International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:9, No:2, 2015

Barrier Properties of Starch - Ethylene Vinyl Alcohol Nanocomposites

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***Abstract*—**Replacement of plastics used in the food industry seems to be a serious issue to overcome mainly the environmental problems in recent years. This study investigates the hydrophilicity and permeability properties of starch biopolymer which ethylene vinyl alcohol (EVOH) (0-10%) and nanocrystalline cellulose (NCC) (1-15%) were used to enhance its properties. Starch -EVOH nanocomposites were prepared by casting method in different formulations. NCC production by acid hydrolysis was confirmed by scanning electron microscopy. Solubility, water vapor permeability, water vapor transmission rate and moisture absorbance were measured on each of the nanocomposites. The results were analyzed by SAS software. The lowest moisture absorbance was measured in pure starch nanocomposite containing 8% NCC. The lowest permeability to water vapor belongs to starch nanocomposite containing 8% NCC and the sample containing 7.8% EVOH and 13% NCC. Also the lowest solubility was observed in the composite contains the highest amount of EVOH. Applied Process resulted in production of bio films which have good resistance to water vapor permeability and solubility in water. The use of NCC and EVOH leads to reduced moisture absorbance property of the biofilms.

***Keywords*—**Starch, EVOH, nanocrystalline cellulose, Hydrophilicity.

I. Introduction

IN recent years replacing synthetic plastics by suitable biodegradable materials which leave less environmental pollution has attracted the attention of investigators. Edible films with high biodegradability from renewable agricultural resources seem an appropriate replacement for conventional plastics [1]. More attentions have been paid to production of biodegradable packaging materials due to increasing environmental pollution caused by the use of synthetic polymers. Organic or inorganic nanofillers with different geometric shapes (fibers, flakes, spherical particles) reinforced into the matrix of biopolymers and the obtained material is called nano-biocomposites [2], [3].

Nanocellulose has been used in sodium caseinate nanocomposites which were made by casting method. The obtained films were less transparent than pure sodium caseinate film and had increased hydrophilic surface, water absorption was not affected by the concentration of the Nanocellulose generally [4]. Teixeira et al have been made starch biofilms containing nanocellulose, they studied hydrophilic properties of the obtained nanocomposites. They used cassava starch and cellulose nanoparticles extracted from cassava to produce nanocomposites. They also used glycerol and glycerol and sorbitol mixture as a plasticizer in the ratio of 1 to 1. The use of cellulose nanoparticles in the matrix of starch film is reduced hydrophilic properties, particularly when the used plasticizer is glycerol [5]. Nano-cellulose is used in polyvinyl acetate film, applying of nanocellulose increases the tensile strength and viscose modulus of the obtained film [6].

The cheap manufacturing and convenient features of plastics has led to variety of applications for them and the use of synthetic polymers has gained popularity in recent years. On the other hand, non degradable oil derived polymers has created many environmental problems in natures. In this project, starch nanocomposite making was studied in order to find an appropriate alternative to the plastic polymers. Ethylene vinyl alcohol (EVOH) was used instead of some portion of starch to improve the hydrophilicity and inhibitory properties of the composite against water vapor permeation, since net starch film will not be able to establish the desired properties of the polymer. On the other hand nanocrystalline cellulose (NCC) and the glycerol as a plasticizer are used to boost functional properties of the nanocomposites.

II. Materials and Methods

In this study nanocrystalline cellulose was extracted from cotton linter. Cotton linter was cut into small pieces about 2 cm lengths by scissors then washed with distilled water. Then the cut linter was gone under hydrolysis treatment by sulfuric acid (65% w/w). The weight ratio of cotton linter to sulfuric acid was 1:20. Hydrolysis took place at 55˚C and under continuous stirring for 2.5 h. In order to neutralize the acidic suspension of NCC, the NaOH solution was used at the concentration of 10% (w/v). Finally, the obtained suspension was treated with ultrasound waves. A40 kHz frequency ultrasound equipment was performed and treatment applied for 15 min.

Casting method was used to prepare nanocomposites in this study. 5 g of corn starch dissolved in cold water and was brought to a volume of 100 ml; 4 g glycerol as a common plasticizer in starch film production was added to the starch suspension. Gelatinization process of starch suspension performed at 90˚C in water bath as long as 60 min. Nanocrystalline cellulose solution homogenized by ultrasound and was added to gelatinized starch to study the effects of nanocrystalline cellulose on the composites properties. The used amount of NCC in different levels was 1-15% of starch

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weight. Obtained solution was stirred at 70˚C for 15 min to evenly distribute of NCC in starch solution. After this constant amount of mixture was dispersed gently over the polystyrene plate; the film making process was completed by water evaporation of solution in the oven [7], [8]. Drying carried out at 60 ˚C for 16 hours. Finally the nonocomposite removed from the plate surface. Some of starch in formulation replaced by ethylene vinyl alcohol by 10% to evaluate the effects of ethylene vinyl alcohol on made composites properties.

EM 3200 scanning electron microscope (SEM) manufactured by KYKY company was used to determine the shape of obtained nanocrystalline cellulose.

Moisture absorbance by the film was measured by Angles and Dufresne method [9]. 20×20 mm pieces of nonocomposites were cut and all samples were kept at 50˚C oven for 24 h. After initial weighing, samples were kept at hermetic jar containing saturated solution of potassium sulfate. The samples were weighted over period of time until they reached the constant weight. Following equation was used to calculate the absorption of moisture values:

$$MA = \frac{W_0 - W_1}{W_0} \times 100$$

MA: moisture absorbance (%), W0: initial sample weight (g), W1: final sample weight (g) at Rh= 97%

The ASTM E96 method was used to measure the water vapor transmission rate (WVTR) [10]. To do this, a glass container with 2.5 cm diameter and 4.5 cm height was used. A 5 mm pore created at the cap of the container then a piece of nanocomposite equals to the diameter of the container neck inserted under cap. Each container contains 3 g of calcium sulfate which creates zero relative humidity. Samples conditioned for 24 hours at relative humidity of 55% which was created by calcium nitrate saturated solution and then a piece of film placed on the glass jar while cap closed.

Glass containers weighted and then kept in hermetic jar containing saturated solution of potassium sulfate. Saturated potassium sulfate solution creates 97% relative humidity at 25˚C. The glass containers were weighted over time for 4 days. The amount of water vapor transmission rate through the films is determined according to weight gain of the containers. Weight gain is plotted verse the time and the slope of fitted line is calculated. Water vapor transmission rate (WVTR) is obtained by dividing the calculated slope value of each sample to the exposed area of the sample.

$$J = WVTR = \Delta W/tA$$

J: water flux, WVTR: water vapor transmission rate, ΔW: amount of water vapor passed through the film (weight gain), t: test time (h), A: area exposed to water vapor (m2)

WVP (water vapor permeability) can be obtained by dividing of WVTR to water vapor pressure difference between inside of container and outside controlled atmosphere. The inside water vapor pressure is considered zero due to the existed calcium sulfate into the container. Water vapor pressure of the outside is calculated by multiplying of the relative humidity (97%) of the hermetic jar to pure water vapor pressure which equals to 3169 pa at 25˚C. Values for water vapor permeation are calculated by multiplying of WVTR to the thickness of the film.

$$WVP = \frac{WVTR \times X}{P(R_1 - R_2)}$$

X: film thickness (m), P: pure water vapor pressure at 25˚C (3169 Pa), R1: relative humidity in the hermetic jar (100%), R2: relative humidity in the glass container (0%)

Solubility in water is defined as the percentage of dissolved dry matter of the nanocomposite after 24 hours immersion of nanocomposite in water. 20×20 mm samples of nanocomposites are prepared and dry at 105˚C for 24 h to measure the solubility in water. The initial dry mater of the each sample determined then is immersed in 50 ml distilled water for 24 h at 25˚C. Finally, the films take out of the water and are dried again for 24 h at 105˚C until reaches constant weight. Final dry matter is determined and total soluble matter (TSM) which represents the solubility in water is calculated according to:

$$TSM = \frac{DM_1 - DM_2}{DM_1} \times 100$$

TSM: Total Soluble Materials in water (%), DM1: initial dry matter (%), DM2: final dry matter (%)

Response surface methodology is a statistical technique used in the optimization of processes where the response is influenced by numbers of independent variables. In this study, different formulations of starch nanocomposites containing variable amounts of EVOH and NCC based on a central composite design were produced. SAS and Excel software were used to statistical analysis of the obtained data.

III. Results and Discussion

Among all methods of nanocrystalline cellulose preparation, acid hydrolysis which is followed by crashing is a way to production of nanocrystalline cellulose. The amorphous regions of cellulose molecule will be removed during hydrolysis [11]. Extraction process is based on the fact that crystalline regions remain unsolved in acid solution; in other words, disordered structure of cellulose in the amorphous regions are sensitive to acid hydrolysis [12]. The nanocrystalline cellulose image which is shown in Fig. 1 was obtained by scanning electron microscopy.

Moisture absorbance in nanocomposite samples was measured and the results are shown in Table I. The lowest moisture absorbance was measured in pure starch nanocomposite sample containing 8% nanocrystalline cellulose without EVOH. This can be due to the involvement of nanocrystalline cellulose with starch polymer, then free OH groups decrease and hydrophilic OH groups will be out of reach. While addition of ethylene vinyl alcohol destroys nanocomposite structure and weakens the link between starch

and nanocrystalline cellulose then as a result the number of free OH groups increases. Moisture uptake values increase by increased substitution of ethylene vinyl alcohol instead the starch in nanocomposites but it should be noted that in samples containing equal amounts of ethylene vinyl alcohol the moisture absorption value reduces by using more nanocrystalline cellulose in the nanocomposites formulation.

ANOVA analysis showed that the variables affecting the moisture absorbance are the nanocrystalline cellulose amount and squared ethylene vinyl alcohol amount in nanocomposite. Relation between the moisture absorbance and experiment independent variables can be explained by the below equation with a correlation coefficient (R2) of 77.56%:

$$MA = 29.72515 + 2.213427x_1 - 0.734368x_2 - 0.289775x_1^2 + 0.137746x_1x_2 - 0.043607x_2^2$$

MA: moisture absorbance, x_1: ethylene vinyl alcohol content in the nanocomposite, x_2: nanocrystalline cellulose content in the nanocomposite

Water vapor transmission rate or water vapor flux through the film was obtained for all samples. Water vapor permeability of nanocomposites was calculated according to obtained WVTR. ANOVA analysis indicates that square of nanocrystalline cellulose amount at $p<0.05$ and nanocrystalline cellulose amount at $p<0.1$ have significantly effect on water vapor permeation. The highest water vapor permeation was observed in the samples containing 5% ethylene vinyl alcohol and 1% nanocrystalline cellulose and the sample with 1.5% ethylene vinyl alcohol and 3% nanocrystalline cellulose. The lowest values of water vapor permeability obtained for samples containing starch+ 8% nanocrystalline cellulose, starch+ 8.7% ethylene vinyl alcohol+ 13% nanocrystalline cellulose and starch+ 8.7% ethylene vinyl alcohol+ 3% nanocrystalline cellulose as 7.66713×10-7, 7.66713×10-7 and 7.91472×10-7 respectively (Table I). Layered and homogeny structure of starch nanocomposites maybe prevents the penetration of water vapor. More interactions establish between starch molecules and nanocrystalline cellulose by increasing of nanocrystalline cellulose content in the nanocomposite formulation, this can create a barrier against the water vapor permeation through the closed structure of the biofilm. Below equation with a correlation coefficient (R2) of 64.46% was obtained to demonstrate relation between the water vapor permeation and experiment independent variables.

$$WVP = 1.896 \times 10^{-6} + 1.926 \times 10^{-8}x_1 - 2.408 \times 10^{-7}x_2 - 3.003 \times 10^{-9}x_1^2 + 6.9 \times 10^{-10}x_1x_2 + 1.202 \times 10^{-8}x_2^2$$

WVP: water vapor permeability, x_1: ethylene vinyl alcohol content in the nanocomposite, x_2: nanocrystalline cellulose content in the nanocomposite

Solubility of the produced nanocomposites is shown in Table I. The lowest solubility belongs to the composite that contains the highest amount of ethylene vinyl alcohol; this sample contains 10% ethylene vinyl alcohol and 8% nanocrystalline cellulose. This can be due to low solubility of ethylene vinyl alcohol compared to hydrophilic polymers like starch. On the other hand the maximum solubility in water is observed in pure starch nanocomposite containing 8% nanocrystalline cellulose. Increased amount of the ethylene vinyl alcohol in nanocomposites samples caused solubility to decrease. Insoluble properties of ethylene vinyl alcohol in water prevent dissolving of composites containing of this polymer. Statistical analysis indicate that ethylene vinyl alcohol content and squared nano crystalline cellulose content in nanocomposites affect the solubility property in the produced nanocomposites significantly ($P< 0.05$). Following equation with a correlation coefficient (R2) of 81.01%demonstrate the relation of solubility property and the independent variables of the experiment:

$$WS = 70.4971 - 2.461887x_1 - 2.077648x_2 + 0.154285x_1^2 - 0.03773x_1x_2 + 0.148989x_2^2$$

WS: water solubility, x_1: ethylene vinyl alcohol content in the nanocomposite, x_2: nanocrystalline cellulose content in the nanocomposite.

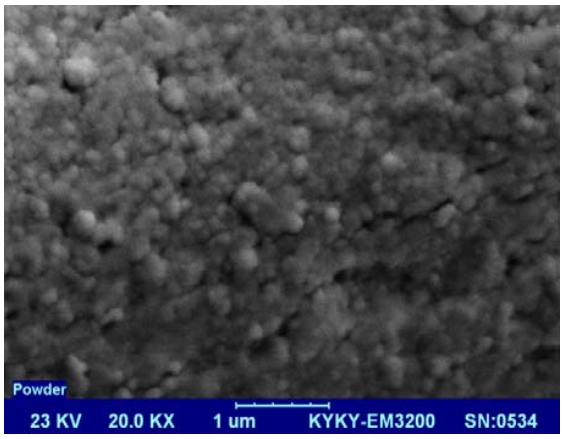

Fig. 1 Obtained scanning electron microscopy image for nanocrystalline cellulose

TABLE I
OBTAINED MOISTURE ABSORBANCE (MA), WATER SOLUBILITY (WS) AND WATER VAPOR PERMEABILITY FOR NANOCOMPOSITES

Samples	MA (%)	WS (%)	WVP	Samples	MA (%)	WS (%)	WVP
1	33.81295	60.54306	1.05E-06	7	31.31313	60.24725	2.15E-06
2	21.50538	64.22222	9.8E-07	8	21.11111	60.17103	9.5E-07
3	28.69565	56.33663	7.91E-07	9	26.78571	56.53886	8.09E-07
4	26.36364	57.28337	7.67E-07	10	31.61765	54.84777	7.63E-07
5	17.14286	64.9866	7.67E-07	11	32.91139	48.52595	8E-07
6	24.44444	48.62456	9.78E-07	12	30.43825	53.3042	7.91E-07

IV. Conclusion

Films used in food packaging are often required to prevent or at least reduce the moisture transfer between the food and the surrounding atmosphere. More reduction in water vapor permeability is observed while the amount of nanocrystalline cellulose increases in the nanocomposites formulations. This reduction can be attributed primarily to the lower hydrophilicity property of nanocrystalline cellulose rather than starch. Lower hydrophilicity property of nanocrystalline cellulose is related to the crystalline structure and hydrophobic characteristic of cellulose fibers in compare to starch matrix. Water solubility of produced films decreased significantly by increasing of used EVOH and NCC in the nanocomposites. This is due to the insoluble properties of EVOH and stabilizing effect of NCC on the nanocomposites matrix. Future researches will show that if increasing amount of ethylene vinyl alcohol and nanocrystalline cellulose in the starch nanocomposite can have a positive effect on the measured characteristics or not.

References

[1] S. K. Park, N. S. Hettiarachchy and L. Were, Degradation behavior of soy protein-wheat gluten films in simulated soil conditions. *J. Agr. Food. Chem*. 2000, 48: 3027-3031.

[2] A. Sorrentino, G. Gorrasi and V. Vittoria, Potential perspectives of bionanocomposites for food packaging applications. *J. Trends. Food. Sci. Tech.* 2007, 18: 84-95.

[3] S. Fischer, J. De Vliegar, T. Kock, L. Batenburg and H. I, Fischer. Green nanocomposite materials-new possibilities for bioplastics. *Mater. Res. Soc. Simp*. 2001, 661: 221-226.

[4] M. G. Pereda, Amica, I. R. and N. E. Marcovich, Structure and properties of nanocomposite films based on sodium caseinate and nanocellulose fibers. *J. Food. Eng*. 2011, 103 (1): 76-83.

[5] E. M. Teixeira, D. Pasquini, A.A.S. Curvelo, E. Corradini, M.N. Belgacem and A. Dufresne, Cassava bagasse cellulose nanofibrils reinforced thermoplastic cassava starch. *Carbohyd. Polym*. 2009, 78 (3): 422-431.

[6] G. Gong, J. Pyo, A. P. Mathew and K. Oksman, Tensile behavior, morphology and viscoelastic analysis of cellulose nanofiber-reinforced (CNF) polyvinyl acetate (PVAc). *Compos. Part A-Appl. S*. 2011, 42 (9): 1275-1282.

[7] P. R. Chang, R. Jian, P. Zheng, J. Yu and X. Ma, Preparation and properties of glycerol plasticized starch (GPS)/cellulose nanoparticle (CN) composites. *Carbohyd. Polym*. 2010, 79: 301-305.

[8] X. Cao, Y. Chen, P. R. Chang, A. D. Muir and G. Falk, Starch-based nanocomposites reinforced with flax cellulose nanocrystals. *Exp. Polym. Let*. 2008, 2 (7): 502-510.

[9] M. N. Angles and A. Dufresne, Plasticized starch/tunicin whiskers nanocomposites. *Macromolecules*. 2011, 34: 2921-2931.

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

[11] W. E. Gacitua, A. A. Ballerini and J. Zhang, Polymer nanocomposites: synthetic and natural fillers a review. *Cienciay. techn*. 2005, 7 (3): 159-178.

[12] D. Bondeson, A. Mathew and K. Oksman, Optimization of the isolation of nanocrystals from microcrystalline cellulose by acid hydrolysis. *Cellulose*. 2006, 13: 171-180.