Effect of Polyvinylpyrrolidone on Biodegradable Film Derived from Chitosan-Poly(Vinyl Alcohol) for Plastic Packaging Application

Nurul Umirah binti Idris and Dr. Istikamah binti Subuki

Faculty of Chemical Engineering, Universiti Teknologi Mara

Abstract— ***Plastic waste disposal has become a very serious problem because of its high volume of solid waste and takes a very long period of times to decompose because it was made up from non-biodegradable synthetic polymer. Blending of natural polymer and synthetic polymer is one of the options to reduce the time of decomposition. Various study of blending of chitosan with PVA is conducted in the past to overcome this issue. It shows that the blended film of chitosan and PVA have good film forming properties. In this study, it covers the effects of addition of PVP into those blended film. PVP is synthetic polymer that also has good film forming properties. Plastic film is prepared by using different ratio of chitosan-PVA with addition of different concentration of PVP solution. The plastic films were subject to mechanical property testing using testing machine. It was found that the addition of PVP does improve the properties of the chitosan in terms of mechanical properties. Swelling test and FTIR Analysis was conducted to determine the chemical nature of film and to determine the functional group of the plastic films. The swelling test of plastic film was carried out to determine the degree of swelling of the plastic polymers.***

Keywords— Biodegradable, Chitosan, PVA, PVP, Blending

I. INTRODUCTION

The redundant of non-biodegradable plastic in this world has grown concern from all sides. Most plastics are derived from synthetic polymers such as polyethylene, polypropylene, polystyrene, poly(vinyl chloride) and poly(ethylene terephthalate) which are non-biodegradable material. A very long period of time are require in order to decompose this material; up to 1000 years or maybe more has bring worry from all people as it involving environmental concern and bring impact to health. Non-biodegradable plastic also may produce toxic in content.

So, a solution must come in order to replace the non-biodegradable plastics into plastics that are derived from biodegradable polymers, which are environmentally friendly and obtained from renewable resources to reduce solid waste from petroleum-based packaging material.

Biodegradable polymer can reduce the environmental pollution as it will reduce the amount of solid waste at the landfill. Biodegradability is not only functional requirement but also an important environmental attribute. So, the use of natural polymer in manufacturing edible or biodegradable material for packaging has greatly increased. There three types of natural polymers which are polynucleotide, polypeptides and polysaccharides. The examples of natural polymer are protein, lipids, and polysaccharides (cellulose, starch and chitin/ chitosan).

The blending of natural polymer with synthetic polymer is one of the solutions to produce biodegradable plastic film. A study conducted by the

Chitosan is types of polysaccharides that are very useful in broad range of applications including medical, pharmaceutical, chemical, agricultural and environmental fields. This has grown a lot of interest **in** the development of the characteristics of the chitosan. Chitosan is a natural polymer that has unique properties which are biodegradability, biocompatibility, non-toxicity and antibacterial and hydropholicity.

The blending of natural polymer with synthetic polymer occupies a special position in various applications including packaging application. Polymer blending is one of the most effective methods to have new material with desired properties. The main purpose of blending the polymers is to obtain materials of additional properties with minimum sacrifice to their original properties (Gaikwad,U.V. & Pande,.S.A.,2013).

Polyvinyl Alcohol (PVA) is nontoxic, water –soluble synthetic polymer, which is widely used in polymer blends because of its good physical and chemical properties and excellent film forming characteristics and emulsifying capability. The addition of cross linkers also has been widely studied in improving the textural properties of the film.

Polyvinylpyrolidone (PVP) which has good properties such as good film formation, has good adhesiveness is added to the plastic film. PVP is an excellent film-former that forms stiff, transparent and shiny films. PVP has the benefits in conjunction with other polymers to boost performance.

II. METHODOLOGY

A. *Materials*

Chitosan in the form of powder, with medium molecular weight, deacetylated chitin was obtained from Agensi Nuklear Malaysia,Selangor, Poly(D-glucosamine). Poly(vinyl alcohol), in the form of powder, 98 – 98.8% hydrolyze with molecular weight of 146 000 – 186000). Polyvinylpyrrolidone(molecular weight 40 000), 1.0 M Acetic acid to dissolve chitosan.1.0 M Sodium Hydroxide use to was away excess acetic acid in blended film.

B. *Preparation of the Solutions*

Chitosan solution was prepared by dissolving chitosan in 1%(w/v) aqueous acetic acid. This is because chitosan is not soluble in water, so acetic acid is use as a solvent to dissolve chitosan. The solution is continuously stirred by using magnetic stirrer at speed 2000 rpm at room temperature for 48 h. Then, the chitosan solution was put into centrifuge for 1 hr at 5000 rpm to remove any impurities in the solution. Then, the solution was filtered by Vacuum Pump Filter to remove any entrapped air. Then, the PVA solution was prepared by diluting it in distilled water. The PVA solution was stir at 2000 rpm at 50℃ to make sure that the PVA was dissolved completely in the solution. The PVP solution was prepared by dissolved in distilled water. The solution was swirled properly to make sure that the PVP dissolved in distilled water. Different concentration of PVP solution was prepared. 1%(w/v),3%(w/v) and 5%(w/v) of PVP solution was prepared.

C. *Preparations of Chitosan/PVA Blended Solutions*

The method use in the preparation of the chitosan/poly(vinyl alcohol)- polyvinylpyrrolidone blended solution is casting method. Chitosan solution and PVA solution are mix in various proportion. Continuous stirring was performed by using magnetic stirrer for 30 min after mixing both solutions. The composition of chitosan and PVA (CS/PVA) were varied from 90/10 to 50/50 by volume. Table 1 shows the designated compositions for the solutions for the Chitosan/PVA blending.

Table 1: Composition of Chitosan/PVA Blending

Sample	Chitosan (%)	PVA(%)
CS/PVA 90/10	90	10
CS/PVA 70/30	70	30
CS/PVA 50/50	50	50

D. *Preparations of Blended Films*

The preparation of the blended films was carried out at various proportions. The chitosan and PVA solution was mixed according to the ratio and stirred by using magnetic stirrer for 30 min to make sure that the solution was fully mixed Then, 10 ml of each of composition of chitosan and PVA mixture are casting in petri dish by using syringe. The thickness of the film was controlled by the volume of the solution. Then, step followed by drying the plastic film at room temperature for 48 h. Then, the dry film was immersed with 25 ml of sodium hydroxide for 60 min in the petri dish to remove excess acetic acid. Then, the film was washed with distilled water to remove the sodium hydroxide at the surface of the films. Then, PVP solution was added to the CS/PVA films in the petri dish for 15 minutes. Then, the films were dry for 48h before it was carefully peeled. Table 2 shows the designated concentration of PVP solution added into CS/PVA films.

Table 2: Concentration of PVP solution added to the blended film

Ratio of CS-PVA	Concentration of PVP,%
9:1	Without PVP
	1
	3
	5
7:3	Without PVP
	1
	3
	5
5:5	Without PVP
	1
	3
	5

E. *FTIR Analysis*

FTIR Analysis was conducted to determine the chemical nature of film and to determine the functional group of the plastic films.

F. *Thickness of the film*

Film thickness was determined by using Mitutoyo thickness gauge. Measurements of five different spots of each film samples were taken and the average thickness of the films is calculated and recorded.

G. *Mechanical Testing*

Tensile strength of the film was measured by using Tinius Olsen H50KT Tensile Machine in accordance with ASTM D882 method. The films were cut into 10 mm wide and 60 mm long. The testing was done with speed at 3 mm/min and 2.5kN load. The average value is taken after five specimens of each sample were tested. Gripping of the films need to be carry out carefully to prevent any failure and slipping of the films from the clamps.

H. *Swelling Tests*

The swelling test was performed to determine the water uptake ability of the prepared films. Swelling test is conducted to check whether the films retain the original properties (Yaradoddi, 2016). Swelling test is performed by immersed the films in distilled water at room temperature for 13 h. Before that the weight of the film was measured and recorded. Then, the excess water on the surface of the films was removed by blotting the surface with tissue paper and the weight of the films was recorded. The degree of the swelling is determined by using the formula below

$$Degree\ of\ swelling = \frac{W_2 - W_1}{W_1} x\ 100\% \qquad (1)$$

Where, W_1= Weight of completely dries sample
W_2= Weight of swelled sample

III. RESULTS AND DISCUSSION

A. *Appearance of the films*

Figure 1: Plastic Film

Figure 2 shows the plastic film made up from the blending of chitosan with PVA and crosslink with PVP. The appearance of the plastic films showed that there is small bubbles appeared on the surface of the films. The bubble formation is commonly known as blistering which is a buckling phenomenon normally found in various film deposition process (Kyeong *et.al,*2012). During the stirring process by using magnetic stirrer, the bubble was started to form and it was still existed even the blended solution was poured into the petri dish. The formation of bubbles will automatically affect the mechanical properties of the film including affect the stability and cause to rupture (Kosior *et.al*, 2013)

B. *Tensile Strength Properties*

Tensile strength is a material that can support a maximum load without any fracture when being stretched. The tensile strength of the plastic films is shown in Figure 2. With the addition of PVP onto the Chitosan-PVA films, the tensile strength of the film was observed. From the Figure 2, it shows that the tensile strength is affected by the addition of PVP solution. The tensile strength with the addition of PVP solution increased as the concentration of PVP solution increased compare to the blended films without the addition of PVP solution. This shows the addition of PVP does help increasing the tensile properties of the film. The increasing of the tensile strength is due to the intermolecular interaction and interfacial adhesion among the components (Ravindra *et.al*, 2015) through hydrogen bonding. The hydrogen bond between hydroxyl group (-OH) of PVA with (-NH_2) of chitosan and carbonyl group (-C=O) of PVP help in increasing the tensile strength of the films. From figure 3, the tensile strength of ratio 7:3 of CS/PVA with 5% PVP shows the highest tensile strength. This shows that the plastic films made up ratio of chitosan:PVA 7:3 with addition of 5% PVP is toughest one compare to the other plastic films.

Figure 3 also shows that increasing amount of chitosan and decreasing amount of PVA increase the tensile strength of the films. The study conducted by Esam *et.al,* 2010 and Abraham, 2016, also shows the similar result. This is because of the positively-charged polysaccharide chitosan moved toward the negatively charge of the hydroxyl group of the PVA which improved the tensile strength of the film. This happens because of the occurrence of intermolecular interactions with chitosan and PVA through hydrogen bond formation (Abraham *et.al,* 2015).

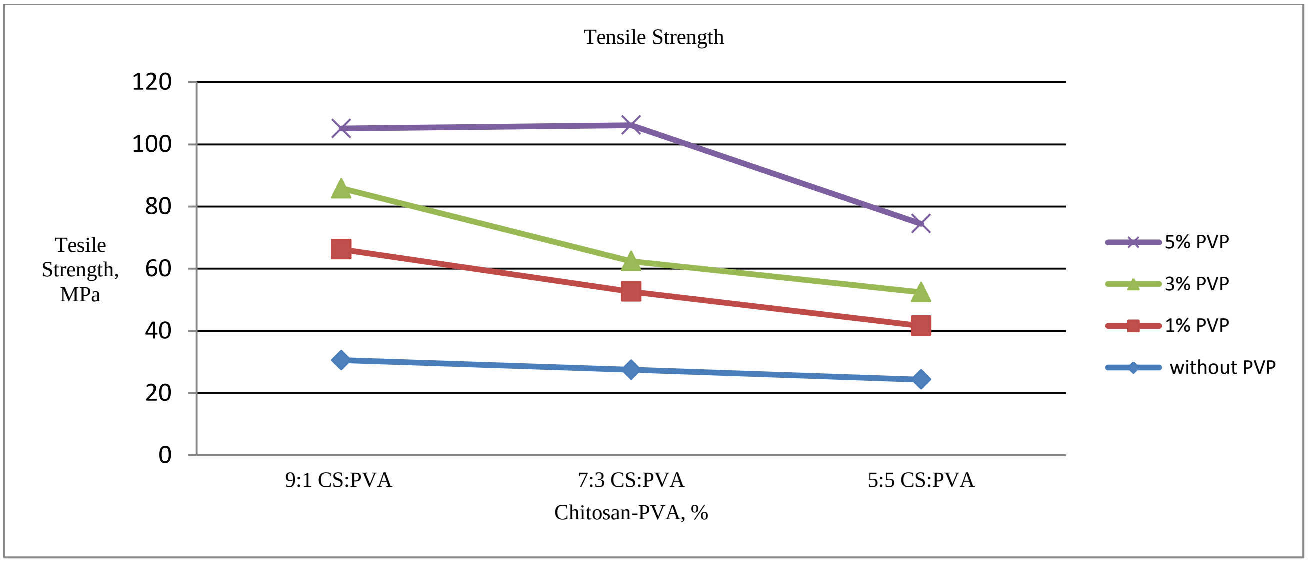

Figure 2: Tensile Strength of the Plastic Fil

C. *Elongation at Break*

Elongation at break or fracture strain showed the final length of the specimen after breakage of the test specimen. The elongation at break is determined with tensile strength. From the Figure 4, it shows that as the concentration of PVP solution increased, the elongation at break increased. This indicates that the film with increasing amount of PVP is tougher.

The graph also shows that the same ratio between chitosan and PVA with increasing concentration of PVP is higher compare to the other films. This also indicates that the films are tougher compare to the films.

It also shows that as the amount of chitosan increased in blending of CS/PVA, the elongation at break decreased. It also shows that the addition of PVP solution into the ratio of 9:1 CS:PVA has low value of elongation at break. This indicates that the film is brittle made it easy to degrade.

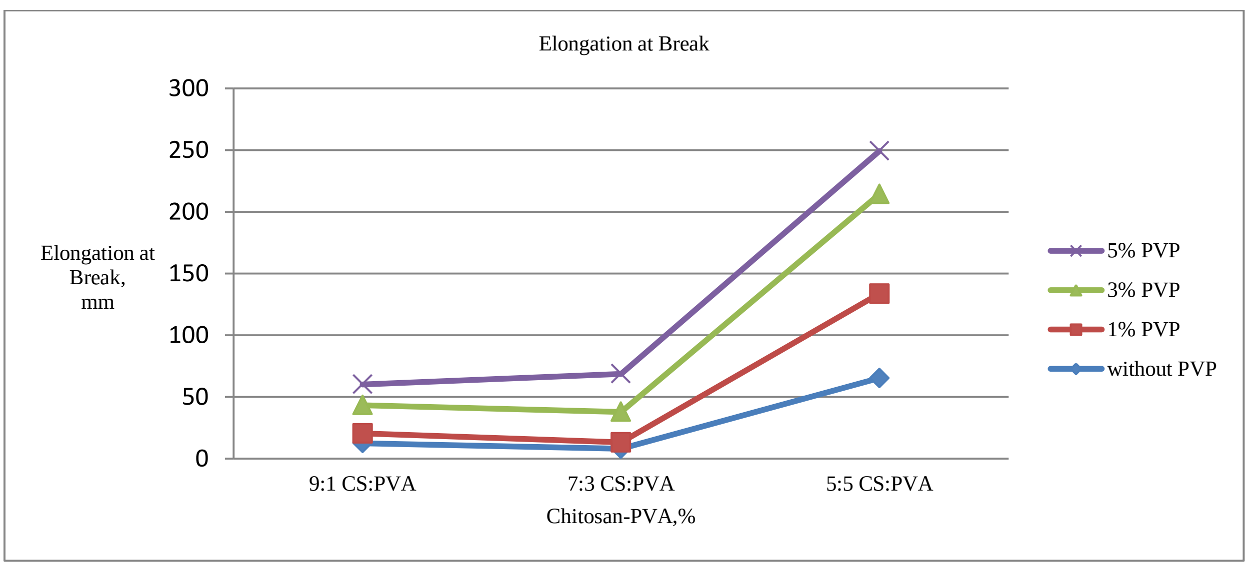

Figure 3: Elongation at Break of Films

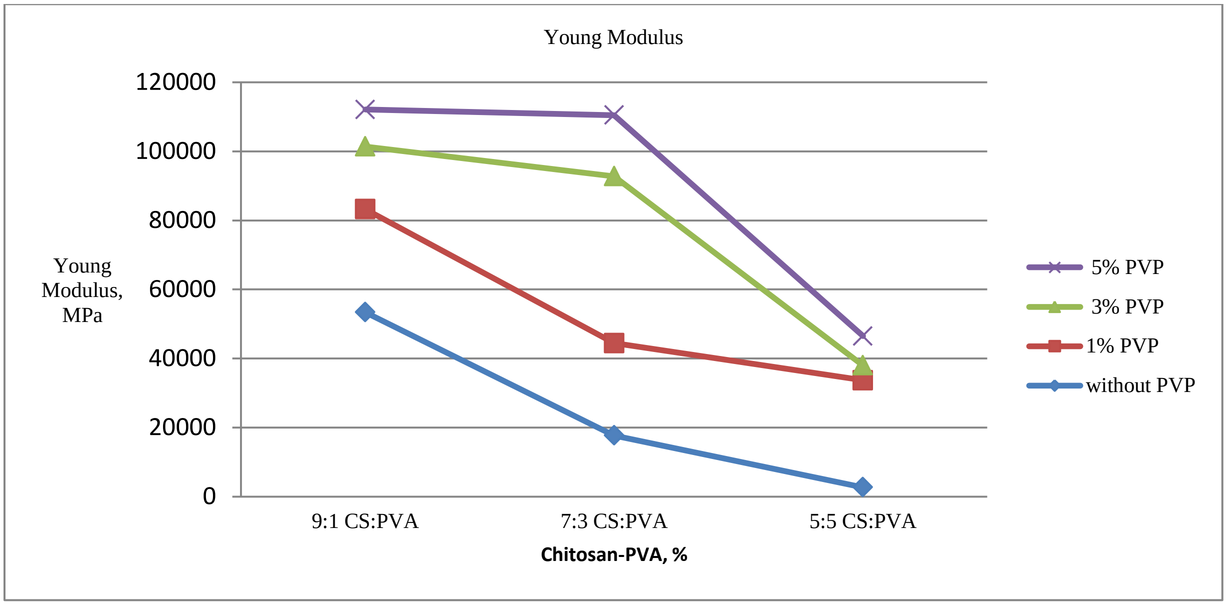

Figure 4: Young Modulus of Plastic Films

D. Young Modulus

Young Modulus is calculated to describe the elastic properties of the plastic film undergoing tension or compression in only one direction. From Figure 4, it shows that as the concentration of PVP solution is increasing, the Young Modulus of plastic films increased. It also shows that the as the amount of chitosan increased in the blending solution, the Young Modulus also increased. According to the Jason *et.al*, 2001, the values of the Young's Modulus are dependent to the value of tensile strength and elongation at break. Young Modulus is an indicator of the stiffness of the film. Figure 4 shows the Young Modulus of the plastic films. The graph shows that as the concentration of the PVP solution added to the blended films increased the Young's Modulus increase. It shows that addition of PVP solution increase the ability of the plastic films to withstand changes when under force.

E. Swelling Test

Based on the observation on the plastic film, the film containing higher amount of PVP solution swell more compare to the other film. Based on Figure 5, as the concentration of PVP increase, the degree of swelling also increased. This is because PVP is water soluble polymer. It also shows that as the amount of chitosan decreased in the blending film, the degree of swelling increased. This happens because PVA is a water-soluble polymer and the blending of chitosan with PVA tends to increase the water uptake due to the increasing hydrophilics groups (-OH) in the blends. The higher degree of the plastic film's swelling makes it easier to absorb water. Figure 5 show that ratio of CS: PVA 5:5 with addition of 5% PVP solution has high degree of swelling compare to the other plastic films. High degree of swelling indicates that the films are low quality material (Yaradoddi *et. al*,2016) . Since chitosan is not soluble in water, the degree of swelling of plastic films containing high amount of chitosan has low degree of swelling. So, film containing higher amount of chitosan is high quality plastic compare to other films.

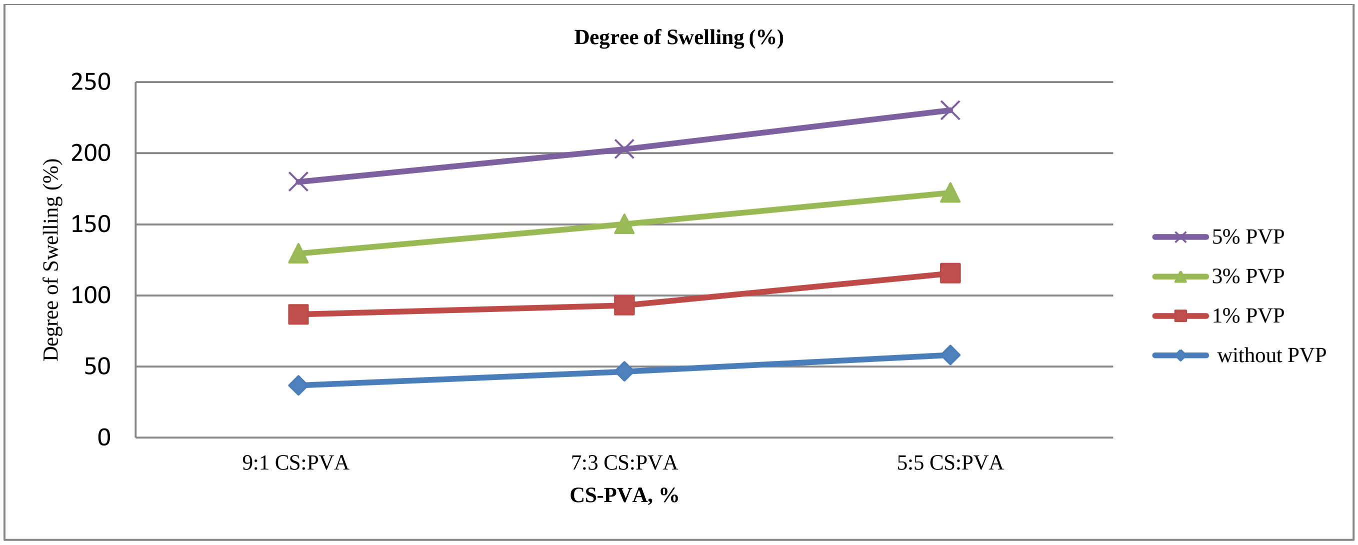

Figure 5: Degree of Swelling of Plastic Film

F. *FTIR Analysis*

The Chemical nature of the plastic film was determined by using FTIR Analysis. Figure 6 shows the peak in absorbance wavenumber for the plastic film 7:3 CS:PVA. Figure 7 shows the peak in absorbance wavenumbers for the plastic film 7:3 CS:PVA 5%PVP. This two figure was chose in order to investigate the difference in peak between films with addition of PVP and films without addition of PVP. Both of the film show absorbance wavenumber spectrum range from 1000-1300 which is C-O-C Stretch. Both films show the highest peak with –NH amide since both film contains same ratio of chitosan. Both plastic films show the absorption rate in the range of 2100-2660 cm^{-1}. The functional group Alkynyl C≡ C Stretch.

The difference in Figure 6 & 7 is , Figure 7 shows the absorbance wavenumbers spectrum range from 3550-3200. The functional group is Alcohol –OH Stretch. This is due to the fact PVP solution is added to the blended film between Chitosan and PVA. The absorbance wavenumber spectrum range of Alkyl C-H stretch is higher in Figure 8 compare to the Figure 7. This is due to the addition of PVP solution into the blended film increase the intermolecular hydrogen bond between the components.

.

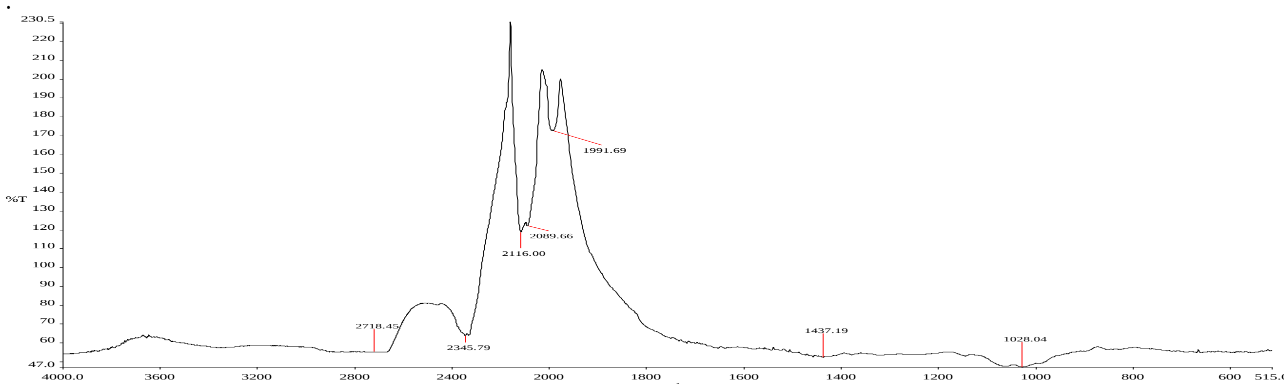

Figure 6: FTIR Analysis for CS: PVA 7:3

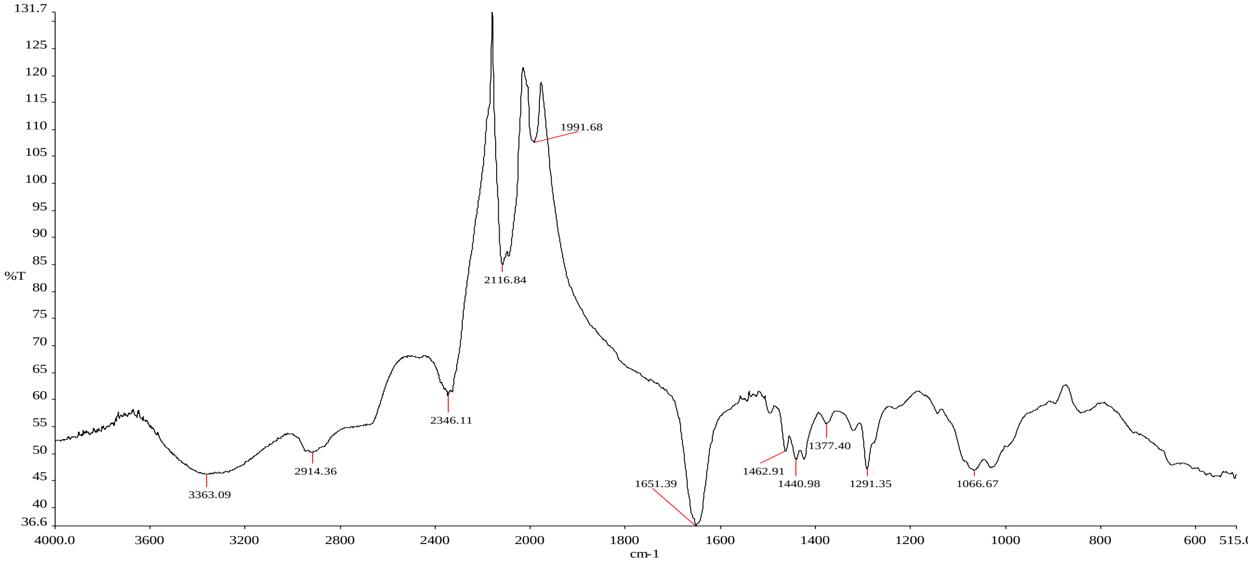

Figure 3: FTIR Analysis for CS:PVA 7:3 5% PVP

IV. CONCLUSION

As the conclusion, the addition of PVP solution to the blended film does improve the properties of the plastic films. The mechanical properties of the cross-linked films were successfully enhancing the mechanical properties of the plastic film. It shows that the addition of synthetic polymer to the chitosan (natural polymer) has changed its characteristics without changing its behavior. Addition of PVA and PVP increase the mechanical properties of the plastic films. It also shows that the addition of PVA and PVP increase the degree of swelling of the plastic films.

ACKNOWLEDGMENT

Thank you to Dr Istikamah Subuki and Universiti Teknologi Mara.

References

[1] A, G. U. V. P. S. (2013). A review of biopolymer chitosan blends in polymer system. *Journal of Science & Engineering, 1*, 13-16.

[2] Abdul Aziz, N. A. e. a. (2014). Synthesis Of Chitosan-Grafted-Poly(Methyl Methacrylate) With Fenton's Reagent (Fe2+ - H2o2) As A Redox Initiator. *The Malaysian Journal of Analytical Sciences, 18*(2).

[3] Abraham, A., Soloman, P. A., & Rejini, V. O. (2016). Preparation of Chitosan-Polyvinyl Alcohol Blends and Studies on Thermal and Mechanical Properties. *Procedia Technology, 24*, 741-748. doi: http://dx.doi.org/10.1016/j.protcy.2016.05.206

[4] Bahrami, S. M., Kordestani,S.S., Mirzadeh, H. & Mansoori, P (2002). Poly (vinyl alcohol) - Chitosan Blends: Preparation, Mechanical and Physical Properties. *Iranian Polymer Journal, 12*, 139-146.

[5] C. M. A. Cruz, C. A., Dabu, E. P. Rescober. (2006). Effect of blend ratio of PVA-Chitosan-Glycerol films in their mechanical properties. 21-30.

[6] Chauhan, D. S., Bhattacarya, S. & Mueen, A.K.K. (2012). Comparative in vitro antioxidant evaluation of different extracts of *Camelis sinesis* leaves from different geographical locations in India. *Department of Pharmacuetical Sciences*.

[7] Chiefari, J., Chong, Y. K., Ercole, F., Krstina, J., Jeffery, J., Le, T. P. T.,et al. . (1998). Living free-radical polymerization by reversible addition fragmentation chain transfer: The RAFT process. *Journal of Macromolecules, 31*.

[8] Destarac, M., Bessiere, J. M., & Boutevin, B. (1998). Atom transfer radical polymerization of styrene initiated by polychloroalkanes and catalyzed by CuCl/2,2 '-bipyridine: A kinetic and mechanistic study. *Journal of Polymer Science Part A – Polymer Chemistry, 36*(16).

[9] Esam Abdulkder, M. M. N., Abdul Hamid Yahaya. (2011). Preparation and Characterization of Chitosan/Poly(Vinyl Alcohol) Blended Films:Mechanical, Thermal and Surface Investigations. *J. Chem.Soc.Pak, 8*(1), 11.

[10] Esam Abdulkder, M. M. N., Abdul Hamid Yahaya. (2014). Chitosan-Based Polymer Blend: Current Status and Applications *J. Chem.Soc.Pak*.

[11] Haweel, C. K. A., S.H. (2008). Preparation of Polyvinyl Alcohol from Local Raw Material. *Iraqi Journal of Chemical and Petreoleum Engineeering, 9*, 15-21.

[12] Honarkar, H. B., M. (2009). Applications of biopolymers I : Chitosan

[13] Hua, D., Tang,J., Cheng, Jianxin.,Deng,Weicai., Zhu,X. (2007). A novel method of controlled grafting modification of chitosan via RAFT polymerization using chitosan-RAFT agent. *Journal of Carbohydrate Polymers, 73*, 98-104.

[14] Keong, K. H. P., O.V., Kim, H.J. & Kim, D.E. (2012). Effectiveness of bubble structure in contact damage the redustion of the film. *Tribology international*, 40-45.

[15] Kosior, D., Zawala,J.,Todorov, R., Exerowa, D. & Malsya,K. (2013). Bubble bouncing and stability of liquid films formed under dynaic and static conditions from n-octanol solutions.

[16] Liu, Z., Wu, G. & Liu, Y. (2006). Graft copolymerization of methyl acrylate onto chitosan initiated by potassium diperiodatoargentate (III). *Journal of Applied Polymer Science, 101*(1), 799-804.

[17] Mitelut, A. C., Tanase, E.E., Popa, V.L., . (2015). Sustainable Alternative for Food Packaging: Chitosan Biopolymers-A Review. *Agrolife Scientific Journal, 4*(2).