The Effect of Plasticizers towards the Characteristics of Methylcellulose Film Packaging

Nurul Aishah Nazihah binti Hamzah, Siti Fatma binti Abd Karim

Faculty of Chemical Engineering, Universiti Teknologi Mara

***Abstract*— The usage of petroleum-based film packaging cause a serious environmental problem, which it will affect the human health as well as human especially 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) are used as the plasticizers. The films were prepared by using solution-casting method. Then, the films are characterized on chemical properties by using FTIR, light transmission and transparency properties by using UV-Vis Spectrophotometer and tensile strength properties to observe the strength of the films. From the FTIR spectra, the presences of characteristics bands of MC structure are observed in all films. The result show that sorbitol and RPO are exists in the MC structure. From UV-Vis study, MC/Sor films are more opaque compared to the MC/RPO films. The tensile strength of the film are decreasing, which might occur due to the modified interactions between the plasticizers and the chemical structure of the film. Overall, RPO can be used as the substitute of the sorbitol to incorporate with MC.**

Keywords —.Film packaging, Methylcellulose, Plasticizers, RPO, Sorbitol

I. INTRODUCTION

Food industry is growing from time to time. Hence, the demand of the bio-based food packaging increases due to the concerns on food safety as well as the awareness towards the environmental issue. Food packaging helps in extending the shelf life of the food and provides the physical barrier between the food and outside environment, which may cause the food to be spoiled. 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 the nature materials such as woods, hemp and plant-based materials as well as microorganisms and synthesis of tunicates[2]. The cellulose derivatives can be used as raw material for production of film food packaging.

Methylcellulose (MC) is one of the cellulose derivatives that are widely used as food packaging. Researchers has put much interest in methylcellulose as it can be used as environmental 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 ability to form thermally induced coating, which can be used to cover fried foods [2]. Adding plasticizers can improve the mechanical properties of the films by increasing extensibility, flexibility, elasticity and mechanical properties. The most used plasticizers are glycerol followed by sorbitol and ethylene glycol [6]. In this study, the plasticizers used are sorbitol and red palm oil (RPO). Sorbitol is one of the polyol that are widely used in film packaging to improve the properties of the based films. Sorbitol is chemical based plasticizers that are non-toxic and chemically stable, which make it suitable to be used in food contact films [7]. The advantage of using sorbitol as plasticizers is it helps in enhancing the mechanical properties of the polymer membrane films. Higher concentrations of sorbitol incorporated with the polymer based film will help in decreasing the hardness and elastic modulus 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 it is non-toxic, biodegradable, high resistance to heat renewable and environmental friendly. Furthermore, it also contains high nutritious values due to the presence of carotene and vitamin E. It also can improve the film appearance. From the researches, it was proven that RPO can replace the chemical-based plasticizers in the future [10].

Thus, the objectives of this study are to synthesize and characterized the chemical, light barrier and tensile strength properties of the MC based film food packaging. Other than that, the effect of the different plasticizers on the chemical, light barrier and mechanical properties of MC based film are investigated. The method used in preparing the film is solution casting. FTIR is used to characterize the chemical structure of MC while UV-Vis Spectrophotometer is used to observe the light transmittance and transparency of the films and tensile strength analysis is used to characterize the mechanical properties of the films.

II. METHODOLOGY

A. 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.

B. 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 are 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 concentration of RPO, which are 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 [5].

C. *Thickness of film*

The film thickness measurements were made at 5 different points along the length of the samples using digital micrometer (Mitutoyo Corporation, Japan) with accuracy of 0.001 mm. The mean values of each sample were used to calculate the mechanical properties [5].

D. *Color measurement*

The film color was determined by using Konica Minolta colorimeter (CR 400; Minolta, Japan). The color values L* (Luminosity), a* (red-green) and b* (yellow-blue) were acquired with three measurements around the film samples and white plate was used as standard for calibration. The total color difference (ΔE^*) was calculated by film control (MC) as standard, by using the following equation, Eqn. 1:

$$\Delta E^* = \sqrt{(\Delta L*)^2 + (\Delta a*)^2 + (\Delta b*)^2} \quad \text{Eqn. 1}$$

Where ΔL*, Δa* and Δb* are the difference between the color parameter of the samples and the standard (L* = 37.677, a* = 0.953 and b*=-2.560) [11].

E. *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} resolutions [12].

F. *Light transmittance and transparency*

The transmission of UV and visible light for each film was determined using an UV-Vis Spectrophotometer in the wavelength range of 200 to 800 nm. The transparency of the film was calculated by using the following equation, Eqn. 2:

$$Transperancy = \frac{logT_{600}}{x} \quad \text{Eqn.2}$$

Where, T_{600} is the transmittance at wavelength 600 nm and x is the film thickness (mm) [11].

G. *Tensile strength*

The tensile strength (TS), elongation at break (EAB) and Elastic Modulus (EM) 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 analyzed. The test was carried out in room temperature with regular humidity conditions [13].

$$EAB = \frac{break\ distance, mm}{gauge\ length, mm} \times 100\% \quad \text{Eqn. 3}$$

III. RESULTS AND DISCUSSION

A. *Thickness and Color Measurement*

The thicknesses of the films are shown in the Figure 1 and Figure 2. The film thickness depended on the film nature as well as the compositions of the material used.

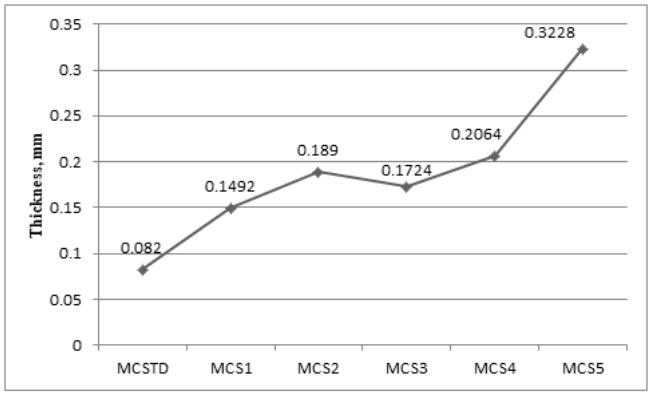

Figure 1: Thickness of MC control and MC/Sor films

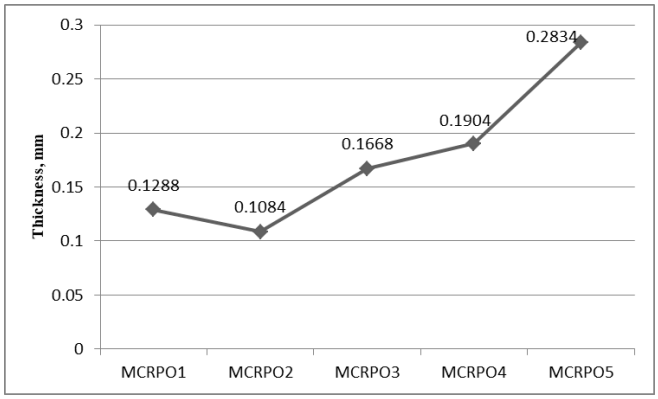

Figure 2: Thickness of MC/RPO films

The thickness values are varies between 0.2064 mm to 0.0820 mm. MC control film is the thinnest film compared to other MC incorporated with the plasticizers. The films thicknesses are increasing as the concentration of the plasticizers are increasing. The MC film incorporated with 5% sorbitol (MCS5) is the thickest among the others. This shows that addition of sorbitol and RPO increases the solid content of the films. Comparing the MC/Sor film with MC/RPO film, MC with incorporations of sorbitol is much thicker than MC/RPO film. This might due to higher content of hydroxyl groups in sorbitol compared to RPO [14]. Higher content of hydroxyl may lead to higher degree of protein-protein hydrogen bonding, which this will affect the thickness of the films.

Table 1: Colour values and total colour difference of films

Sample	L*	a*	b*	ΔE^*	Results
MCSTD	37.68	0.95	-2.56	N/A	Transparent
MCS1	35.47	0.59	-1.69	2.40	Slightly white
MCS2	41.22	0.40	-2.98	3.61	Slightly white
MCS3	44.59	0.22	-2.25	6.96	Moderately white
MCS4	46.45	0.31	-1.46	8.87	White
MCS5	61.32	-0.63	-0.35	23.80	White
MCRPO1	36.12	0.47	-0.66	2.50	Slightly yellowish
MCRPO2	36.20	-0.18	-0.06	3.12	Slightly yellowish
MCRPO3	36.19	-0.61	1.53	4.63	Moderately yellowish
MCRPO4	36.72	-0.84	3.98	6.85	Yellowish
MCRPO5	36.50	-1.01	5.88	8.74	Yellowish

The color value and total color difference are shown in Table 1. The L* value indicates the lightness or darkness of the films. Increasing value of L* shows an increase of the lightness of the films. The value of a* shows a greenness or redness of the films, which higher value of a* means the color of the films are more to redness while the value of b* shows the yellowness or blueness of the film, where the higher the value of b* indicates the film is leading more to yellowness. From the result, MC/Sor has increasing values of L*, which shows that the lightness of the film is increasing. The value of the L* is increasing from 35.470 (MCS1) to 61.320 (MCS2). The decreasing value of a* of MC/Sor film shows the greenness of the film compared to MC control film. The value of b* for MCS2 are higher than MC control film while the rest of MC/Sor film has lower b* value than MC control film. Film of MCS5 has the highest total color (23.799) difference compared to other MC/Sor. For MC/RPO films, the value of L* of MC/RPO films are slightly fluctuated with the increasing of the concentration of the RPO and the value of a* is decreasing. The value of b* of MC/RPO film increases as the concentration of RPO increases. The value of ΔE* shows significant increase, which lead to more colored films [15].

B. *Fourier Transform Infrared Spectroscopy (FTIR)*

The FTIR spectra obtained for the MC control and MC/Sor films are shown in Fig. 3 while MC control and MCRPO films are shown in Fig. 4. From Fig. 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 peaks at 1642 cm^{-1} and 1124 cm^{-1} related to the C-O stretching and the band at 1435 cm^{-1} is correspond to the C-H stretching. Comparing the MC control spectra with the MC incorporated with sorbitol, the presence of characteristic bands of the MC structure can be seen in all films. The broad absorption band of O-H stretching are getting narrowed and shifted from the peaks of 3361 to 3305 cm^{-1}. This changes can be seen in the MCS1 to MCS5 films [16]. Furthermore, with 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 are appear in MCS2 to MCS5 films. These similar spectra of sorbitol are shown in the study done by *Lele Cao et al* [17]. In Fig. 4, the FTIR spectra of the MC/RPO films are shown. The peaks of the MC structure can be seen in all MC/RPO films. Nevertheless, the peak that indicates the O-H stretching is shift from 3358 cm^{-1} (MC control) to 3451 cm^{-1} to 3361 cm^{-1} for MC/RPO films. In addition, the peaks in the range of 2925 cm^{-1} to 2853 cm^{-1} that correspond to the C-H stretches of the alkanes of RPO appear in all MC/RPO films. The other peaks, which are 1642 cm^{-1} and 1124 cm^{-1} that represent the C-O stretching bands are appear in all MC/RPO films. From the results, it indicates that sorbitol and RPO are successfully crosslink with the MC [8]. The FTIR spectra of MC/Sor and MC/RPO have similar patterns with the spectra of MC control.

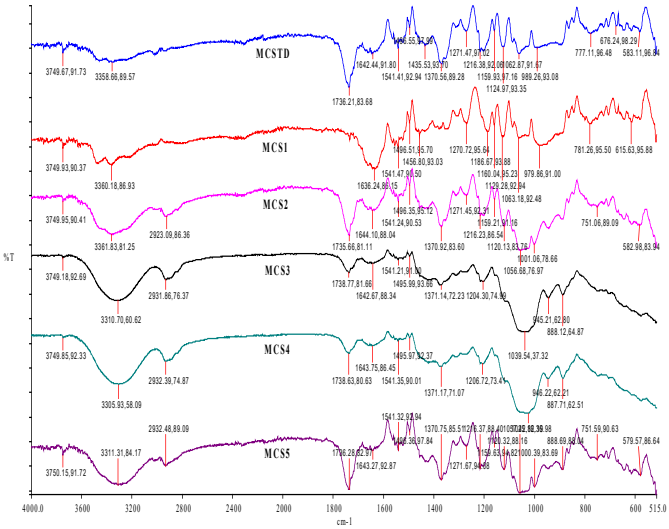

Figure 3: FTIR Spectra of MC control and MC/Sorbitol

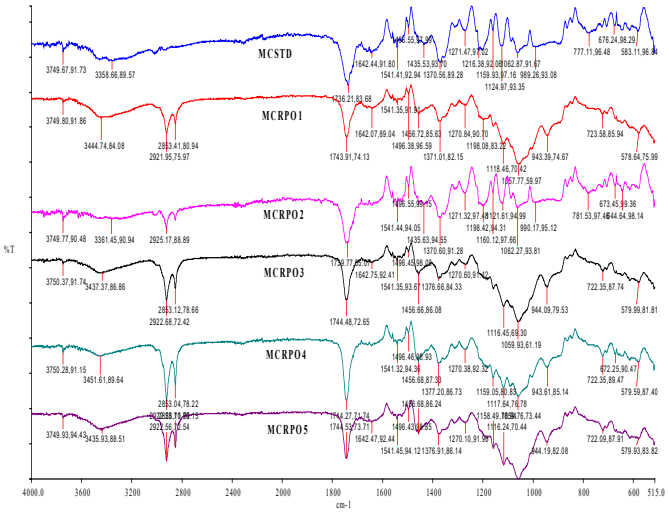

Figure 4: FTIR Spectra of MC control and MC/RPO

C. *Light transmittance and transparency*

The transparency of the films is investigated by using the UV-Vis Spectrophotometer. Table 2 shows the % transmittance and the transparency value of the films.

Table 2: Light transmittance and transparency value of the films

% Transmittance			Transparency value (TV)
Sample name	T_{280}	T_{600}	
MC control	2.254	2.636	5.138
MCS1	1.928	1.972	1.980
MCS2	6.637	17.865	6.623
MCS3	26.424	22.646	7.858
MCS4	2.805	69.024	8.911
MCS5	1.656	90.991	6.068
MCRPO1	1.00E+10	3.963	4.641
MCRPO2	3.565	4.046	5.598
MCRPO3	95.280	4.130	3.695
MCRPO4	2.904	5.728	6.928
MCRPO5	2.198	6.918	2.963

The % transmission (%T) of the light through MC control film at 280 nm is 2.254%. From Table 2, at wavelength of 280 nm, the highest value of %T for MC/Sor films is 26.424% of MCS3 and the lowest value of the %T is 1.656% for MCS5. Furthermore, the value of %T of MC/RPO films shows higher reading of %T compared to MC control film except for MCRPO5, which has lower %T (2.198%). MCRPO1 also indicates the highest value of %T at 280 nm (1.00E+10). Higher %T illustrates that the films absorb greater amount of the light. The %T of the MC/Sor films indicates that the concentration of the plasticizers added to the films might affect the % transmission of the light to the films. From the results of both plasticizers, it can be said that 5% concentration of plasticizers reduce the UV light penetration compared to the MC control film, which lower value of %T influenced better barrier properties towards the UV light [6]. Contrast to the %T at 280 nm, the %T at the visible light, T_{600} shows that the addition of sorbitol and RPO to the films increases the %T of the films. This depicts that the addition of the sorbitol are more likely due to the transparent nature of the sorbitol. This

result are similar to the study done by *Bakry et al* [14]. The transparency value (TV) of the MC/Sor films shows an increment compared to the MC control, which has the transparency value of 5.138. The increment of transparency value illustrated higher opacity of the film. This might due to the higher polymer chain compaction, which limits the light to pass through the films [6]. However, the value of the MCS5 is decreased from 8.911 of MCS4 to 6.608 for the MCS5 film. Moreover, the value of transparency for MC/RPO films shows a fluctuation, where MCRPO4 has the highest transparency value (6.928) and MCRPO5 has the lowest transparency value (2.963). These results indicate that the addition of the sorbitol to the films cause higher opacity to the films compared to the addition of RPO.

D. Mechanical properties

The mechanical properties of the films are studied by using the standard method and the results of the test are shown in Figure 5 to Figure 8.

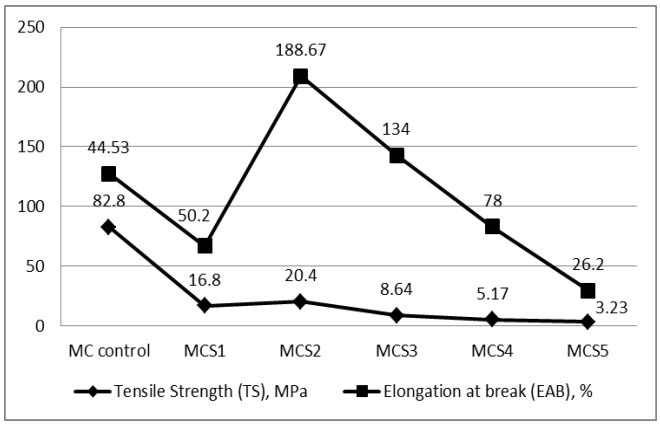

Figure 5: Tensile strength and elongation at break of MC control and MC/Sor films

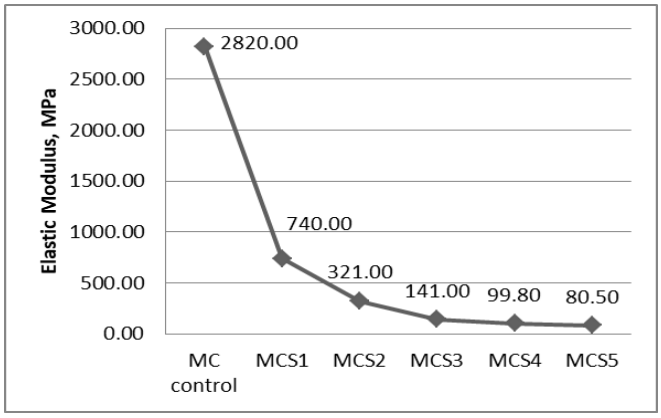

Figure 6: Elastic Modulus of MC control and MC/Sor films

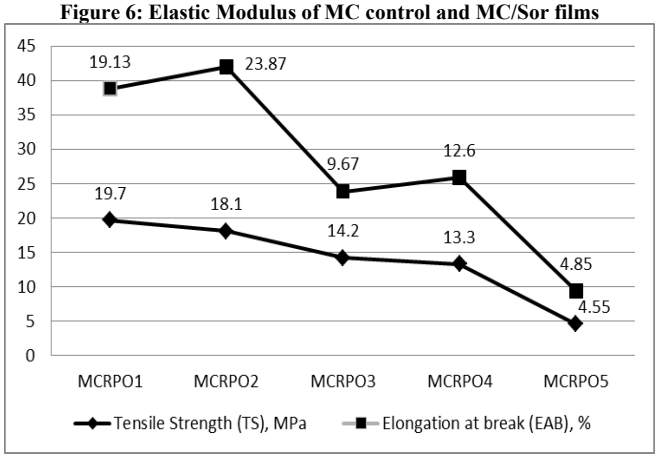

Figure 7: Tensile strength and elongation at break of MC/RPO films

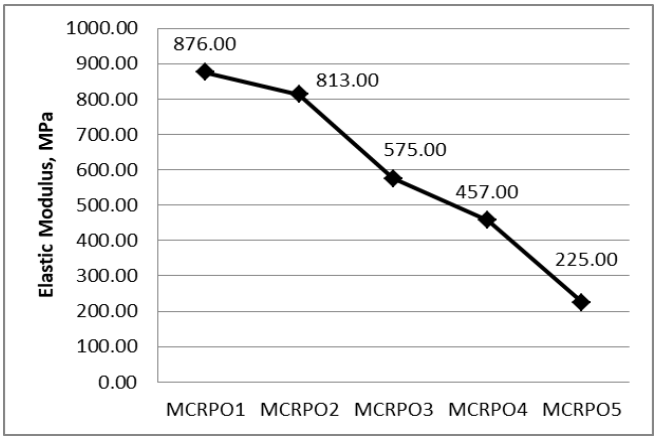

Figure 8: Elastic Modulus of MC/RPO films

Tensile strength is a measurement of maximum strength of film to withstand stress applied to it. From Figure 5, MC control shows that the tensile strength of the film is 82.8 MPa. However, TS value of MC film incorporated with 1% sorbitol (MCS1) is significantly decreasing from 82.8 MPa to 16.8 MPa. The TS value was then increase from 16.8 MPa to 20.4 MPa (MCS2). This might due to the greater thickness of MCS2 (0.1890 mm) compared to MCS1 (0.1492 mm). Nevertheless, the tensile strength decreases from 20.4 (MCS2) to 3.23 MPa (MCS5). For different concentration of RPO in Figure 7, tensile strength decreases from 19.7 (MCRPO1) to 4.55 MPa (MCRPO5) as the concentration of the RPO increases. The decreases value of TS might occur due to the modified interactions between the plasticizers and the chemical structure of the film. These results are similar to the study done by *N. R. Saha et al* [4]. The elongation at break is measure to study the ability of the film to stretch before it breaks. From Figure 5 and Figure 8, the MC film incorporated with 2% of sorbitol, MCS2 (188.67%) indicates the highest EAB and MC incorporated by 5% RPO, MCRPO5 (4.85 %) indicates the lowest EAB. Other than that, the result shows that MC films that incorporate with sorbitol shows higher EAB than EAB of MC control film (44.53%) compared to the MC film incorporated with RPO. This proves that sorbitol helps in increasing the flexibility of the MC films. Elastic modulus is define as the ratio between stress and strain caused by the load applied to the film, which means the value of EM is the maximum stress that the film can withstand without undergoing permanent deformation. From the result in Figure 6, MC control film has the highest EM value of 2820 MPa while MC with addition of 5% sorbitol has the lowest EM value (80.50 MPa). Although MCRPO5 has the lowest EAB, but the value of EM of MCRPO5 (225.00 MPa) is quite high compared to MCS3 (141.00 MPa), MCS4 (99.80 MPa) and MCS5 (80.50 MPa) as shown in Figure 8. This shows that the addition of the RPO to the film increase the elasticity of the MC film compared to incorporations of sorbitol.

IV. CONCLUSION

Environmental friendly packaging is highly in demand for a better future. Methylcellulose is one of the bio-sources that can be the substitute of the petroleum-based packaging. These results suggested that RPO improved most of the MC properties. The FTIR spectra of both plasticizers show the crosslink of the MC with the plasticizer added to the films. The chemical structures of the added plasticizers are appeared in the MC structure. The light barrier properties have slightly improvement with the addition of the plasticizers. The transparency values of MC/RPO films are lower than MC/Sor films that indicate lower opacity of MC/RPO films. Further study on the light barrier properties should be done in order to improve the light transmission on the visible light penetration to the films. The tensile strength of the films shows a reduction with the increment of plasticizers concentration. However, the values of EAB are increase with the addition of sorbitol to the films compared to EAB of MC/RPO films. Lastly,

the elasticity of RPO films are much better compared to the MC/Sor films. Overall, RPO shows better results compared to sorbitol, which indicates that bioorganic plasticizers can be the substitute of the chemical based plasticizers.

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