Preparation and characterization of microcrystalline cellulose / chitosan films

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Abstract The microcrystalline cellulose (MCC) chitosan film was produced through solution casting with different composition of chitosan and different plasticizers. This MCC chitosan film was a biodegradable polymer due to all the ingredient was natural resources. MCC and chitosan can be found abundantly in the earth, and thus, can be obtained easily. Several testing were conducted such as tensile test, scanning electron microscope and Fourier transform infrared. The optimum ratio for the MCC chitosan was 90: 10 (MCC: chitosan). At this ratio, MCC chitosan has the highest tensile strength which was 42.16 MPa for the film without adding the plasticizer. MCC chitosan film also having the addition of plasticizer to improve film’s properties. Results show that addition of plasticizer able to improve properties of MCC chitosan film such as high tensile strength, high elongation at break and low Young’s modulus value. The percentages when compared MCC chitosan film with glycerol as plasticizer than the control film on the optimum ratio for tensile strength was higher 106%; while for film with PEG as plasticizer was higher 102%, elongation at break was higher 121% and 110% for both glycerol and PEG respectively when compared to control film.

1 Introduction

Nowadays, there are many bio-waste from animals and plants that are useful to human being. Scientists and researchers are now more focus on environmental friendly material which is useful and harmless to human health. Therefore, bio-waste such as chitin, cellulose, starch, lignin and so on giving attention from tem to developing and modifying products [1-5]. There are many researchers have savor in environmental friendly and biodegradable materials, which can be obtained from renewable and natural resources. It is due to the advance properties compare to non-environmental friendly films such as low cost, easy availability and biodegradability. biological degradability, the lessening volume of waste and compostability, conservation of fossil-based raw materials, decreasing amount of carbon dioxide release to atmosphere, and also increase utilization of agricultural resources for production of natural polymer [6].

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The discovery of renewable sources of polymeric materials has maintained the suitable expansion in economically and ecologically attractive skills. There are many interesting discoveries of renewable sources from polymeric materials such as the complete discovery of biodegradable polymers, which gave researchers ideas to handle waste disposal problems created from traditional petroleum derived plastics. Bio-based composites are a class of composite materials that are defined as having at least one of their component phases (i.e. matrix or reinforcement) derived from biomass. Recent heightened research in the development of bio-based composites for solving the escalating problem of end-of-life disposal of plastic materials and reducing the number of available landfill sites. There is a development in bio-composites research on the conversion from petroleum-based polymer, for example, polypropylene and polyethylene to naturally derived biopolymer such as starch, chitosan and resin matrices to produce composites [7]. Therefore, the present study is focused on microcrystalline cellulose (MCC)/chitosan film. Chitosan is reinforced into MCC matrix to enhance the film properties. Effect of glycerol and polyethylene glycol (PEG) as plasticizers to MCC chitosan film has also been studied. With addition of plasticizer, MCC chitosan film becomes more flexible and improve the mechanical properties of the films.

2 Experimental

2.1 Materials

Chitosan acts as the main component in this chitosan MCC film. Chitosan was manufactured at Sigma Aldrich. MCC was obtained from Sigma Aldrich which follows United States Pharmacopeia (USP) Reference Standard (Material number: 1098388; CAS Number 9004-34-6). Glycerol was used as plasticizer in this film. Glycerol was obtained from HmbG Chemicals (Germany; Code: C0347-91552409). Polyethylene glycol (PEG), also sometimes referred to as polyethylene oxide (PEO) was obtained from Sigma Aldrich. Lithium chloride was obtained from Avantor Performance Materials. N,N-Dimethylacetamide is the organic compound which is miscible with most other solvents, but it is poorly soluble in aliphatic hydrocarbons. DMAc was obtained from Avantor Performance Materials (Germany; CAS number: 127-19-5).

2.2 Preparation of the sample

2.2.1 Preparation of MCC solution

First, the amount of MCC powder, DMAc solution and lithium chloride (dry in oven 24 hours at 110°C) needed was weighed. MCC powder was added into DMAc solution and stirred for 15 minutes. Lithium chloride was then added into DMAc solution and stirred for 45 minutes until MCC powder fully dissolved and formed a colourless solution.

2.2.2 Preparation of MCC chitosan films with glycerol and polyethylene glycol

Glycerol as plasticizer was added into MCC chitosan solution and then stirred for 15 minutes to get homogeneous solution. Similar steps were used for polyethylene glycol as plasticizer. Then, the solution was casted to the glass plate (50 ml). Finally, the film was taken out when it was fully dried. The formulation of MCC chitosan films was shown in Table 1.
Table 1. Formulation of MCC chitosan film.

| Sample name        | MCC: Chitosan ratio (%) | Glycerol (%) | Polyethylene glycol (%) |
|--------------------|-------------------------|--------------|-------------------------|
| MCC film           | 100:0                   | 0            | 0                       |
| MCC/chitosan (95/5) film | 95:5               | 0            | 0                       |
| MCC/chitosan (90/10) film  | 90:10             | 0            | 0                       |
| MCC/chitosan (85/15) film  | 85:15             | 0            | 0                       |
| MCC/chitosan (80/20) film    | 80:20             | 0            | 0                       |
| MCC film           | 100:0                   | 3            | 0                       |
| MCC/chitosan (95/5) film | 95:5               | 3            | 0                       |
| MCC/chitosan (90/10) film  | 90:10             | 3            | 0                       |
| MCC/chitosan (85/15) film  | 85:15             | 3            | 0                       |
| MCC/chitosan (80/20) film    | 80:20             | 3            | 0                       |

3 Characterization and Testings

The mechanical testing used was tensile testing according to ASTM D 882 by using Instron machine. The thickness of the plastic test specimen was prepared according to the ASTM D 6988. The shape of the specimen was in a rectangular shape. Tensile test was used to find the tensile strength, Young’s modulus and elongation of the film specimen. There should be at least 3 specimens was use for testing for each batch of the film composition in order to have more accurate result. Structural analysis was performed by Fourier Transform Infrared (FTIR) Perkin Elmer Spectrometer 2000. It was the technique use to get the infrared spectrum. The spectrum was obtained through emission or absorption of the film. The spectra were obtained at resolution of 4 cm⁻¹ in the range of 4000-6000 cm⁻¹. The specimens were scan for 32 times for a better resolution on the reading.

4 DISCUSSION

4.1 Structural analysis

FTIR spectroscopy is an analytical technique used to identify mainly organic materials which provides information about the chemical bonds and molecular structure of a material. The existence of a specific chemical bond in any material is indicate from the presence of a peak at a specific wavenumber after scanning the test samples in the infrared light source. Fig. 1 shows the peak of MCC film with and without plasticizer. MCC film with plasticizer exhibit similar peak with that of original MCC film. MCC film with and without plasticizer was compared base on unchained peak, which was at region 2346.16 cm⁻¹. The unchained peak act as reference peak which was used to compare any different peaks occur between the samples due to it will not to be changed whenever what condition
for MCC chitosan film. Spectrum band of 3342.9 cm\(^{-1}\) was attributed to the O-H stretching vibration of hydroxyl group in the cellulose. The band at 2893 cm\(^{-1}\) corresponds to C-H stretching vibration of \(-\text{CH}_2-\) groups. The band at 1644.5 cm\(^{-1}\) was assigned for C=O in the aldehyde on the terminal anhydroglucose unit [8]. Peak at 1436.9 cm\(^{-1}\) was due to CH\(_2\). The 3342.9 cm\(^{-1}\) peak from MCC film was shifted a bit to 3328.1 cm\(^{-1}\) and 3332.5 cm\(^{-1}\) when adding with plasticizer PEG and glycerol. This prove that the interaction bonding between the MCC chains with plasticizer were stronger than that of without adding plasticizer [9]. Band found at 1324.1 cm\(^{-1}\), 1355.4 cm\(^{-1}\) and 1323.9 cm\(^{-1}\) was associated with C-O stretching vibration of CH\(_2\)- OH groups. Also a band observed at 1015.4 cm\(^{-1}\), 1014.3 cm\(^{-1}\) and 1014.0 cm\(^{-1}\) were for -C-O-C- in the cellulose molecules [10].

From Fig. 2, the broad absorption band, which appears in the range of 3600–2800 cm\(^{-1}\) is related to collective absorption by both N–H and O–H groups in the polymer, is an indication of the bonding of chitosan with MCC through hydrogen bond [11]. The presence of chitosan is also revealed by its typical peak shown only by treated samples at 1650–1580 cm\(^{-1}\) which assigned to N–H bending. A strong absorption peak appears at 1999.1 cm\(^{-1}\) for chitosan react with MCC signifies the formation of Schiff base (C=\(\equiv\)N double bond) between aldehydic carbonyl group of MCC and amino group of chitosan. While C–H were observed at 2892.4 cm\(^{-1}\) and 2894.4 cm\(^{-1}\). The absorption peaks at 1643.8 cm\(^{-1}\), 1636.8 cm\(^{-1}\) and 1644.3 cm\(^{-1}\) were associated with the presence of the C=O stretching of the amide I band, while range from 1450 cm\(^{-1}\) to 1470 cm\(^{-1}\) was stand for C-H bending, 1356.2 cm\(^{-1}\) and 1322.7 cm\(^{-1}\) were O-H bending. The peak at 1014.04 cm\(^{-1}\), 1014.5 cm\(^{-1}\) and 1019.1 cm\(^{-1}\) were assigned for anti- symmetric stretching of C–O–C bridge [12]. The FTIR spectrum of the MCC chitosan film showed that, the broad peak for -OH and -NH groups were shifted from 3342.9 cm\(^{-1}\) to 3330.4 cm\(^{-1}\). This shift indicated that interaction between amine groups in chitosan and OH groups in cellulose occurred. The sharp peak of –OH at 3330.4 cm\(^{-1}\) indicated the availability of free –OH group of MCC. The carbonyl band of the composite was shifted to a lower frequency, from 1644.5 cm\(^{-1}\) to 1643.8 cm\(^{-1}\). This FTIR spectrum showed that the composite may be prepared by the interaction of -NH group of chitosan and –OH group of MCC [13].

![Fig. 1. FTIR spectrum of MCC film with and without plasticizer.](image-url)
4.2 Tensile properties

Tensile test is a very important test used to determine tensile strength, Young’s modulus, and elongation at break. Tensile testing involves measuring the force required to elongate a specimen to its breaking point and determining the material properties from the result obtained. A film requires some tensile strength for its application, such as packaging. Besides, it also requires a certain elongation and modulus to maintain or carry product weight. Figure 3 shows the tensile strength of MCC chitosan film with different ratios of filler, chitosan added into microcrystalline cellulose (MCC) film. From the graph, it can be seen that the tensile strength of MCC film was increased until 10% of chitosan in MCC chitosan film and then decreased. From that, the maximum amount of chitosan that can enhance MCC film properties was 10%. The tensile value of MCC film is 32.2 MPa, increasing gradually to 42.16 MPa when loaded with 10% of chitosan as filler. However, starting from 10% of chitosan, the tensile value decreased from 42.16 MPa to 34 MPa when 15% of chitosan and 27.25 MPa when 20% of chitosan is loaded with MCC film.

The mechanical properties of the composites are determined by several factors, such as the nature of the reinforcement fiber, fiber aspect ratio, fiber–matrix interfacial adhesion, and also the fiber orientation in the composites [14]. The improvement in tensile strength at the presence of chitosan was expected as it was very compatible with MCC matrix with high strength properties and as a result it adds stiffness to the composites. In addition, from the graph, the elongation at break for MCC chitosan film also increased with the increased amount of chitosan. This is due to the higher amount of chitosan making MCC chitosan film brittle and easy to break. Furthermore, this improvement in the interfacial bonding also enables a more efficient transfer of stress from the matrix phase to the chitosan phase. This result is consistent with previous findings on cellulose-polymer composite systems [15,16].
Fig. 3. Tensile strength of MCC chitosan films.

Chitosan was very compatible with MCC from the formation of hydrogen bond between hydroxyl group of MCC matrix and chitosan filler. Therefore, it able to enhance properties of MCC once it load in MCC film. However, at higher concentration of chitosan, the MCC film will become brittle and easily to break. Hence, the tensile strength will be affected and shows decreasing trend. From Fig. 4, elongation at break of film with 10% of chitosan, MCC chitosan is the highest compare to elongation break of other ratio. Start from 15% of chitosan and beyond the tensile strength and elongation break was decreased and lower than the original MCC film which without adding chitosan. In order to enhance the bonding strength between the cellulosic materials and the matrix polymer, plasticizing agent was used. Fig. 4 shows tensile strength of different ratio of MCC chitosan films with and without plasticizer, polyethylene glycol (PEG). From the graph, tensile strength of MCC chitosan film with polyethylene glycol (PEG) as a plasticizer was higher when compare to MCC chitosan film without plasticizer. There was increased in tensile value from MCC film without chitosan to 10phr of chitosan in MCC chitosan film which is 43.12MPa, the optimum followed by decreasing value to 28MPa at 20% of chitosan in MCC chitosan film.

The same tensile strength result get for glycerol as plasticizer in MCC chitosan film which shown in the graph. There was increased in tensile strength of MCC chitosan film at 10% of chitosan and followed by decreased of tensile value from 44.96MPa, the optimum value at 10% of chitosan to 29.17MPa at 20% of chitosan in MCC chitosan film. This is because PEG and glycerol act as plasticizer which enhanced the tensile properties of MCC matrix. It embedded within the MCC chains to make the film more flexible and tightly hold the MCC chains [17-19]. Hence, MCC chitosan film with plasticizer more resistant to break when the external force applied as compared to MCC chitosan film without plasticizer. Furthermore, the reorganization of the polymeric network due to strong polymer-plasticizer interactions favoured the crystallization process, ultimately leading to the increased chain stiffness and decreased flexibility of the material [20]. However, MCC chitosan film with PEG exhibited lower tensile strength when compare to the MCC chitosan film with glycerol which bigger molecular size of PEG decreased the efficiencies to embed into MCC matrix. Elongation at break is also known as fracture strain which
expresses the capability of film to resist changes of shape without crack formation. In general, elongation at break of MCC film will increase as the chitosan filler increased. The optimum elongation at break of MCC chitosan film was at 10% amount of chitosan. As the material’s stiffness increased with increasing content of chitosan, and thus the film demonstrated a lower elongation at break in comparison to MCC film.

By adding plasticizer into MCC chitosan film make it becomes more flexible and elastic. Thus, the elongation at break of MCC chitosan film with polyethylene glycol (PEG) as a plasticizer higher compare to that without plasticizer as shown in Fig. 4. From the reference sample, the value of elongation at break was 23.2% while MCC chitosan film with PEG was 24.4%. At 10% of chitosan in MCC chitosan film, the elongation at break for MCC chitosan film without plasticizer was 27.6% while MCC chitosan film with PEG was 30.3%. Although the value of elongation at break decreased after that, the MCC chitosan film with PEG was still higher than that of without PEG. There is same positive result get for MCC chitosan film with glycerol as plasticizer. There was 33.44% elongation at break for MCC chitosan film with glycerol at 10% of chitosan, 121.1% increased as compared to control samples counter parts. Besides, there was improvement of chemical bond between plasticizer with matrix which it make MCC chitosan film resist to break. However, effect of glycerol as plasticizer is more obvious compared to that of PEG. The improvement of break elongation of MCC chitosan film with glycerol was higher than that of PEG. There was because the molecular size of glycerol was small enough and easier to join with MCC chains to poses plasticized effect as compared to PEG.

![Fig. 4. Tensile strength of MCC/chitosan films with different type of plasticizer.](image-url)
Fig. 5. Tensile strength of MCC/chitosan films with different type of plasticizer.

5 Conclusions

The development and study of microcrystalline cellulose (MCC) chitosan film had been done in simple and economic method. In this study, chitosan had been added into MCC to produce a better properties film with different composition of chitosan added. Incorporation of chitosan in MCC chitosan film will improve mechanical strength of films. The optimum composition of chitosan in MCC chitosan film is 10phr where its tensile strength, elongation at break, moisture absorption and degree of degradation is the highest. However, as the chitosan content increases, the tensile strength and elongation at break decrease significantly due to possible aggregation of chitosan.

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References

1. A.W.M. Kahar, M. Lingeswarran, M.Z. Amirah Hulwani, H. Ismail, Polym. Bull., 76(2), (2019)
2. A.W.M. Kahar, H. Ismail., N. Othman, J. Vinyl Add. Technol.18(3), (2012)
3. R. J. Walster, R. Rahman, A. W. M. Kahar. IOP Conf. Series: Mater. Sci. Eng., 429, (2018)
4. H. Zaman, J. Song, L.S. Park, I.K. Kang, S.Y. Park, G. Kwak, K.B.Yoon. Polym. Bull. 67(1), (2011)
5. A. W. M. Kahar, H. Ismail, A. Abdul Hamid, A J. Therm. Anal. Calorim., 123(1), (2016)
6. N. Ibrahim, A.W.M. Kahar, D.L. Ngoc, H. Ismail, H. Bio-res., 12(2), (2017)
7. F. Vilaplana, E. Strömberg, S. Karlsson, Polym. Degrad. Stabil., 95(11), (2010)
8. A.W.M. Kahar, H. Ismail. J. Vinyl Add. Technol. 22(3), (2017)
9. A.W.M. Kahar, N. Sarifuddin, H. Ismail, H., Ira. Polym. J., 26 (2), (2017)
10. D. Trache, A. Donnot, K. Khimeche, R. Benelmir, N. Brosse, Carbohydr. Polym., 104, (2014)
11. S. Yasmeen, M. Kabiraz, B. Saha, M. Qadir, M., Gafur, S. Masum, Intern. Resear. J. Pure Appl. Chem., 10(4), (2016).
12. A.H. Mohd Zain, A.W.M. Kahar, I. Hanafi, 2018. J Polym Environ, 26(2), (2008)
13. H. Salmah, H., Ismail, A. Bakar, J. Appl. Polym. Sci., 107(4), (2007)
14. N.F. Alias, H. Ismail, A.W.M. Kahar, Bio-res, 12(4), (2017)
15. Z.Lin, C. Chen, Z. Guan, S. Tan, X. Zhang, J. Appl. Polym. Sci., 122(4), (2011).
16. Z. Xiaju, S. Juncai, Y. Huajun, L. Zhidan, T. Shaozao, J. Thermo. Compos. Mater., 24(6), (2011).
17. O.S. Dahham, N.Z. Noriman, A.W.M. Kahar, H. Ismail, S.T. Sam, J. Appl. Sci. & Agric., 10(5), (2015).
18 A.H. Mohd Zain, A.W.M. Kahar, N.Z. Noriman, Procedia Chem., 19, (2016)
19. A.W.M. Kahar, H. Ismail., N. Othman, J. Appl. Polym. Sci., 128(4), (2013)
20. H. Liu, R. Adhikari, Q. Guo, B. Adhikari, J. Food Eng., 116(2), (2013)