisture content and appearance of the biofilm

The moisture content for each carrageenan-cellulose films with different percentage of MCC used are shown in Table 1. The increasing value of the percentage of MCC had increased the value of the moisture content for the films. At 1% of MCC, the value of moisture content was the lowest with only 13.28% of moisture inside the film obtained. Meanwhile, the highest value of moisture content was at 3.5% of MCC which is 16.72%. The increasing value of the moisture content in the film has increased due to the presence of the MCC. MCC increased the tendency for the films to absorb more water. Hydrophilicity properties of carrageenan increased with the incorporation of MCC due the intermolecular interaction between carrageenan and MCC had increased the number of H bonding which increasing the affinity for the films obtained to adsorb more water [20]. Since carrageenan is hydrophilic and soluble in water, carrageenan is more sensitive towards water compared to MCC, hence it mobilize more water [16]. Thus this would reflect the result of moisture content where at 0.5% MCC concentration, the moisture content is higher than the subsequent of 1% and 1.5% MCC concentration.

Table 1
Moisture content of the carrageenan-cellulose films.

Concentration of MCC (%)	Moisture Content (%)
0.5	15.20 ± 0.43
1	13.28 ± 0.31
1.5	13.72 ± 0.31
2	14.75 ± 0.86
2.5	16.08 ± 0.33
3	16.62 ± 1.02
3.5	16.72 ± 0.25

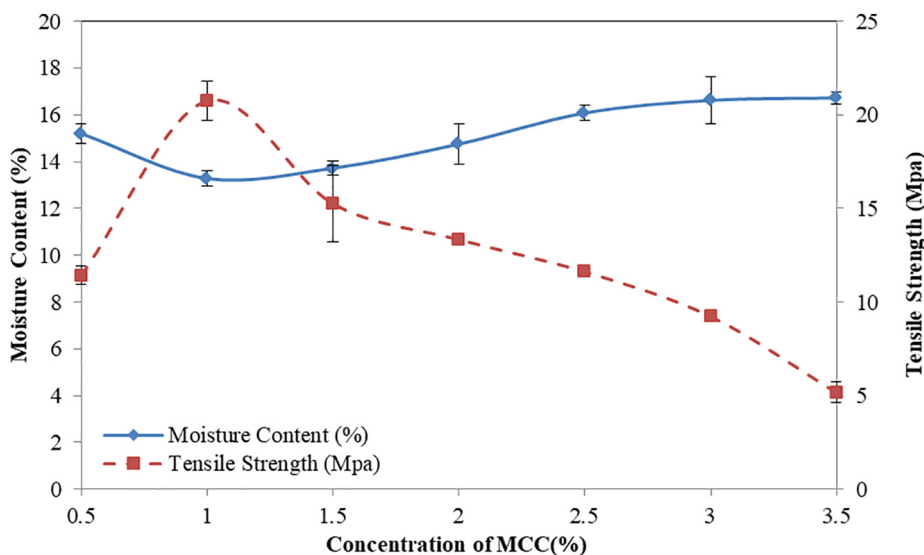


Fig. 1. Moisture content and tensile strength of carrageenan-cellulose films.

Fig. 1 shows the relationship between moisture content of the biofilms obtained and the tensile strength. The presence of more water molecule in the moisture content was increased; it decreased the tensile strength of the films. 1% of MCC shows the highest value of tensile strength with the lowest value of moisture content which was 13.28%. Meanwhile, 3.5% of MCC had the high-

est value of moisture content with 16.72% achieved the lowest value of tensile strength. When the water adsorption of biofilms was high, the properties of the biofilms obtained would change by reducing the value of tensile strength and resulting to the brittle biofilms [21]. Hence, this characteristic demonstrated that 1% of MCC film is more favorable compared to the other film obtained.

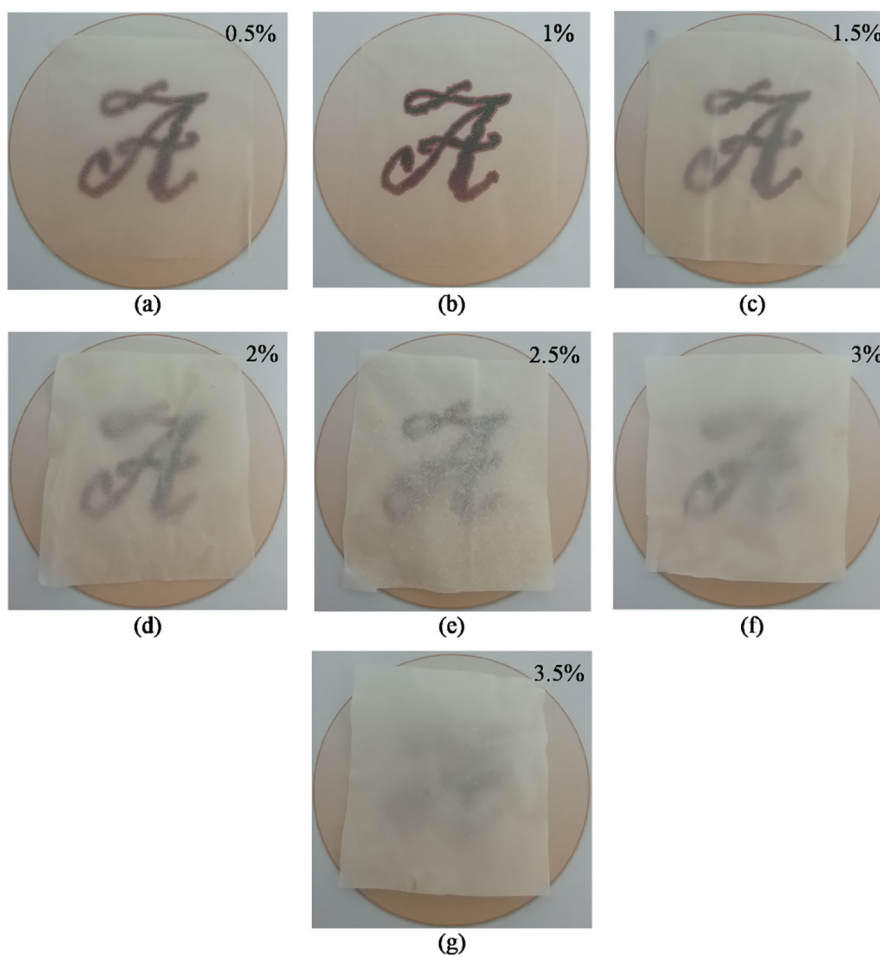
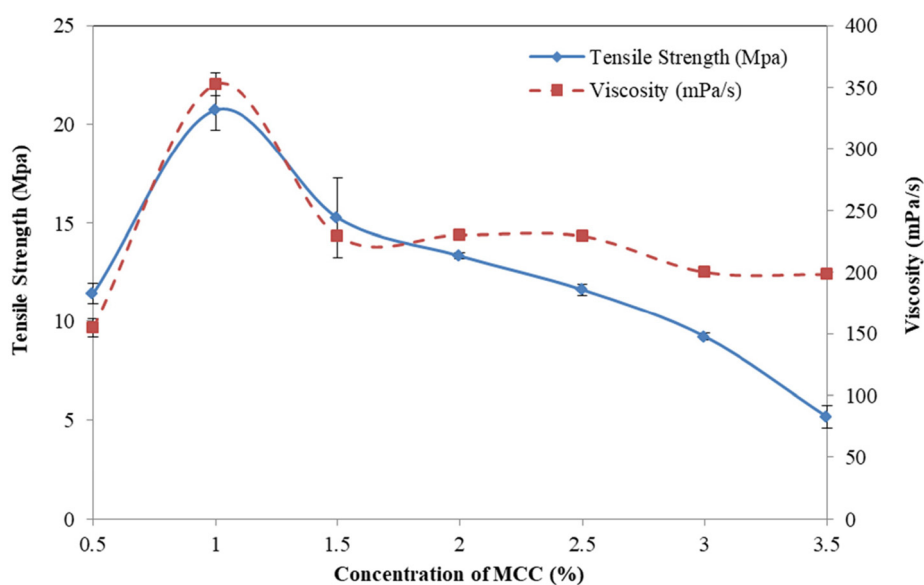


Fig. 2. Physical appearance of carrageenan-cellulose films.

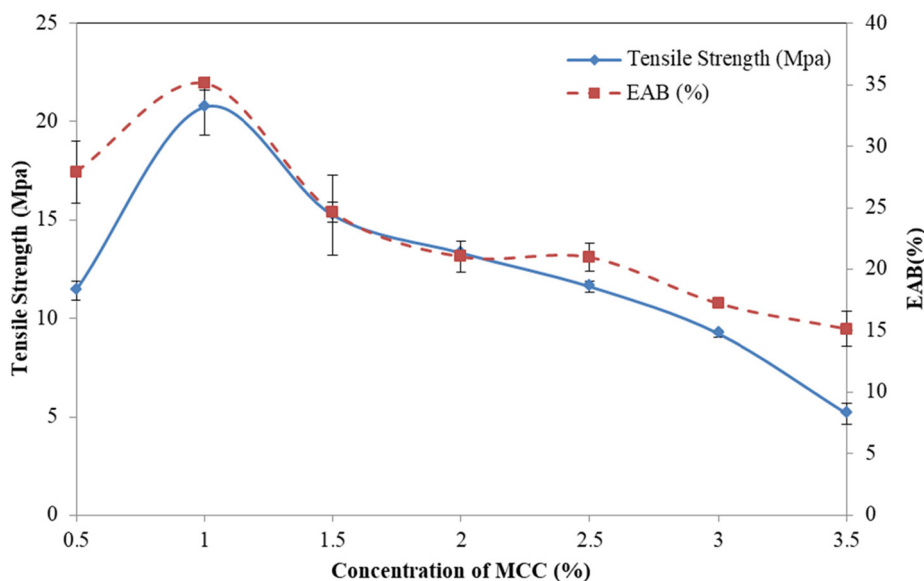
The moisture content also affected the appearance of the film obtained. As the concentration of MCC increased the biofilms obtained was thicker and less opacity. Fig. 2 (a) and (b) shows the film with 0.5% and 1% of MCC, respectively have the smoothest surface and more transparent compared to the other films. Meanwhile, the films with 3.5% of MCC shows the high opacity compared to the other films. A similar effect of MCC on the surface appearance of the avocado seed starch biocomposite films also was observed [22]. MCC is insoluble in water [23] and the surface opacity at the higher concentration of MCC tends to retard the intermolecular relation between the compounds which resulting aggregate and heterogeneous film surface was obtained [22]. The transparency of the film appearance has a relation with the concentration of MCC used into the matrix at the higher concentration of MCC. Thus, cloudier solutions of the films were obtained.

3.2. Viscosity and strength analysis

Viscosity represents the intermolecular interaction among the chemical compound in the film matrix. Viscosity also can be correlated with the tensile strength of the biofilms obtained [24]. Fig. 3 (a) shows the graph that indicates the connectivity between viscosity and tensile strength of the film. Fig. 3(a) shows that 1% of MCC has the higher value of viscosity which is 352.55 mPa/s compared to other films. 3.5% of MCC films have the lowest value of viscosity at 198.26 mPa/s. This pattern of results is due to the complementary number of carboxymethyl group of MCC with carrageenan and other material in the matrix which leads to the increasing of intermolecular interaction between the composite chains of the films [25]. Meanwhile, 3.5% of MCC has the lowest value in both viscosity and tensile strength might suggest to the agglomeration of MCC in the biocomposite matrix [26].



(a)



(b)

Fig. 3. Relationship of (a) tensile strength and viscosity and (b) tensile strength and EAB of carrageenan-cellulose films.

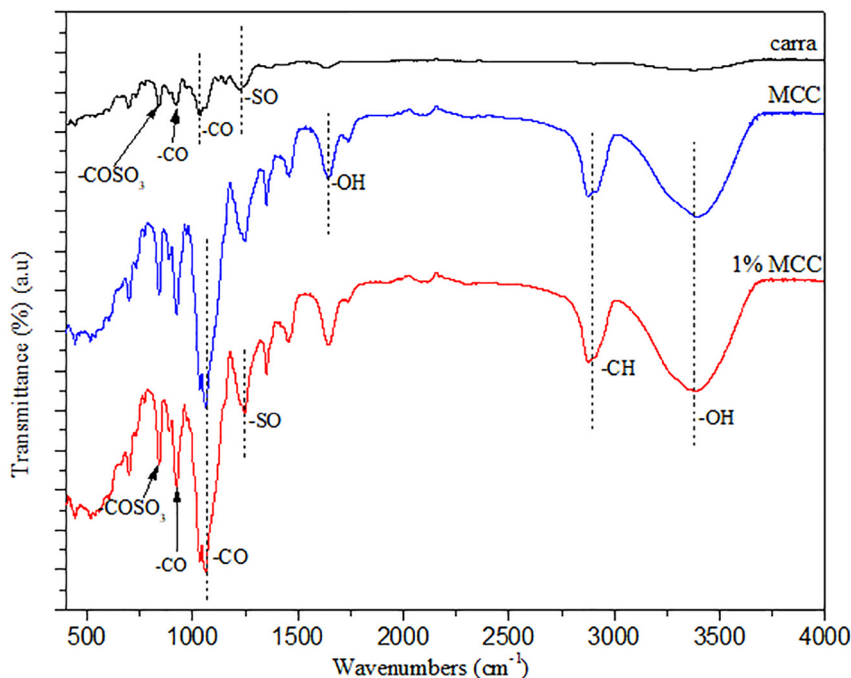


Fig. 4. Infrared spectra of carrageenan, MCC and carrageenan-cellulose film.

EAB indicates the capability of the sample to endure the pressure being applied and the breaking point of the samples. Fig. 3 (b) shows the relationship between tensile strength and EAB of the films obtained. The graph shows that 1% of MCC has the highest value of tensile strength and EAB of 20.74 MPa and 35.12%, respectively. Meanwhile the lowest value of tensile strength and EAB are 5.16 MPa and 15.15%, respectively for 3.5% MCC. Both tensile strength and EAB usually is caused by the presence of plasticizer. Hence the decrement in tensile strength and EAB as the concentration of MCC increased is due to the insufficient amount of plasticizer in the compound that inhibits the flexibility and continuity in the matrix chain [27]. The sample without reinforcement tends to have poor mechanical and physical properties [28]. Hence, the addition of MCC as the reinforcement agent into the biocomposite matrix is to improve the mechanical and physical properties of the films obtained. 1% addition of MCC improved the mechanical & physical properties of film at the optimum concentration.

3.3. FTIR functional group determination

Fig. 4 shows the infrared spectra of carrageenan, MCC and 1% of MCC film. All films at different concentration of MCC exhibited an identical spectrum with the existence of the identical functional group as in 1% of MCC addition.

Infrared spectrum of carrageenan shows significant functional groups that present in carrageenan molecular structure. Peak at 1223 cm^{-1} in the spectrum indicates the $-\text{SO}$ sulphate esters in carrageenan and peak at 1034 cm^{-1} shows the glycosidic linkage ($-\text{CO}$) of carrageenan. The glycosidic linkage usually appeared in the range from 1010 to 1080 cm^{-1} [29]. Meanwhile, band that appeared at 923 cm^{-1} and 841 cm^{-1} attribute to 3,6-anhydro-D-galactose ($-\text{CO}$) and D-galactose-4-sulfate ($-\text{COSO}_3$) of carrageenan, respectively. 3,6-anhydro-D-galactose usually appears in the range of 925 – 935 cm^{-1} and D-galactose-4-sulfate appears in the range from 840 to 850 cm^{-1} [29]. Thus, the sample is confirmed as the κ -carrageenan chemical structure.

The infrared spectrum of MCC in the figure indicates several functional groups that are usually found in the MCC. Broad band of 3381 cm^{-1} in the figure is due to the stretching vibration of $-\text{OH}$

OH groups of the MCC and this band usually appeared in the range of 3200 – 3500 cm^{-1} [30,31]. Peak at 2875 cm^{-1} belongs to the asymmetrically stretching vibration of $-\text{CH}$ groups of MCC, peak at 1647 cm^{-1} indicates the $-\text{OH}$ adsorbed water vibration and finally peak at 1062 cm^{-1} shows the $-\text{CO}$ groups of cellulose [32]. The infrared spectrum of 1% of MCC shows the fingerprint from carrageenan and MCC. However, it can be seen that the peaks is slightly shifted and increased in intensity which indicates the intermolecular interaction between carrageenan and MCC had occur in the biocomposite matrix. As can be seen peak at 1247 cm^{-1} was belongs to the carrageenan however shows increasing in the intensity of the peak as the peak appeared more obvious compared to the original carrageenan spectrum. Same goes to the peak at 924 cm^{-1} and 842 cm^{-1} which also belong to carrageenan and the intensity of the peak was increased higher compared to the original peak which also shows that there were also highly interaction occur at the functional group of 3,6-anhydro-D-galactose and D-galactose-4-sulfate of carrageenan with MCC.

4. Conclusion

In conclusion, the addition of the MCC into the matrix of carrageenan biocomposite improved the tensile strength, EAB, water content and the appearances of the films. However, as the percentage of the MCC increased from 0.5% until 3.5% the mechanical and physical of the films changed where the results shows that biofilm with 1% of MCC give the most favorable properties for bioplastic. The film has the highest value of viscosity, tensile strength and EAB which were 352.55 mPa/s , 20.74 MPa and 35.12% , respectively. Thus, 1% of MCC bioplastic holds the priority to be further explored as a potential packaging material.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] F. Gironi, V. Piemonte, Bioplastic and petroleum-based plastic: Strength and weaknesses, *Energy Sources: Part A*. 33 (2011) 1949–1959.
- [2] N. Rajendran, S. Puppala, R.M. Sneha, A.B. Ruth, C. Rajam, Seaweeds can be new source for bioplastics, *J. Pharm. Res.* 5 (3) (2015) 1476–1479.
- [3] F. Bilo, S. Padini, L. Sartore, L.E. Depero, G. Gargiulo, A. Bonassi, S. Federici, E. Bontempi, A Sustainable Bioplastic Obtained from Rice Straw, *J. Cleaner Prod.* 200 (2018) 357–368.
- [4] L. Sartore, A. D'Amore, L. Di Landro, Ethylene vinyl acetate blends with cellulosic fillers and reinforcements, *Polym. Compos.* 36 (2015) 980–986.
- [5] L. Sartore, F. Bignotti, S. Pandini, A. D'Amore, L. Di Landro, Green composites and blends from leather industry waste, *Polym. Compos.* 37 (2016) 3416–3422.
- [6] M. Sletmoen, B.T. Stokke, Review: higher order structure of (1,3)-beta-D-glucans and its fluence on their biological activities and complexation abilities, *Biopolymers* 89 (2008) 310–321.
- [7] Adam F., Hamdan M.A., Abu Bakar S.H. Carrageenan: A novel and future biopolymer. *Industrial Applications of Biopolymers and Their Environmental Impact*. CRC Press. In Press
- [8] S.H. Abu Bakar, F. Adam, Determination of physical crosslink between carrageenan and glyoxylic acid using density functional theory calculations, *Malaysian J. Anal. Sci.* 21 (4) (2017) 979–985.
- [9] V.K. Thakur, M.K. Thakur, Processing and characterization of natural cellulose fibers/thermoset polymer composites, *Carbohydr. Polym.* 109 (2014) 102–117.
- [10] L. Brinchi, F. Cotana, E. Fortunati, J. Kenny, Production of nanocrystalline cellulose from lignocellulosic biomass: technology and applications, *Carbohydr. Polym.* 94 (1) (2013) 154–169.
- [11] S. Ummartyotin, H. Manuspiya, A critical review on cellulose: from fundamental to an approach on sensor technology, *Renew. Sustain. Energy Rev.* 41 (2015) 402–412.
- [12] D. Trache, H.M. Hazwan, C.T.H. Chui, S. Sabar, M.R. Nurul Fazita, O.F.A. Taiwo, T.M. Hassan, M.K. Mohamad Hafiz, Microcrystalline cellulose: Isolation, characterization and bio-composites application—A review, *Int. J. Biol. Macromol.* 93 (A) (2016) 789–804.
- [13] Z.N. Izzati, N. Samat, H. Anuar, N. Zainuddin, Mechanical properties and failure modes of recycled polypropylene/microcrystalline cellulose composites, *Mater. Des.* 69 (2015) 114–123.
- [14] X. Sun, C. Lu, Y. Liu, W. Zhang, X. Zhang, Melt-processed poly(vinyl alcohol) composites filled with microcrystalline cellulose from waste cotton fabrics, *Carbohydr. Polym.* 101 (2014) 642–649.
- [15] A. Merci, A. Urbano, M.V.E. Grossmann, C.A. Tischer, S. Mali, Properties of microcrystalline cellulose extracted from soybean hulls by reactive extrusion, *Food Res. Int.* 73 (2015) 38–43.
- [16] M.A. Hamdan, F. Adam, K.N. Mohd Amin, Investigation of mixing time on carrageenan-cellulose nanocrystals (CNC) hard capsule for drug delivery carrier, *Int. J. Innov. Sci. Res. Technol.* 3 (1) (2018) 457–461.
- [17] J.W. Rhim, L.F. Wang, Preparation and characterization of carrageenan-based nanocomposite films reinforced with clay mineral and silver nanoparticles, *Appl. Clay Sci.* 97–98 (2014) 174–181.
- [18] M. Lubis, A. Gana, S. Maysarah, M.H.S. Ginting, M.B. Harahap, Production of bioplastic from jackfruit seed starch (*Artocarpus heterophyllus*) reinforced with microcrystalline cellulose from cocoa pod husk (*Theobroma cacao* L.) using glycerol as plasticizer, *IOP Conf. Ser. Mater. Sci. Eng.* 309 (2017) 012100.
- [19] Maulida., Siagian M., Tarigan P. 2016. Production of starch based bioplastic from cassava peel reinforced with microcrystalline cellulose avicel PH101 using sorbitol as plasticizer. *J. Phys. Conf. Ser.* 710: 012012.
- [20] N.E. Wahyuningtiyas, H. Suryanto, Analysis of biodegradation of bioplastics made of cassava starch, *J. Mech. Eng. Sci. Technol.* 1 (1) (2017) 24–31.
- [21] A. Jones, M.A. Zaller, S. Sharma, Thermal, mechanical and moisture adsorption properties of egg white protein bioplastics with natural rubber and glycerol, *Progr. Biomater.* 2 (1) (2013) 12.
- [22] Lubis M., Harahap M.B., Ginting M.H.S., Sartika M., Azmi H. 2016. Effect of microcrystalline cellulose (MCC) from sugar palm fibres and glycerol addition on mechanical properties of bioplastic from avocado seed starch (*Persea Americana* Mill). Full Paper Proceeding ECBA-2016. 331(3): 1-10.
- [23] S. Suvachittanont, P. Ratanapan, Optimization of microcrystalline cellulose production from corn cob for pharmaceutical industry investment, *J. Chem. Chem. Eng.* 7 (12) (2013) 1136–1141.
- [24] S.L. Hii, J.Y. Lim, W.T. Ong, C.L. Wong, Agar from Malaysian red seaweed as potential material for synthesis of bioplastic film, *J. Eng. Sci. Technol.* 7 (2016) 1–15.
- [25] P. Rachtanapun, N. Rattanapanone, Synthesis and characterization of carboxymethyl cellulose powder and films from *mimosa pigra*, *J. Appl. Polym. Sci.* 122 (2011) 3218–3226.
- [26] H. Kargarzadeh, M. Mariano, J. Huang, N. Lin, I. Ahmad, A. Dufresne, S. Thomas, Recent developments on nanocellulose reinforced polymer nanocomposites: A Review, *Polymers.* 132 (2017) 368–393.
- [27] Munthoub D.I., & Wan Abdul Rahman W.A. 2011. Tensile and water adsorption properties of biodegradable composites derived from cassava skin/polyvinyl alcohol with glycerol as plasticizer. *Sains Malaysiana.* 40(7): 713-718.
- [28] D. Preechawong, M. Peesan, P. Supaphol, R. Rujiravanit, Characterization of starch poly(ϵ -caprolactone) hybrid foams, *Polym. Test.* 23 (2004) 651–657.
- [29] V. Webber, S.M. de Carvalho, P.J. Ogliaeri, L. Hayashi, P.L.M. Barreto, Optimization of the extraction of carrageenan from *Kappaphycus alvarezii* using response surface methodology, *Ciência e Tecnologia de Alimentos.* 32 (4) (2012) 812–818.
- [30] M. Rahimi Kord Sofia, R.J. Brown, T. Tsuzuki, T.J. Rainey, A comparison of Cellulose nanocrystals and cellulose nanofibers extracted from bagasse using acid and ball milling methods, *Adv. Nat. Sci. Nanosci. Nanotechnol.* 7 (3) (2016) 035004.
- [31] J. Li, Y. Wang, X. Wei, F. Wanf, D. Han, Q. Wang, L. Kong, Homogeneous isolation of nanocelluloses by controlling the shearing force and pressure in microenvironment, *Carbohydr. Polym.* 113 (2014) 388–393.
- [32] N. Jia, S.M. Li, M.G. Ma, J.F. Zhu, R.C. Sun, Synthesis and characterization of cellulose-silica composite fiber in ethanol/water mixed solvents, *Bioresources.* 6 (2) (2011) 1186–1195.