The Effect of Plasticizers towards the Characteristics of Methylcellulose Film Packaging

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Abstract. The usage of petroleum-based film packaging causes a serious environmental problem, which affects human health as well as marine life. The main objective of this study is to study the effect of different plasticizers on the methylcellulose (MC) based film food packaging. Sorbitol and red palm oil (RPO) were used as plasticizers. The films were prepared by using solution-casting method before being characterized. FTIR spectrum showed the presence of 3361 to 3305 cm⁻¹ peak as the presence of hydroxyl group in sorbitol and 2925 cm⁻¹ to 2853 cm⁻¹ peak corresponded to the C-H stretches of the alkanes of RPO. All films appeared in white colour for sorbitol while yellowish for films with RPO. Tensile strength and elastic modulus decreased over increasing amount of sorbitol or RPO due to the modified interactions between the plasticizers and the chemical structure of the film. Overall, RPO can be used as the substitute of sorbitol to incorporate with MC.

1. Introduction

Food packaging helps in extending the shelf life of the food and provides the physical barrier between the food and outside environment. The advantages of using bio-based food packaging are it is biodegradable, renewable and usually edible [1]. Food packaging can be in various forms such as films, plastics, trays and foamed products. The most commonly used bio-based polymers, as food packaging are polyhydroalkanoates (PHAs), polylactide (PLA), PLA blends, starch blends and cellulose derivatives. Cellulose can be gained from nature materials such as woods, hemp and plant-based materials as well as microorganisms and synthesis of tunicates [2].

Methylcellulose (MC) is one of the cellulose derivatives that are widely used as food packaging because it can be used as environmentally friendly products due to its large availability, inexpensive and easy processability [3]. Methylcellulose has various advantages such as biodegradable, biocompatible, non-toxicity and good film-forming polymer [4]. Methylcellulose are very effective oxygen, carbon dioxide and lipid barriers even though it has poor water vapour transport [5]. Methylcellulose also has the ability to form thermally induced coating, which can be used to cover fried foods [6]. However, methylcellulose is very brittle. Adding plasticizers can improve the mechanical properties of the films by increasing extensibility, flexibility, elasticity and mechanical properties.

The most used plasticizers in films are glycerol followed by sorbitol and ethylene glycol [6]. Sorbitol is usually used in food packaging film because non-toxic and chemically stable. Sorbitol concentration in polymer based film affecting the hardness and elastic modulus (EM) of the film. Sorbitol is one of...
common plasticizers used in film food packaging application which is non-toxic and chemically stable [7]. Different concentration of sorbitol will affect the hardness and elastic modulus (EM) of the films [8]. The other plasticizer that is being investigated is red palm oil (RPO), which is a bio-based plasticizer [9]. The benefits of RPO are non-toxic, biodegradable, high resistance to heat, renewable and environmentally friendly. It also can improve the film appearance and expected to improve the elongation of the films because plasticizer able to improve the elongation of film [10]. It had been proven that RPO can replace the chemical-based plasticizers in the future [11]. Therefore, the objective of this paper was to synthesize and compare the characteristics, light barrier and tensile strength of MC based film with different type of plasticizer.

2. Methodology
2.1. Materials
Methylcellulose (MC) type A4C (powder form, viscosity: 400 cP) was purchased from Take It Global Sdn. Bhd. Sorbitol with MW of 182.17 g/mol was purchased from Merck Sdn. Bhd (Millipore, Darmstadt, Germany) in white powder form. Pure red palm oil food grade (NaOH: 0.141, KOH: 0.1974, INS: 145) was purchased from IKO store, Malaysia.

2.2. Preparation of Methylcellulose based-film
The films were prepared by using solution casting method. Three grams of MC was dissolved in 100 ml distilled water under continuous stirring. Different concentration of sorbitol, which were 1%, 2%, 3%, 4% and 5% (MCS1, MCS2, MCS3, MCS4 and MCS5 respectively) were incorporated in the homogenous MC solutions. The MC incorporated with red palm oil (RPO) were prepared by using same step with different concentrations of RPO, which were 1%, 2%, 3%, 4% and 5% (MCRPO1, MCRPO2, MCRPO3, MCRPO4 and MCRPO5 respectively). Pure MC film, which is the film control (MCSTD) and the MC solution films were prepared by pouring 30 ml of the solutions on the petri dishes. The films were then left in the oven at 80°C until completely dried. The dried films were peeled manually by using spatula and cut into desired size for further analysis.

2.3. Fourier Transformation Infrared (FTIR) Spectroscopy
The film samples were cut into 3 x 3 cm sizes and IR spectra of the samples were taken in the range of 500 to 4000 cm\(^{-1}\). The sample was placed on the metallic slit sample holder and analysed with over 10 cumulative scans at 2 cm\(^{-1}\) resolution [12].

2.4. Tensile Strength
The tensile strength, elongation at break (EAB) and Elastic Modulus were measured by using ASTM-D882 as the guideline. The machine was equipped with 2.5 kN static load cell and velocity of the crosshead used was 500 mm/min. The samples were cut into strips of 15 mm wide and 60 mm long and placed at the grip to be analysed. The test was carried out at room temperature with regular humidity conditions [13].

3. Results and Discussion
3.1. Thickness, Color Measurement and Transparency
Figure 1 shows the average thickness of MC films at different concentration of sorbitol or RPO. The thickness was increased as sorbitol concentration increased except at 3% sorbitol having decreased condition. Similar situations occur for RPO except for 2% RPO where the thickness slightly decreased. The MC film at 5% sorbitol (MCS5) was the thickest where similar results found by [14]. The present of sorbitol and RPO had resulted in thicker films due to formation of hydrogen bonding between the plasticizer and MC film. The addition of sorbitol and RPO increased the solid content of the films. However, sorbitol having better thickness at same concentration of RPO because sorbitol had higher content of hydroxyl [13], [15]. Therefore, greater interaction occur between MC and sorbitol during
gelatinization, resulting thicker films. The thickness of film was important for packaging industry because affecting the value of tensile strength and elastic modulus of the film [16].

![Figure 1. Thickness of MC films at different concentration of Sorbitol or RPO](image.png)

3.2. **Fourier Transform Infrared Spectroscopy (FTIR)**

Figure 2 showed the FTIR result for MC films with sorbitol. From Figure 3, the peak at the 3558 cm\(^{-1}\) shows the most relevant feature of MC structure, which this peak indicates O-H stretching band of hydroxyl group of MC. The broad absorption band of O-H stretching are getting narrowed and shifted from the peaks of 3361 to 3305 cm\(^{-1}\) because the presence of hydroxyl group in sorbitol that lead towards formation of more hydrogen bonding [13], [15]. This indicate crosslink occur between sorbitol and MC. These changes can be seen in the MCS1 to MCS5 films [17] and also supported by increasing the thickness of the film when sorbitol was added into the film. Furthermore, with the addition of sorbitol, peak in the range of 2932 cm\(^{-1}\) to 2923 cm\(^{-1}\) that represent the C-H asymmetric and symmetric stretching of the sorbitol structure appear in MCS2 to MCS5 films. These similar spectra of sorbitol are shown in the study done by Lele Cao et al [17].

FTIR spectra of the MC/RPO films are shown in Figure 3. The peaks of the MC structure can be seen in all MC/RPO films. The spectrum that showed the present of RPO was the methyl and methylene groups at 2921 cm\(^{-1}\) and 2853 cm\(^{-1}\) as also being found by [18].The peaks in the range of 2925 cm\(^{-1}\) to 2853 cm\(^{-1}\) corresponded to the C-H stretches of the alkanes of RPO appear in all MC/RPO films and indicate successful crosslink between RPO and MC [19].

3.3. **Mechanical Properties**

Figure 4 showed the tensile strength of MC film at different concentration of sorbitol or RPO. MC control shows that the tensile strength of the film is 82.8 MPa. However, tensile strength value of MC film incorporated with 1% sorbitol (MCS1) is significantly decreased from 82.8 MPa to 16.8 MPa. The tensile strength value was then increased from 16.8 MPa to 20.4 MPa (MCS2). This might be due to the greater thickness of MCS2 (0.1890 mm) compared to MCS1 (0.1492 mm). Nevertheless, the tensile strength decreased from 20.4 (MCS2) to 3.23 MPa (MCS5) because the plasticizer amounts exceed the compatibility and sorbitol disturb the polypeptide chain [13].
Figure 2. FTIR Spectra of MC control and MC/Sorbitol

Figure 3. FTIR Spectra of MC control and MC/RPO
For different concentration of RPO, tensile strength decreased from 19.7 (MCRPO1) to 4.55 MPa (MCRPO5) as the concentration of the RPO increased. The decreased value of tensile strength might occur due to the modified interactions between the plasticizers and the chemical structure of the film. These results are similar found by N. R. Saha et al. from the results in Figure 5, MC control film had the highest EM value of 2820 MPa while MC with addition of 5% sorbitol had the lowest EM value (80.50 MPa). The value of EM of MCRPO5 (225.00 MPa) was quite high compared to MCS3 (141.00 MPa), MCS4 (99.80 MPa) and MCS5 (80.50 MPa). This showed that the addition of the RPO to the film increased the elasticity of the MC film compared to incorporations of sorbitol. The smaller molecular weight of sorbitol compared to RPO had allowed increasing of molecular attraction and concurrently discourage the interaction of biopolymer chains. Therefore, plasticization better for sorbitol compared to RPO.

4. Conclusion
Sorbitol and RPO can be used as plasticizers for MC film. The present of solid content in plasticizer had improved the thickness of the film. The impact of redness of RPO had led the film to show yellowish colour but colourless film obtained for MC film with sorbitol. The thickness of the film and hydroxyl group of sorbitol had affected the transparency of MC film where the transparency level decreased over increasing value of sorbitol concentration. Higher concentration of RPO decreased the transparency level because lack of hydrogen bonding formed. The new peaks occurred at 3600 – 3020 cm⁻¹ were referred to formation of hydrogen bonding in the polymer chains of MC and sorbitol while addition of RPO showed new peak in the range of 2925 cm⁻¹ to 2853 cm⁻¹. This represent the C-H stretches of the alkanes of RPO. Elastic modulus of MC film with RPO gives better result compared to MC film with sorbitol. Therefore, this research need to be improved by adding compatibilizer to improve TS and EAB of film so that able to fulfill film packaging requirements.

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References
[1] Piñeros-Hernandez D, Medina-Jaramillo C, López-Córdoba A and Goyanes S 2017 Food Hydrocoll. 63 488
[2] Nasatto P L, Pignon F, Silveira J L M, Duarte M E R, Noseda M D, and Rinaudo M 2015 Polymers (Basel). 7 777
[3] Orasugh J T et al. 2018 Carbohydr. Polym. 188 168
[4] Esmaeili A and Fazel E M 2016 Flavour Fragr. J., 31 341
[5] Suderman N, Isa M I N, and Sarbon N M 2018 Food Biosci. 24 111
[6] Nguyen Vu H P and Lumdubwong N 2016 Carbohydr. Polym. 154 112
[7] Ma X, Qiao C, Zhang J, and Xu J 2018 Int. J. Biol. Macromol., 119 1294
[8] Liu W et al. 2018 Polymer (Guildf). 148 109
[9] Tee Y B, Talib R A, Abdan K, Chin N L, Basha R K, and Yunus K F M 2014 Agric. Agric. Sci. Procedia 2 289
[10] Manshor N M, Rezali M I, Jai J, and Yahya A 2018 IOP Conf. Ser. Mater. Sci. Eng. 358 1
[11] Halim A L A, Kamari A, and Phillip E 2018 Int. J. Biol. Macromol. 120 1119
[12] Saha N R et al. 2016 Carbohydr. Polym. 136 1218
[13] Bakry N F, Isa M I N, and Sarbon N M 2017 Int. Food Res. J. 24 1753
[14] Gutiérrez T J and González G 2017 Food Biophys. 12 11
[15] Noronha C M, De Carvalho S M, Lino R C, and Barreto P L M 2014 Food Chem. 159 529
[16] Datta D and Halder G 2018 Process Saf. Environ. Prot. 114 143
[17] Cao L, Liu W, and Wang L 2018 J. Clean. Prod. 175 276
[18] Jia P, Xia H, Tang K, and Zhou Y 2018 Polymers (Basel). 10 12
[19] Sharif Z I M et al. 2019 507 1