

Effect of Clove Essential Oil and Zein Nanoparticles towards Improving Food Film Packaging

Nik Nurilya Nazlin bt Nik Lah and Siti Fatma bt Abd Karim

Faculty of Chemical Engineering, Universiti Teknologi Mara

Food packaging is importance for manufacturer in order to accomplish consumers demand for fresh, convenient and flavorful food demands [1]. The biodegrade film with satisfying UV barrier properties is rarely seen and used by the consumer. The objective of this study ere to determine the effect if the temperature used for solvent casting and clove essential oil (CLO) concentration on the characteristic and biodegradability of the film using Zein and CLO. The film was prepared using solvent casting at several temperature 20°C, 35°C and 90°C. UV-vis and FTIR were used to characterize the effect of temperature and concentration of CLO on film packaging. Degradation rate measurement was carried out using degradation test at room temperature, 25°C. It was found that increasing of CLO increased the UV-barrier properties and also lowering the degradation rate.

Keywords— Zein, food packaging, clove essential oil and biodegradable.

I. INTRODUCTION

Food is the daily life needs by human and in depth scientific definition, food is the substance that living things consume for their energy and also nutrient. Food industry is an industry with acceptable estimation of growth since human population is increasing and also their need for food.

Food packaging more concern to protect the food from unwanted material such as fly, fungi and dust. In the production view, food packaging is also used and design as a way to attract potential customer to buy their product. Food packaging can comes in many form such as can, bags, film, containers or wrapper. A lot of researcher is making their way to find cheaper, biodegradable and also satisfying mechanical performance of the food packaging with enhance properties using many means of knowledge.

Film is use to protect and preserve food quality and it can be flexible than can which make it customizable to fit the consumer needs [2]. Food packaging films is used as cereal box liners, bags for bread, frozen food or snacks and food wrappers. Most of the commercialize food film packaging using petroleum based of film which make it non-biodegrade and promote the increasing of the volume of the waste in the landfill over the time.

Food film packaging consists of two major part which are the base usually used is starch and also additive in this case essential oil to improve the food film packaging properties. Semolia flour had been used to make a food film packaging incorporated with the Zinc Oxide. It was found that Semolia flour have great gluten content which can enhance the biopolymer film's nutritional properties [3]. Other than that, Hydroxypropyl-methylcellulose (HPMC) had been reported to have low flavor and aroma properties [4]. Essential Oil (EO) is classified as the Generally Recognized as Safe (GRAS) and widely used in the food film packaging to improve the antimicrobial properties of the film [5]. *Zataria multiflora* Bioess essential oil (ZEO) had been reported

that it increased the antioxidant and also antimicrobial properties of the film [6] [7]. Another EO that had been used to improve the antimicrobial properties is Cinnamon essential oil (CEO) with the main component of cinnamaldehyde. However, no degradation test was completed in these papers.

Zein being a water-insoluble protein form a bright, transparent and elastic like solution when dissolves in ethanol with heating. Most of the researcher used this material as the base of the film but Moradi and Tajik had discover that this material had potential of being antimicrobial agent [7]. Zein also shown excellent resistance water vapor and oxygen which can give extra protection towards the food [8]. Clove or *Eugenia Caryophyllata* essential oil (CLO) is one of the GRAS natural antimicrobial. This CLO consists of the carvacol, thymol and mainly eugenol [5, 9, 10]. Essential oil (EO) generally more effective in inhibit the growth of the gram positive compares to the gram negative bacteria however, this CLO capable of inhibit the *E. coli* which is one of the gram negative bacteria.

The study conducted using nanoparticle (NP) is wide and varies. The impact of the NP in the study of food packaging towards the UV protection and degradation properties are rarely seen. According to Reed, the study of the reaction occur between the UV light and vast type of beverage are complex and gave negative impact to the color, flavors and nutrition value [11].

The main purpose of this research were to synthesis film packaging using Zein, glycerol and also clove essential oil. Besides that, this study aiming to determine the impact of temperature of solvent casting and the concentration of CLO towards the characteristic and also the UV barrier properties. It was initially expected that increasing in the CLO concentration will increase the barrier properties but decrease in the degradation rate.

II. METHODOLOGY

A. Materials

Zein powder or maize for Sigma Aldrich, clove essential oil from Young Living as the antimicrobial agent, ethanol-water solution as the solvent and glycerol as the plasticizer.

B. Preparation of the film

16 gram of the zein powder is dissolved in the 80 v/v ethanol water solution and stirring for 30 minutes at 80°C. 2.4 gram of glycerol (15% g glycerol/ g dry zein powder) was added to the solution and it was stirred again for 8 minutes at 30°C. Then the clove essential oil at 2.5%, 5%, 7.5%, 10% and 12.5 % (g essential oil/ g dry zein powder) was incorporated. Then this solution is stirred for another 8 minutes.

The pure zein film was undergo solvent casting for 24 hours in at 20°C, 8 hours for 35°C and 20 minutes for 90°C. Then the casting method at 90°C was used for the solution incorporated with the various concentration of CLO. Lastly the film was cool down for 24 hours before peeled.

C. Fourier transform infrared spectroscopy (FTIR)

The samples are tested for the wavelength in range of 4000 and 400 cm^{-1} to detect the vibration characteristics of the functional group in the film solution and also the film [12]. This test is carried out using Fourier Transform Infra-Red (FTIR) Perkin Elmer/ Spectrum One from Perkin Elmer Sdn. Bhd. in the instrument 2 laboratory.

D. UV-Vis

A 60 mm $\times$ 4 mm of biofilms is diluted into 5 ml of 80% of ethanol water solution. The result is compared with the range of ultra violet (UV) wavelength in range of 180 to 290 nm of UVC [3] and the transparency is evaluate at 600 nm .

E. Biodegradation test

Six set of batch reactor were set up. The reactor was filled with the same type of soil in an aerobic condition at room temperature which is 25 – 37 $^{\circ}\text{C}$ [13].

III. RESULTS AND DISCUSSION

A. The effects of temperature of solvent casting to the control film

i. Prepared Film

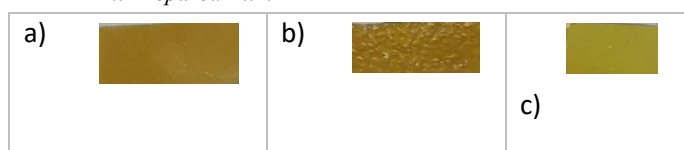


Fig. 1: : Film using solvent casting method a) at 20 $^{\circ}\text{C}$, b) at 35 $^{\circ}\text{C}$ and c) at 90 $^{\circ}\text{C}$.

From Fig. 1: : Film using solvent casting method a) at 20 $^{\circ}\text{C}$, b) at 35 $^{\circ}\text{C}$ and c) at 90 $^{\circ}\text{C}$., it can be seen that film that undergo solvent casting method at 90 $^{\circ}\text{C}$ produce yellowish color instead of brown and more transparent compared to the 20 $^{\circ}\text{C}$ and 30 $^{\circ}\text{C}$. Besides that, the film at the higher temperature of solvent casting process have better strength and easier to be peeled.

ii. FTIR

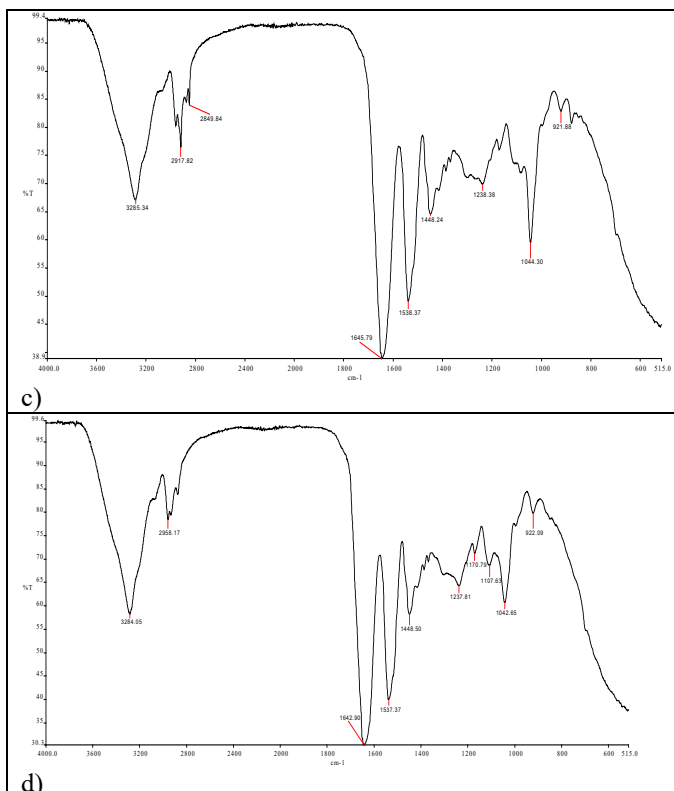
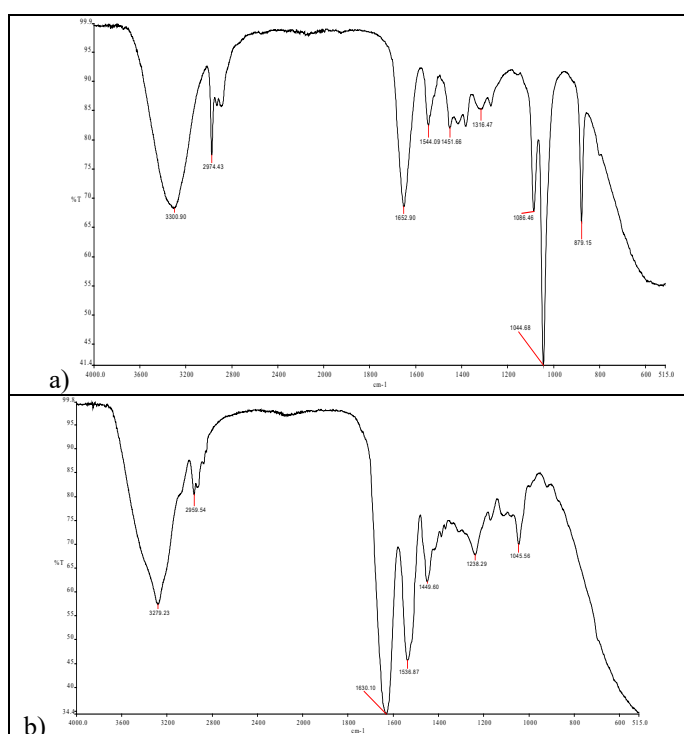


Fig. 2: FTIR for a) solution, b) solvent casting at 20 $^{\circ}\text{C}$, c) solvent casting at 35 $^{\circ}\text{C}$ and d) solvent casting at 90 $^{\circ}\text{C}$.

From Fig. 2: FTIR for a) solution, b) solvent casting at 20 $^{\circ}\text{C}$, c) solvent casting at 35 $^{\circ}\text{C}$ and d) solvent casting at 90 $^{\circ}\text{C}$. Fig. 2(a) for the solution the possible function group that had been detected by the FTIR at 3300.90, 2974.43, 1652.90, 1544.09, 1451.66, 1316.47, 1086.46, 1044.68 and 879.15 cm^{-1} suggest that there it C-H stretch, CH₃ stretching, primary CO, primary amides and secondary NH₂ of amide or aromatic benzenes compound, carbonyl C=O stretch, C-O deformation from carboxylic acid compound and strong nitrogen or oxygen stretch for nitro component.

From Fig. 2 (b,c and d) the functional group that appear in Fig. 2 (a) disappear when it became film which supposed to be the secondary and tertiary CO in aromatic Benzamides or Acetate for aromatic ester. There are also no peak observed in the wavelength at range of 1680 cm^{-1} to 1630 cm^{-1} for the solution.

As the conclusion, with the different of certain functional group that exist in the film but not in solution suggesting that there are chemical conversion occur during the solvent casting method. Therefore, more study for this particular type of film will be needed.

The different temperature of the solvent casting process take place also contribute a significant different to the film packaging. From Fig. 2, FTIR shows that there is a different peak and intensity resulting from different temperature using the same solution. Solvent casting at temperature of 35 $^{\circ}\text{C}$ and 90 $^{\circ}\text{C}$ had been observe to have 12 type of possible functional group functional group. At 35 or 90 with the room temperature, there 10 possible functional group that observed in these two films.

The different occur at the wavelength of 2975-2950, 1650; 3320 – 307, 2840 -3870, 950-900 and 1170 cm^{-1} . Film at room temperature consist of CH₃ symmetric stretching at 2975~2950 cm^{-1} and secondary N-H stretching at 3320~3070 cm^{-1} while the other two does not have this peaks. For the film at 35 degree Celsius the functional group that only appear on this film is CH₃ absorption at wavelength of 2840~2870 cm^{-1} . Lastly, no isopropyl group discover at any films besides the film that under solvent casting at 90 $^{\circ}\text{C}$.

Based on the analysis, at 35 $^{\circ}\text{C}$ and 90 $^{\circ}\text{C}$, the functional group from solution is sustain but 90 $^{\circ}\text{C}$ provide shorter time to be prepared. Therefore the film will undergo solvent casting at 90 $^{\circ}\text{C}$.

Table 1: Functional group detected using the FTIR analysis.

Description	Wavelength (cm ⁻¹)	Solution	Film		
			Temperature (°C)		
			27	35	90
Strong C-H stretch (Alkynes)	≈3300	/	/	/	/
CH ₃ asymmetric stretching (Hydrocarbons)	2975~2950	/	/	-	-
Carboxylic acid OH stretch	3000~2000	/	/	/	/
Secondary NH ₂ (Amide / Aromatic Benzamides)	1570~1515	/	/	/	/
CH ₃ asymmetric deformation (Hydrocarbon)	1470~1440	/	/	/	/
C-O stretch and OH deformation (carboxylic acid)	1320~1210	/	-	-	-
Primary Amide	1080~1040	/	/	/	/
Carbonyl stretch C=O	≈1650	/	-	/	/
Strong Nitrogen/Oxygen stretch	≈870	/	-	-	-
Secondary NH stretching (Amide / Aromatic Benzamides)	3320~3070	-	/	-	-
CH ₃ absorption (Hydrocarbons)	2840~2870	-	-	/	-
Secondary CO (Amide / Aromatic Benzamides)	1680~1630	-	/	/	/
Tertiary CO (Amide / Aromatic Benzamides)	1670~1630	-	/	/	/
C-O stretch and OH deformation (carboxylic acid)	1320~1210	-	/	/	/
Acetate (Aromatic Ester)	1250~1230	-	/	/	/
C-N stretch	1300~1100	-	/	/	/
C-O stretch and OH deformation (carboxylic acid)	950~900	-	-	/	/
Isopropyl group	≈1170	-	-	-	/

- Means does not exist;

/ means that the functional group is possible to be exist

[14]

B. The effects of concentration of clove essential oil on the characteristic of the film.

i. Prepared film



Figure 1: a) pure control film, b) 2.5 wt% of CLO with zein, c) 7.5% of CLO with zein and d) 12.5 wt% of CLO with zein.

Film with higher amount of CLO tend to be more brownish and better in term of strength. This observation is contradict with the result when *Zataria multiflora* Bioess essential oil (ZEO) was added where the film was reported to be more yellowish instead of brownish [6].

Besides that, separation phase occur on 2.5 to 12.5 wt% of the CLO. The size of the separation phase significantly increase with increasing of concentration of CLO.

ii. FTIR

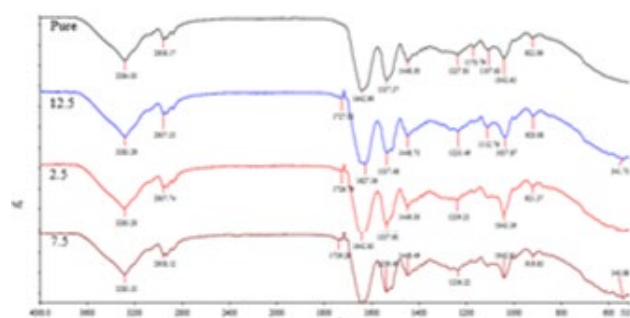


Fig. 3: FTIR spectroscopy for various concentration of clove essential oil.

From the Fig. 3, the film containing the essential oil have similar peak except for two peaks are in the range of 1720-1740 cm⁻¹ and 550 cm⁻¹ compared to the pure zein film. At the wavelength of 1754 to 1695 cm⁻¹ the possible functional group is COOH for amino acids which is observed at all of the film containing essential oil only. Besides that, it is also possible that these films containing aromatic ester for C=O stretch at wavelength of 1715 to 1730 and C=O saturated for 7.5 wt% of essential oil.

iii. UV-vis

Table 2: Absorption value at different solvent casting temperature

Temperature (°C)	Abs (nm)					
	255	360	400	500	600	795
Room Temperature	3.642	0.191	0.098	0.057	0.041	0.020
35	3.745	0.475	0.132	0.064	0.041	0.020
90	4.014	0.392	0.113	0.060	0.042	0.023

From the Table 2, film which undergo solvent casting at 20°C consist the lowest absorption value compared to the other two at range of 255 cm⁻¹. At lower the transmittance value means that better ultra violet screening at the range of 280 nm [15]. From Table 2: Absorption value at different solvent casting temperature, the lowest absorption value in this range is the film at undergo solvent casting at room temperature compared to the other two. Then, transparency is observed at the range of 600 cm⁻¹. The absorption value of these film does not significantly different. This shows that the temperature play little effect on the film transparency.

iii. UV-vis

Table 3: Absorption value at different solvent casting temperature

wt% of Clove Essential Oil	Abs (nm)					
	200	390	395	595	600	800
2.5 wt% CLO	3.466	0.218	0.210	0.062	0.062	0.037
7.5 wt% CLO	3.449	0.134	0.127	0.037	0.037	0.015
12.5 wt% CLO	3.433	0.095	0.092	0.039	0.04	0.021

For wavelength in range of 200 to 600 nm, there is a clear trend for the absorbance behavior. As the concentration of essential oil increased, the absorbance value decreased. This same result had been seen in the Kashiri et al. (2017) [6]. However, in the wavelength with the range above 600 to 800 nm the absorbance value increased for 2.5 to 7.5 wt% and decreased from 7.5 to 12.5 wt% of essential oil. At wavelength of 200 nm, the lowest absorption value is identify as the better ultra violet screening. Hence, zein film incorporated with 12.5% of clove essential oil is better in ultra violet barrier compared to the others.

However, there is no possible trend observed at the wavelength of 600 nm. Since the higher absorption value will gave the more transparent film, film with the 7.5 wt% clove essential oil have to be more transparent and see through compared to the 2.5 and 12.5 wt%.

iv. The effects of concentration of clove essential oil degradation rate.

Table 4: Changes in mass of film after 4 days.

Film	Change in Mass (g)
Pure	0.293
2.5%	0.161
7.5	0.245
12.5	0.128

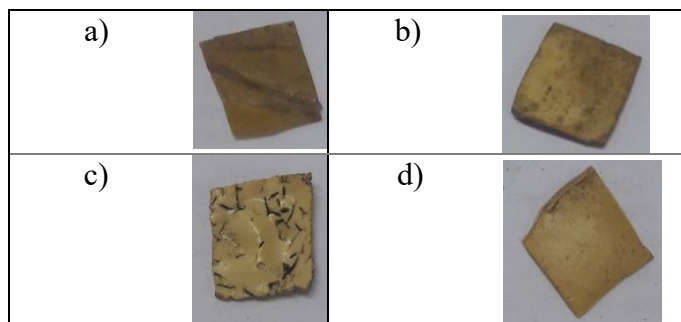


Fig. 4 Film after biodegrading test at day 3 a) pure zein film. b) Zein with 2.5 wt% clove essential oil, c) 7.5 wt% CLO and d) 12.5 wt% CLO

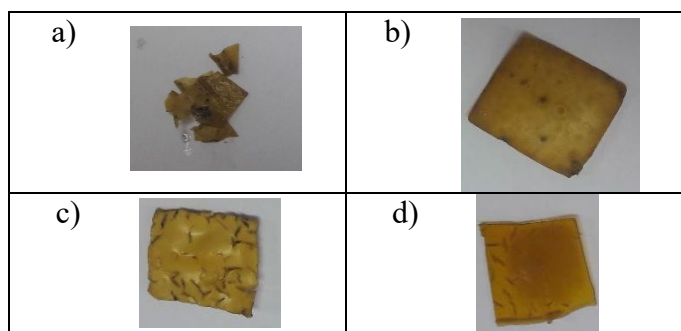


Fig. 5 Film after biodegrading test at day 4 a) pure zein film. b) Zein with 2.5 wt% clove essential oil, c) 7.5 wt% CEO and d) 12.5 wt% CEO.

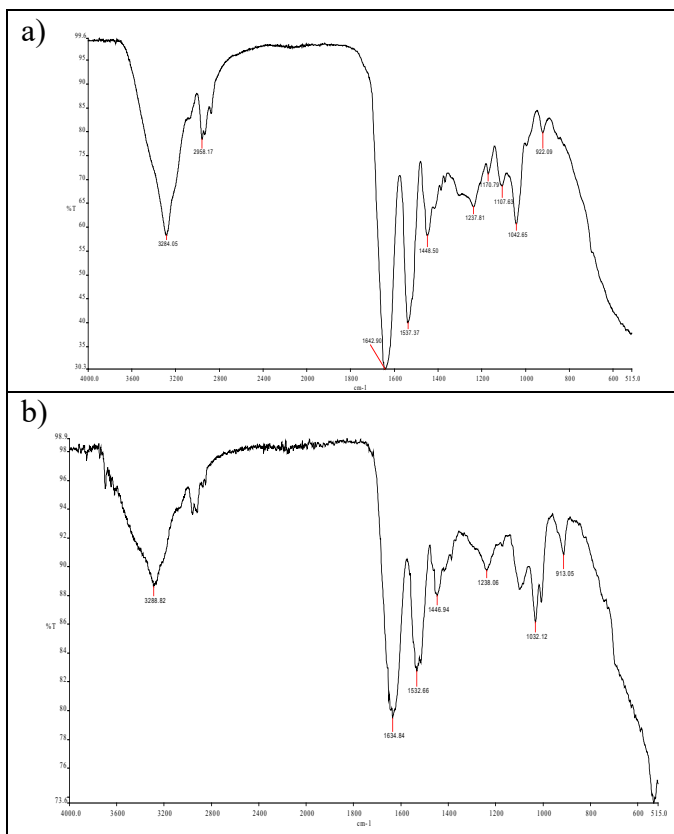


Fig. 6 FTIR result of pure zein film a) before degradation b) after degradation test

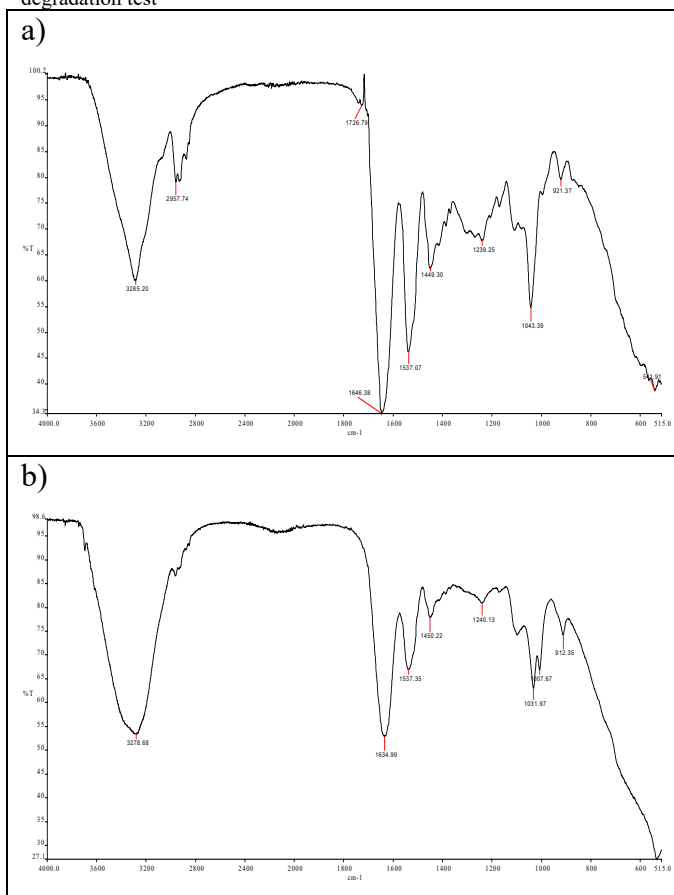


Fig. 7: FTIR result of 2.5 wt% CEO zein film a) before degradation b) after test.

a)

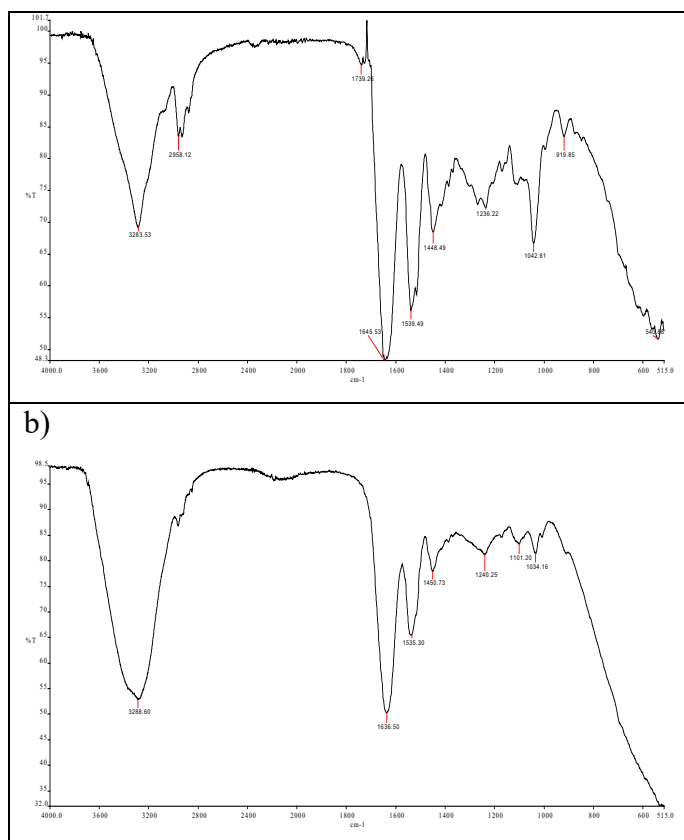


Fig. 8: FTIR result of 7.5 wt% CEO zein film a) before degradation b) after test.

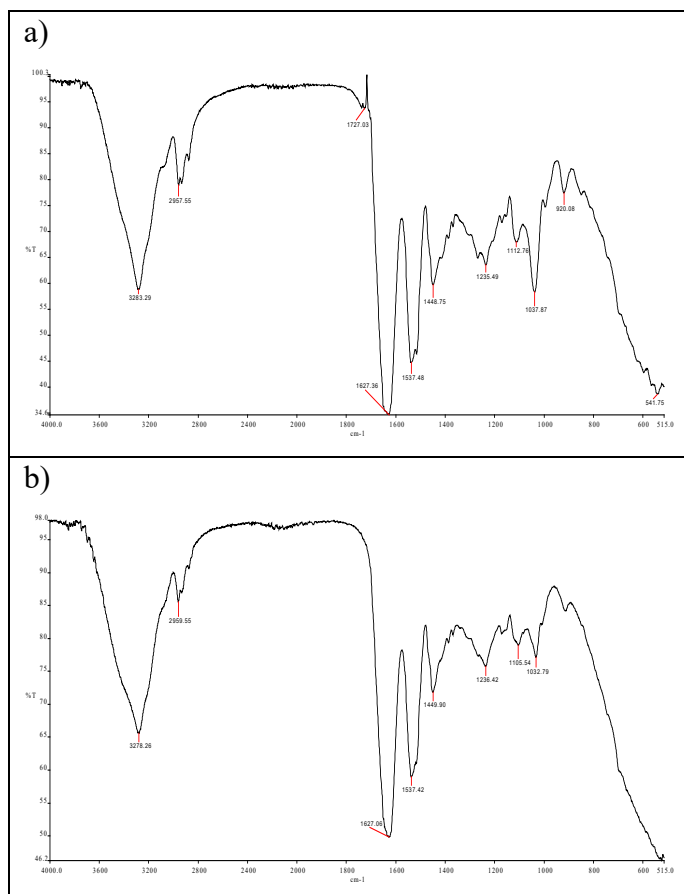


Fig. 9: FTIR result of 12.5 wt% CEO zein film a) before degradation b) after test.

Table 4 shows that film without the CLO undergo the degradation faster than with the CLO. From observation, pure zein film much more brittle and easily broke after the degradation test while the others film still does not lost the flexibility to be bend.

From Fig. 4 and Fig. 5, addition of the CLO does slower the degradation process where the film does not undergo reduction of size easily. At day 3, all of the films is observe to undergo change in color from orange-like color to the yellowish. However at day 4, the film containing 12.5 wt% of CLO reverted back to orange-like color. This film also observed to undergo the lowest change in mass after the degradation. The 7.5 wt% of CLO incorporated into the zein film is undergo highest change in mass compared to the 2.5 and 12.5 wt% of CLO in zein film. This is due to the separation of CLO and zein film is observed at this film. This separation is believe to promote the degradation process of 7.5 wt% zein film. These effect can be observed in the Fig. 4 and Fig. 5 where the separation boundary is covered by the soil. From the Fig. 7 and Fig. 8: FTIR result of 7.5 wt% CEO zein film a) before degradation b) after test. Fig. 8, both film containing 2.5 and 7.5 wt% CLO undergo reduction of peaks detected. Those peaks are at 2957.74, 1726.79, 921.37 and 550 cm⁻¹ which conclude 4 peaks start to disappear from the films. In the other hand, only 3 peaks start to diminish for the case of 12.5 wt% of CLO which conclude that this film undergo the degradation slowest than other three films.

As for 7.5 wt% of CLO in Fig. 8, the peaks at 1649 cm⁻¹ start to change from stiff to board peaks which indicate that this film undergo some changing. However for 12.5 wt% of CLO in Fig. 9 the peaks detected by the FTIR before and after degradation does not have any significant changes compared to the pure zein film.

Even though 7.5 wt% of CLO in zein film is the most favorable for easily degrade film the separation of the phase indicates that the properties of the CLO does not fully utilize in this film therefore zein film with 2.5 wt% is chosen.

Thus, FTIR result in Fig. 6, Fig. 7, Fig. 8 and Fig. 9 support the value from the Table 4. Therefore, pure zein film is the best film in term of biodegradation properties.

IV. CONCLUSION

In this work, food film packaging was prepared and the characteristic tested using the FTIR and UV-vis in order to assess the effect of concentration and temperature on the UV barrier properties and degradation rate.

The result of UV-vis of the film indicate that the transparency and UV barrier properties. The result shows that increasing the concentration of the CLO also increase the UV barrier properties but have no significant effect on the transparency. In this study, film with moderate (7.5 wt %) CLO have the highest degradation rate compared to 2.5 and 12.5 wt% of CLO. This observation was due to the separation phase that occur for this film which make it easier to loss in weight and for essential oil to dissolve in soil.

Overall, addition of CLO into the zein film improved the barrier properties of the film but decreased the rate of degradation compared to the pure film. Therefore, further study on active essential oil that could improve the degradation properties should be done in the future. Besides that, an experiment with lower concentration of CLO should be used in order to observe limitation of it concentration in order to prevent separation phase. An experiment with different temperature for incorporated zein also should be done in order to access the capability of the solvent casting method to sustain all the functional group from solution to its film.

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REFERENCES

- [1] John WS, Raja P, Sundar RAA, Tiroutchelvamae D. Review on - Nanotechnology Applications in Food Packaging and Safety. *International Journal of Engineering Research*. 2014.
- [2] David M. 7 Advantages of Flexible Packaging. *ABCPACKAGING* 2013.
- [3] Jafarzadeh S, Alias A, Ariffi F, Mahmud S. Characterization of Semolina Protein Film with Incorporated Zinc Oxide Nano Rod Intended for Food Packaging. *Polish Journal of Food and Nutrient Science*. 2017.
- [4] Wrona M, Cran MJ, Nerina C, Bigger SW. Development and characterisation of HPMC films containing PLA nanoparticles loaded with green tea extract for food packaging applications. *Carbohydrate Polymers*. 2017;107-18.
- [5] Khaleque MA, Keya CA, Hasan KN, Hoque MM, Inatsu Y, Bari ML. Use of cloves and cinnamon essential oil to inactivate *Listeria monocytogenes* in ground beef at freezing and refrigeration temperatures. *LWT - Food Science and Technology*. 2016;74:219-23.
- [6] Kashiri M, Cerisuelo JP, Domínguez I, Lopez-Carballo G, Muriel-Gallet V, Gavara R, et al. Zein films and coatings as carriers and release systems of *Zataria multiflora* Boiss. essential oil for antimicrobial food packaging. *Food Hydrocolloids*. 2017:260-8.
- [7] Moradi M, Tajik H, Razavi R. SM, Mahmoudin A. Antioxidant and antimicrobial effects of zein edible film impregnated with *Zataria multiflora* Boiss. essential oil and monolaurin. *LWT-Food Science and Technology*. 2016:37-43.
- [8] Zhang Y, Cui L, Che X, Zhang H, Shi N, Li C, et al. Zein-based films and their usage for controlled delivery: Origin, classes and current landscape. *Journal of Controlled Release*. 2015.
- [9] Anaya-Castro MA, Ayala-Zavala JF, Muñoz-Castellanos L, Hernández-Ochoa L, Peydecastaing J, Durrieu V. β -Cyclodextrin inclusion complexes containing clove (*Eugenia caryophyllata*) and Mexican oregano (*Lippia berlandieri*) essential oils: Preparation, physicochemical and antimicrobial characterization. *Food Packaging and Shelf Life*. 2017;14:96-101.
- [10] Nisar T, Wang Z-C, Yang X, Tian Y, Iqbal M, Guo Y. Characterization of citrus pectin films integrated with clove bud essential oil: Physical, thermal, barrier, antioxidant and antibacterial properties. *International Journal of Biological Macromolecules*. 2018;106:670-80.
- [11] Reed W. UV light may be harmful for PET. *FoodQuality news.com*; 2004. p. 22.
- [12] Mazzaglia A, Kenny JM, M Balestra G, Torre L, Yanga W, Owczarek JS, et al. Antioxidant and antibacterial lignin nanoparticles in polyvinyl alcohol/chitosan films for active packaging. *Industrial Crops and Products*. 2016.
- [13] M. Makhtar NS, Rodhi MNM, Musa M, K. Hamid KH. Thermal Behavior of *Tacca leontopetaloides* Starch-Based Biopolymer. *International Journal of Polymer Science*. 2013.
- [14] SCIENTIFIC T. Knowledge Base Infrared Spectral Interpretation: Thermo Fisher Scientific Inc.; 2009.
- [15] Assifa Rahma Khoirunnisa, I Made Joni, Camellia Panatarani, Emma Rochima, Praseptianga D. UV-screening, transparency and water barrier properties of semi refined iota carrageenan packaging film incorporated with ZnO nanoparticles. *American Institute of Physics*. 2018.