RMUTP Research Journal Special Issue
The 4th Rajamangala University of Technology International Conference

Improvement of Solution-Cast PVA Films Properties by Na-CMC Blending for Biodegradable Applications

Daranee Khunphet[1*], Pimchanok Bunmek[1], Chinanat Witthayaprapakorn[2], and Winita Punyodom[3]

[1]Department of Science (Chemistry), Faculty of Science and Agricultural Technology, Rajamangala University of Technology Lanna, Nan Campus, Phupeang, Nan 55000, Thailand
[2]Department of Science (Chemistry), Faculty of Science and Agricultural Technology, Rajamangala University of Technology Lanna, Chiang Mai Campus, *Chiangmai* 50300, Thailand
[3]Biomedical Polymers Technology Unit, Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

Abstract : Properties of biodegradable polymer, polyvinyl alcohol (PVA) were improved by blending with carboxymethyl cellulose sodium salt (Na-CMC). The blended films were prepared by casting solution technique. Their structure and properties were investigated by varied techniques such as scanning electron microscopy (SEM), differential scanning calorimeter (DSC), water vapor permeability, water solubility and measurement of tensile strength. Results showed that the blended films were thin sheets of uniform thickness of 86.33-95.67 μm, with good coherency, clearness, translucence and flexibility. The SEM analysis showed that surface of the blended films with high PVA ratio was smooth. Based upon the observation on DSC, it was found that the melting temperature of PVA decreased when the amount of Na-CMC in the blended film increased. The blended films exhibited higher water absorption that was indicated by water solubility and the water vapor permeability was also studied. The tensile properties were studied and percentage of strain at break increased with the increasing amount of PVA. From this work, it was found that the 50:50 %wt of PVA and Na-CMC blended film gave the best results as the most optimum miscibility between the two components. Moreover, the addition of glycerol causes a reduction of the TS due to the decrease in the intermolecular. It also shows effect on the percentage of strain at break. When increasing amount of glycerol, it was found that percentage of strain at break also increased.

Keywords : blended film, solution cast, biodegradable

Corresponding Author:* Science_rmutlnan2011@hotmail.com Tel. +66 5471 0259

1. Introduction

Biodegradable polymer films have been studied for application in a variety of fields, such as chemical engineering, medicine, pharmaceuticals, food and agriculture. New polymeric materials are constantly sought for food packaging applications [1]. PVA is one of Biodegradable polymers used as a moisture barrier film for food supplement tablets and for foods that contain inclusions or dry food with inclusions that need to be protected from moisture uptake [2]. The US Food and Drug Administration (FDA) allows PVA utilize for as an indirect food additive in products which are in contact with food. They has also been approved for use in packaging meat products by the Meat Inspection Division of the USDA and approved for use in packaging poultry products by the Poultry Division of the USDA [3].

PVA was produced by the polymerization of vinyl acetate; which is then hydrolyzed into PVA [4]. PVA has good film forming properties and highly hydrophilic water soluble with outstanding chemical stability it was blended different synthetic and natural polymers. It is used as a water-soluble film useful for packaging [5]. Su et al. [6] prepared the soy protein isolate (SPI)/PVA blend films. The results showed that the SPI/PVA blend of biocompatible polymers combined the advantages both components, and sharply improved the flexibility.

The food packaging films must possess the appropriate mechanical properties for extending the shelf life of foods. Cellulose derivatives have good film making properties. Their based films are transparent, flexible, relatively good oxygen, aroma, can act as carbondioxide barrier also have low water vapor. Na-CMC is a naturally polymer occurring water soluble adhesive polymer. It is broadly applied in a lot of industrial sectors such as food, paper making, paints, pharmaceutics, cosmetics and mineral processing [7]. Addition Na-CMC to PVA has a marked influence on its properties depending on its ratio and compatibility of the individual polymers. The aim of this work was to fabricate films with blends of PVA and Na-CMC by solution casting method, and to study their structure and properties using varied techniques such as SEM, DSC, water vapor permeability, water solubility and measurement of tensile strength. Moreover, the effect of glycerol addition in PVA/Na-CMC blended films on mechanical properties such as the stress at break and percentage strain at break were investigated.

2. Materials and Methods

2.1 Chemicals

87% hydrolyzed PVA of average molecular weight *125,000* g mol^{-1} was purchased from *BDH* Chemical Ltd (England). Na-CMC with molecular weight of 700,000 g mol^{-1}was purchased from Acros Organics. Glycerol as the plasticizer was purchased from Sigma aldrich.

2.2 Preparation of blend film

PVA/Na-CMC thin films were fabricated by solution casting technique from solutions in hot water as solvent using a Petri dish as a casting surface. The solution were mixed by varying PVA/Na-CMC mass ratios of 100/0, 80/20, 60/40, 50/50, 40/60, 20/80 and 0/100. The mixed solutions were stirred for 6 hours before casting onto clean Petri-dish. The solvent was allowed to evaporate at room temperature for 48 hours. Then, the dried samples in the form of films were peeled off from the glass and further dried in vacuum desiccators for 3 days. Another series of PVA/Na-CMC mass ratios of 50/50 with addition of glycerol (0 - 25%wt) were prepared using the method above.

2.3 Characterization Methods

2.3.1 Differential scanning calorimetry (DSC)

The DSC was performed with a Perkin-Elmer Pyris DSC7 in a nitrogen atmosphere. The samples were sealed in aluminum pan (3-5 mg) and all the scans were carried out from 0 to 250°C at heating rate of 10 °C/min. The thermal properties of the polymer blends were determined using two scans. The 1st heating conducted to eliminate the residual water and solvent. The T_g, T_m and Enthalpy (ΔH_m) were determined from the second heating scans.

2.3.2 Tensile testin

Tensile strength (TS) and % strain at break were evaluated for each film using the Lloyd's tensile testing machine (LRX model) a according to the ASTM D882-91 with a crosshead speed of 50 mm/min. The gauge length was 50.0 mm. Each specimen had a width of 10 mm. The average thickness of the specimen was about 80-95 μm. The thickness of the films was measured with a digital gauge.

2.3.3 Morphological observation

The blend films were mounted on aluminum stubs with graphite-filled tape and vacuum coated with gold-palladium. The surface morphology of blend films was investigated by scanning electron microscopy (SEM) (JEOL JSM 5910-LV) at an acceleration voltage of 15 kV and spot size 22.

2.3.4 Water solubility

Solubility in water was defined as the percentage of the dry matter of film which is solubilized after 1 hour immersed in water. Film specimens were dried in the vacuum oven at 80 °C untill reached a constant weight (W_1). Then, the 500 mg of each films were immersed in the beaker contain 100 mL of distilled water at 30 °C for 1 hour. Finally, the films were removed from the water then dried in the vacuum oven at 80 °C until reached a constant weight (W_2). The percentage of the total soluble matter (%TSM) was calculated by using equation 1[8].

$$\%TSM = \frac{W_1 - W_2}{W_1} x100 \qquad (1)$$

2.3.5 The water vapor permeability (WVP)

The WVP was carried out by ASTM method E96-95 [9] with some modifications. The test films were cut into Petri dish then placed on another Petri dish with 20 ml distilled water to expose the test films to 100% relative humidity as shown in Figure 1. After that, the cup water test were kept in an incubator at 30 ± 1 °C and 50% humidity. The weights of the films were measured using an analytical balance (± 0.0001 g) every day for 4 days. The relationship between the weight loss and time was plotted then the slope of the linear regression was used to calculate the water vapor permeability (WVP) by equation 2 [11-12].

$$WVP = \frac{Slope * L}{A * S * (RH_1 - RH_2)} \tag{2}$$

Where, A is the area of the exposed film surface (m^2), S is saturation vapor pressure at test temperature (kPa), L is the thickness of the test films (mm) and (RH_1-RH_2) is the relative humidity gradient used in the experiment.

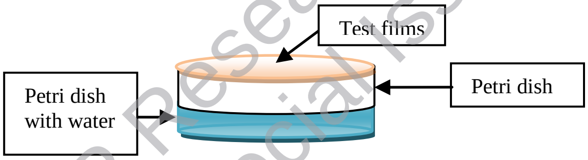


Figure 1 Schematic representation of cup water test

3. Results and Discussion

3.1 Characterizations of the PVA/Na-CMC blended films

3.1.1 Appearance and Thickness

The average thickness of the films was about 86.33-95.67 μm. All of blend films were good coherency, clear, translucent and transparent.

3.1.2 Thermal properties

The thermal properties of pure PVA, pure Na-CMC and PVA/Na-CMC blended are summarized in Table 1. PVA exhibited glass transition temperature (T_g) and melt peak temperature (T_m) at 75 and 185 °C, respectively, otherwise pure Na-CMC exhibited T_g at 123 °C while as T_m peak disappeared. As the content of Na-CMC increased, T_m of PVA became less prominent and disappeared because of the interchain hydrogen bonds between the -OH groups of PVA and C=O groups of Na-CMC [7, 13]. The depression of the melting point of a crystalline polymer component in a blend provides important information about its miscibility. To improve the compatibility between PVA and Na-CMC, suitable plasticizer should be added. The glycerol was used as plasticizers to enhance the dispersion and the interfacial affinity in PVA/Na-CMC blends. So, addition of plasticizers as glycerol make T_m of PVA/Na-CMC (50/50) blends decreased with increasing glycerol concentration.

Table 1 Thermal characteristics of pure PVA, pure Na-CMC and PVA/Na-CMC blend films by using DSC technique.

PVA/Na-CMC	Concentration of glycerol (%wt)	T_g (°C)	T_m (°C)	ΔH_m (J/g)
100/0	0	75	185	8.7
80/20	0	74	182	6.6
60/40	0	74	182	6.8
50/50	0	74	181	5.4
40/60	0	74	180	4.8
20/80	0	121	n/d	n/d
0/100	0	123	n/d	n/d
50/50	10	n/d	173	7.2
50/50	15	n/d	170	6.6
50/50	20	n/d	165	8.8

n/d = not detectable

Mechanical properties

The mechanical properties of blend films were assessed by measuring their tensile strength (TS) and percentage stain at break. The results showed that TS of the films is decreased with increasing the amount of Na-CMC in the blends (Figure 2). The increasing of TS of the blended films can support the reason that there are molecular interaction between PVA and Na-CMC. Figure 3 shows percentage stain at break of PVA/Na-CMC blend films. These percentage stain patterns corresponded well to the result of TS, except for pure PVA film which has a higher percentage stain. These mechanical properties are attributed to the fact that there is molecular interaction between PVA and Na-CMC. The mechanical properties of Na-CMC are improved by blending is mainly due to hydrogen bond interaction in Na-CMC and PVA.

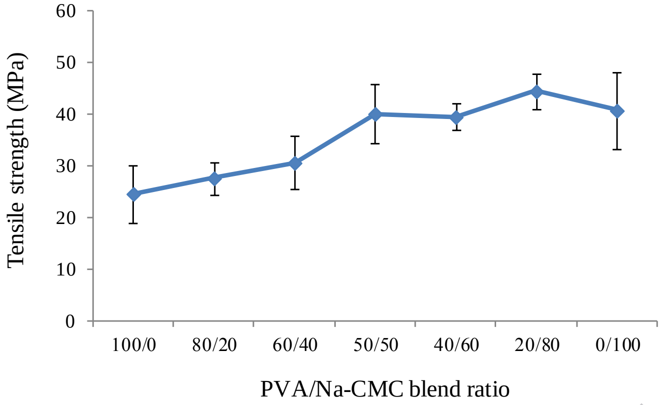


Figure 2 The TS of PVA/Na-CMC blend films

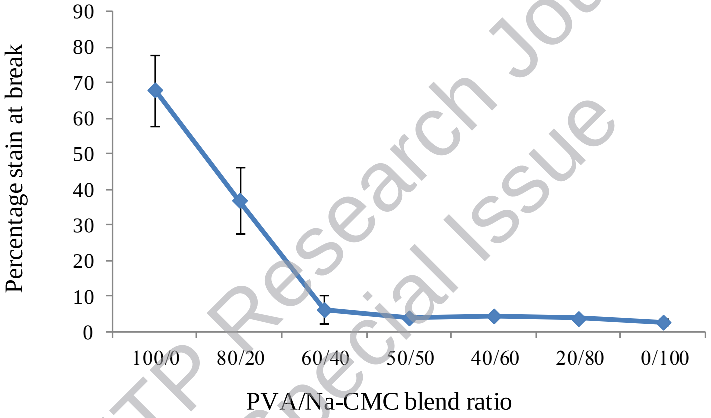


Figure 3 The percentage stain at break of PVA/Na-CMC blend films

From the results were shown in Figure 4, the addition of glycerol causes a reduction of the TS due to the decrease in the intermolecular interactions. Otherwise it shows effect on the percentage strain at break, when increasing amount of glycerol it was found that percentage strain at break decrease. It can discuss that glycerol is plasticizer which can improve the flexibility of the films, that was shown in Figure 5.

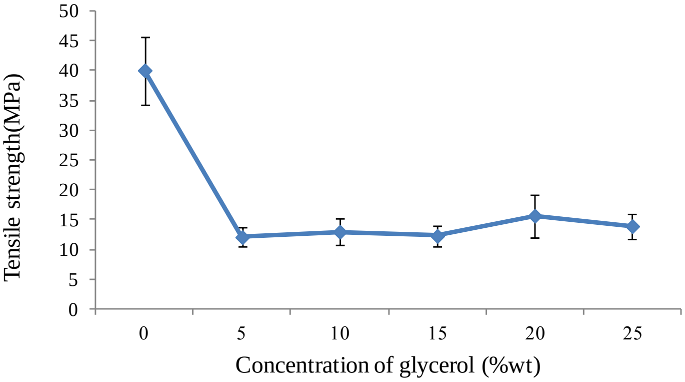


Figure 4 Effect of glycerol on stress at break of the PVA/Na-CMC (50/50) blend films

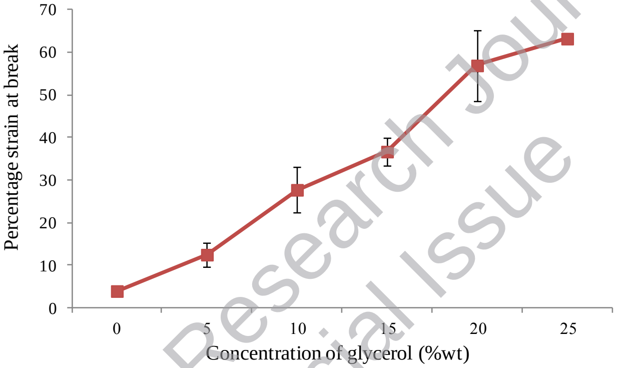


Figure 5 Effect of glycerol on percentage strain at break of the PVA/Na-CMC (50/50) blend films

Surface Morphology

Scanning electron micrographs (SEMs) of blended films are shown in Figure 6. The granules of Na-CMC were demonstrated on the surface of film with PVA/Na-CMC blend ratio of 0/100. While increasing the PVA component on blend the surface of blend films to be relatively smooth, to be homogeneous and continuous matrix without any pores or cracks. The effect of glycerol on scanning electron micrographs (SEMs)of PVA/Na-CMC blend films (50/50) are shown in the figure 7. It was found that, the surface of blend films with 15-25% glycerol concentration were exhibited flat and dense without any phase separation. It can conclude that all PVA and Na-CMC blend films are flat and dense without any phase separation. PVA microdomains are dispersed within Na-CMC matrix in the blend films with relatively good interfacial adhesion between the two components.

Moreover, addition glycerol with 15-25% glycerol concentration can improve compatibility between PVA and Na-CMC.

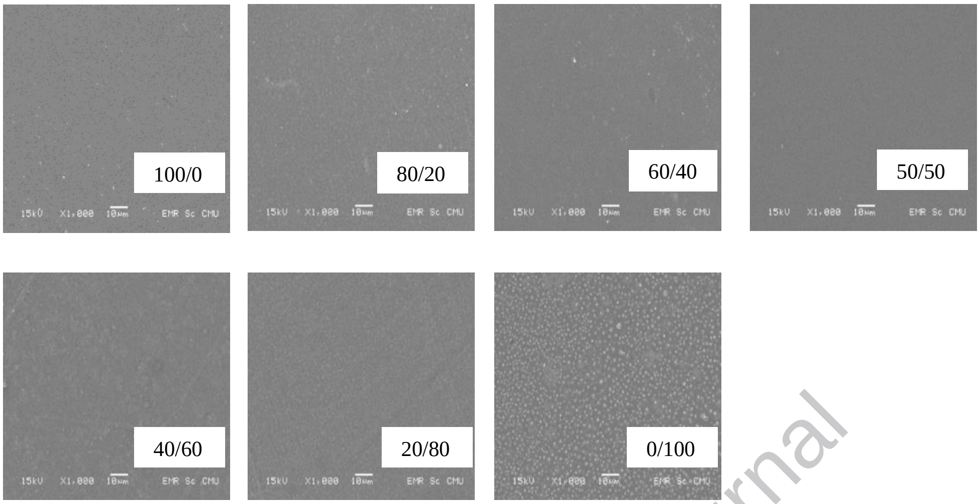
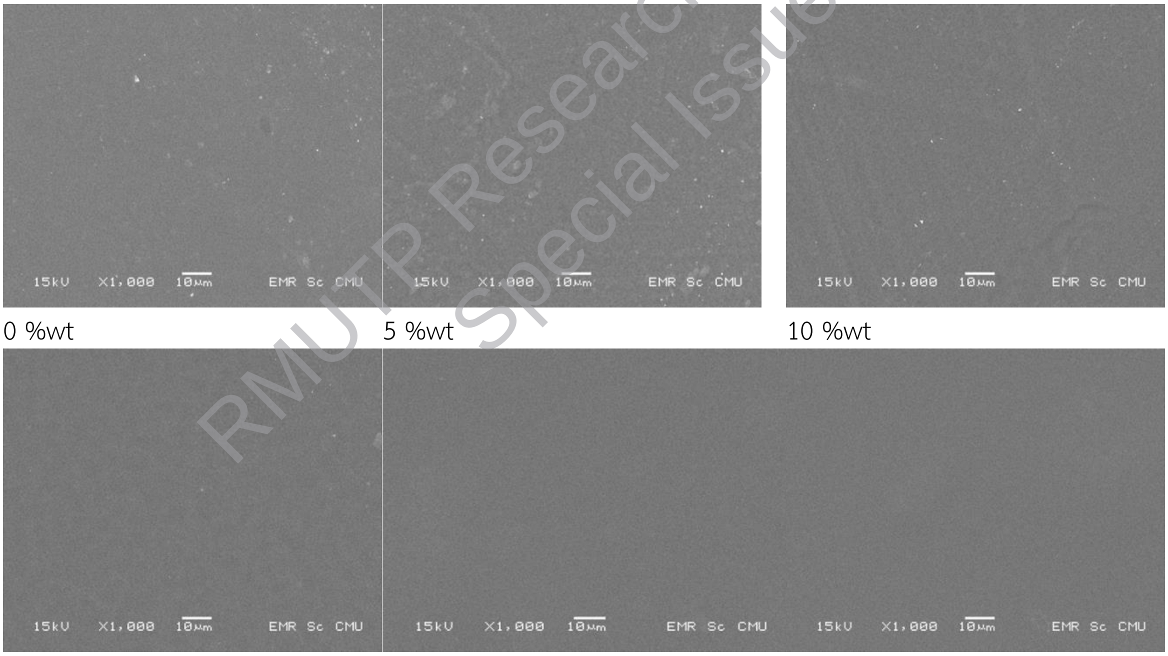


Figure 6 Scanning electron micrographs (SEMs) of the films with PVA/Na-CMC blend ratios of 100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 20/80 and 0/100.



0 %wt

5 %wt

10 %wt

15 %wt

20 %wt

25%

Figure 7 Effect of glycerol concentration on scanning electron micrographs (SEMs)of PVA/Na-CMC blend films (50/50)

Water Solubility Properties

All films are default after being immersed in the water at 30°C for 1 hour. The total soluble matter (%TSM) of PVA/Na-CMC blended films is shown in Figure 8. The %TSM of 0% Na-CMC content was 4.01±0.39%, which increased to 7.87±0.67 and 27.58±3.42% for 10 and 100% Na-CMC, respectively. It can conclusion that %TSM is corresponding with the amount of Na-CMC. At 0% Na-CMC, the film showed the lowest of %TSM value while %TSM was increased when the amount of Na-CMC increased. Under other conditions, %TSM was decreased when the amount PVA increased. It could be briefly explained that water molecules are absorbed by hydrophillic function groups (-OH groups), mainly through hydrogen bonding or weak electrostatic interactions, the film can be easily dissipated with water molecules [14].

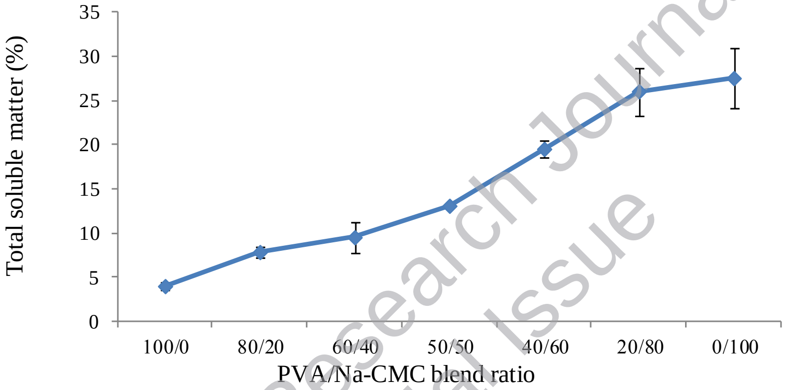


Figure 8 Effect of PVA/Na-CMC blend ratios from 100/0 to 0/100 on %TSM

Water Vapor Permeability (WPV)

WVP values were calculated by the amount of water vapor passing through the unit area of the film per unit time. The WVP of PVA/Na-CMC blend are shown in the Figure 9. The WVP was significantly effect by increasing Na-CMC content. Interestingly, films with Na-CMC 60% up had high WVP values when compared with high PVA content. Because Na-CMC is hydrophilic materials with polar groups in its molecular structures, and the interactions of polar groups with permeating water molecules. The water increases the polymer free volume, allowing the polymeric chain segments to increase their mobility. Higher segment mobility results in higher WVP [6].

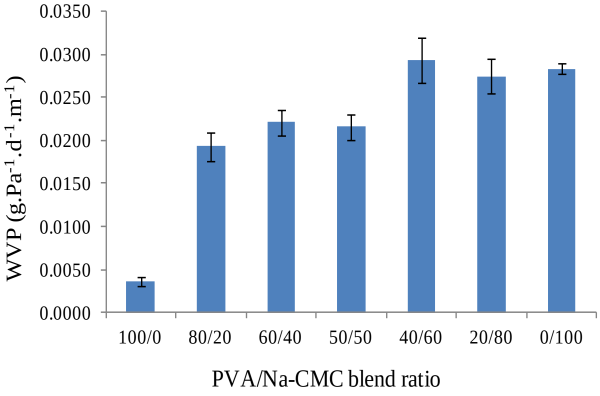


Figure 9 Effect of PVA/Na-CMC blend ratios from 100/0 to 0/100 on WPV of films

4. Conclusion

PVA/Na-CMC blend films with 86.33-95.67 μm wall thickness were fabricated by using solvent casting technique from solutions in hot water as solvent. All films were good coherency, clear, translucent and transparent. The SEM analysis showed that the surface of blend films with high PVA ratio was smooth. Addition glycerol with 15-25% glycerol concentration can improve compatibility between PVA and Na-CMC. From the DSC data, increasing Na-CMC and glycerol content make T_m of PVA became less prominent and disappeared because of the interchain hydrogen bonds between the -OH groups of PVA and C=O groups of Na-CMC. The tensile testing found that percentage stain at break was increased with increasing amount of PVA and glycerol in the blends. In addition, the blend films exhibited the higher water absorption that was indicated by water solubility and the water vapor permeability. The addition of the amount of glycerol decreased TS of PVA/Na-CMC blended films. Otherwise it shows effect on the percentage strain at break, when increasing amount of glycerol it was found that percentage strain at break decrease.

With considering these results, it seems that the 50:50 %wt of PVA and Na-CMC blend film with glycerol as plasticizer the exhibited miscibility between the two components, a little crystallization, and optimal water absorption. PVA/Na-CMC blend films with glycerol as plasticizer have the potential to be used in the food packaging materials.

5. Acknowledgements

The authors wound like to thank Faculty of Science and Agricultural Technology, Rajamangala University of Technology Lanna (RMUTL) for financial support. The authors express appreciation to Biomedical Polymers Technology Unit, Department of Chemistry, Faculty of Science, Chiang Mai University for assistance with preparation and characterizations of blend films.

6. References

[1] S.Y. Parka, S.T. Juna, K.S. Marsh, *Food Hydrocoll.* **15** (2001) 499-502.

[2] S.K. Saxena, *Polyvinyl Alcohol (PVA): Chemical and Technical Assessment,* 61st JECFA, Rome, Italy (2004) pp 3-7.

[3] C.C Demerlis, D.R. Schoneker, Food Chem. Toxi. **41** (2003) 319-326.

[4] N.A. Peppas, D. Tennenohouse, *J. Drug Del. Sci. Tech.* **14(4)** (2004) 291-297.

[5] S. Tripathi, G.K. Mehrotra, P.K. Dutta, *Int. J. Biol. Macromol.* **45** (2009) 372–376.

[6] J.F. Su, Z. Huang, K. Liu, L.L Fu, H.R. Liu, *Polym. Bull*. **58** (2007) 913-921.

[7] W. Li, B. Sun, P. Wu, *Carbohydr. Polym.* **78** (2009) 454 -461.

[8] S. Zivanovic, J. Li, P. M. Davidson, K. Kit, *Biomacromolecules* **8** (2007) 1505-1510.

[9] ASTM (1995). Standard test methods for water vapor transmission of material, E96-95. Annual book of ASTM. Philadelphia, PA: American Society for Testing and Materials.

[10] P. Kumar, K.P. Sandeep, S. Alavi, V.D. Truong, R.E. Gorg, *J. Food Eng.* **100** (2010) 480–489.

[11] W. Tongdeesoontorn , L. J. Mauer2, S. Wongruong, P. Rachtanapun, *As. J. Food Ag-Ind.* **2(04)** (2009) 501- 514.

[12] Y. Zahedi, N. Sedaghat, B. Ghanbarzadeh, *Int. J. Nuts & Related Sci.* **2(2)** (2011) 56-63.

[13] Y. He, B. Zhu, Y. Inoue, *Prog. Polym. Sci*. **29** (2004) 1021-1051.

[14] N. A. Azahari, N. Othman, H. Ismail, *J. Physical Science*, **22(2)** (2011) 15–31.