

Preparation and characterization of biopolymer blends based on polyvinyl alcohol and starch

Received for publication, January 10, 2015
Accepted, March 18, 2015

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Abstract

In recent years, there has been an expanding research for new polymeric materials with high performance and low costs. With growing environmental awareness, the research has particularly focused on eco-friendly materials, with terms such as „renewable”, „recyclable”, „sustainable” and „biodegradable” becoming important features of the materials.

Polyvinyl alcohol (PVA) ranks among the few biodegradable synthetic polymers that are frequently modified owing to their properties. PVA contains numerous polar alcohol groups and may form hydrogen bonds with water. It therefore dissolves easily in water. Starch is a widely used biopolymer which is actually a storage polysaccharide in plants. It is composed of both linear and branched polysaccharides, known as amylose and amylopectin. Starch is one of the most abundant and inexpensive polysaccharide sources which have the unique characteristic of ‘biodegradability’ and it can be easily degraded in water.

This work presents the preparation and characterisation of some PVA and starch polymeric blends. A series of physical-mechanical analysis were performed (such as melt processing characteristics, optical properties, permeability, etc.) in order to determine the suitability of these materials for packaging development and use in food industry.

Keywords: biodegradable, PVA, starch, polymeric blends.

1. Introduction

For many years, plastics like polystyrene (PS), polyethylene (PE), polypropylene (PP) and polyethylene terephthalate (PET) have been widely used in food packaging industry. However, the disposal of these materials after their end use requires hundreds of years to degrade in environmental conditions (MADERA-SANTANA & al., 2014 [1]; YOON & al., 2012 [2]). Therefore, it has been an expanding research for new materials with high performance and at an affordable cost that can be defined by renewability, recyclability, sustainability, biodegradability and biocompatibility (SATYANARAYANA & al., 2009 [3]). Over the years, there have been developed biodegradable polymers made from renewable and natural polymers such as starch, cellulose, clay, pectin, etc. (PEREIRA & al., 2014 [4]).

Starch is a natural polymer, inexpensive and abundant resource, which is biodegradable and can be easily degraded in water being often used as filler for the replacement of petroleum derived synthetic polymers to reduce environmental pollution (KHAN & al., 2006 [5]; YOON & al., 2012 [2]). Starch occurs in the form of discrete and partially crystalline

microscopic granules that are held together by an extended network of associated molecules (SATYANARAYANA & al., 2009 [3]). Starch represents the storage of polysaccharide in plants like wheat, corn or potatoes. The ratio of these polysaccharides varies with their botanical origin and generally, native starches contain around 70-85% amylopectin and 15–30% amylose (REDDY & al., 2013 [6]).

By using conventional polymer processing techniques, starch, like many other polymers, can be produced into different final forms such as extruded, molded, thermoformed or blown articles (XIE & al., 2013 [7]). However, starch-based materials are known to have limitations such as poor processability and properties (e.g. weak mechanical properties, poor long-term stability, and highly water sensitivity) (SATYANARAYANA & al., 2009 [3]; XIE & al., 2013 [7]; YOON & al., 2012 [2]). Great effort has been made to improve these properties by adding different synthetic polymers, like polyvinyl alcohol (PVA), poly (lactic acid) (PLA), and polyester (YOON & al., 2012 [2]).

PVA is a vinyl polymer that is a non-toxic, water-soluble, biocompatible and biodegradable synthetic polymer, in which the main chains are joined by only C-C bonds (MADERA-SANTANA & al., 2014 [1]; HSIEH & LIAU, 2013 [8]). Also it has excellent chemical resistance and good mechanical properties.

Polyvinyl alcohol (PVA) has been widely used for the preparation of blends and composites with several natural, renewable polymers like chitosan, nanocellulose, starch or lignocellulosic fillers. After being used in industry, it is carried away in wastewater treatment plants, where it is more or less successfully degraded (JULINOVA & al., 2010 [9]). PVA also displays low biodegradation when applied in agriculture (JULINOVA & al., 2010 [9]; SANTOS & al., 2014 [10]). Over the years there have been made efforts to improve PVA biodegradability and functionality by blending it with other polymers like PLA (WANG & al., 2006 [11]), PHB (TETSUYA & al., 1998 [12]), chitin (AOI & al., 1995 [13]; AOI & al., 1997 [14]), chitosan (CHEN & al., 2007 [15]; CRISTALLINI & al., 2007 [16]; BONILLA & al., 2014 [17]; HANG & al., 2010 [18]; KRSTIĆ & al., 2014 [19]; NGUYEN & LIU, 2013 [20]; PARPARITA & al., 2012 [21]; SRINIVASA & al., 2003 [22]), starch (COȘEREA & al., 2012 [23]; JELINSKA & al., 2008 [24]; CINELLI & al., 2006 [25]), lignocellulosic fillers (CINELLI & al., 2008 [26]) and nanocellulose (XU & al., 2013 [27]; SRITHEP & al., 2012 [28]; HRBALOVA & al., 2011 [29]; SRITHEP & al., 2012 [28]).

2. Materials and methods

Materials

In order to achieve biodegradable formulations the following raw materials were used: PVA type ELVANOL 75-15 (DU PONT) having a degree of hydrolysis in the range of 99.0 – 99.8 %, 12-15 cP viscosity, max. 5% volatile and 0.398 g/cm³ density. It was used as thermo-plastic matrix.

Starch type AMYZET 100 (AMYLUM România); it has 800 kg/m³ density, pH (30% suspension) 6-8. It was used as biodegradation agent.

Glycerol (SIGMA-ALDRICH) having density of 1.267 g/cm³; it was used as plasticizer in order to decrease the glass-transition temperature (T_g) and to increase the flexibility and processing behaviour of starch and PVA since starch is only partially compatible with PVA.

Processing Procedure

It was carried out four formulations coded: PVA/Starch 0, PVA/Starch 10, PVA/Starch 20 and PVA/Starch 30 containing starch from 0 to 30 wt. %, as it is shown in Table 1. It was

respected the ratio 2:1 between PVA and plasticizer. Before use, the starch was dried for 4 hours at 105°C.

Table 1. Compositions of PVA/starch blends

Code sample	PVA, wt. %	Starch, wt. %	Glycerol, wt. %
PVA/Starch 0	66.67	0	33.33
PVA/Starch 10	60	10	30
PVA/Starch 20	53.34	20	26.66
PVA/Starch 30	46.67	30	23.33

First, PVA was premixed with plasticizer. The melting of blends was performed using a BRABENDER Plastograph, in the following conditions: cuvette of 30 cm³, temperature 170±5°C, mixing time 10 minutes, speeds of rotors 40/70 rpm. Films and sheets with thickness of 0.1 mm and respectively 1 mm were obtained by pressing in the following conditions: temperature: 170 °C; preheating time: 5 min respectively 10 min; pressing time: 2 min respectively 5 min; cooling time: 40 min; pressure: 150 bar respectively 125 atm.

Characterization Methods

(a) Processing Characteristics

Processing behaviour was evaluated by analysis of processing characteristics following the torque – time curves registered during blending in the Brabender mixer. Thus, torque, melt viscosity and power consumption, of the prepared blends were evaluated to constant values of 10 min at 40 rpm based on rheological data reported earlier conforming equations (1) and (2) (BLYLER & DAANE, 1967 [30]):

$$M = C_0 S^a \quad (1)$$

where:

M is torque;
 S is the rotation speed (rpm);
 C_0 is a constant depending on temperature;
 a is a constant.

$$\zeta = K \dot{\gamma}^n \quad (2)$$

where:

ζ is shear stress;
 $\dot{\gamma}$ is shear rate;
 K and n are the power law parameters.

Based on the equations (1) and (2) it can be deduced that the torque recorded on Brabender is an indirect evaluation of shear stress, while the rotor speed (rpm) is an indirect evaluation of shear rate. Thus, the melt viscosity η is given as the ratio of shear stress to shear rate, and herein can be obtained from the ratio of torque to rotor speed (equation (3)) (MENON, 1999 [31]):

$$\eta = K(M/S) \quad (3)$$

where: K is a constant depending on temperature.

Practical process engineering data, P , can be developed using equation (4) (MENON, 1999 [31]):

$$P = M \times \omega \quad (4)$$

where:

P is power(W); M is torque (mkg);
 ω is input shaft rotation ($2\pi S/60$); S is rotor speed (rpm).

(b) Fourier-transform infrared (FT-IR) spectroscopy

The FT-IR analyses were carried out with a FTLA2000-104 spectrophotometer (ABB Canada) equipped with ZnSe crystal, via the Attenuated Total Reflectance (ATR) method in the range of 3700cm^{-1} - 700cm^{-1} . The recording was carried out at 4cm^{-1} resolution, in transmission mode.

(c) Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was performed using a DSC 823^e from Mettler Toledo, calibrated with indium standard. The samples weighting between 2.3 and 9 mg were cut in square plates, packed in aluminium pans and placed in the DSC cell. Samples were first heated from ambient temperature to 250°C at a heating rate of $10^{\circ}\text{C}/\text{min}$, in order to erase any previous thermal history. Then, the samples were cooled to ambient temperature and heated again to 250°C at a rate of $10^{\circ}\text{C}/\text{min}$. The degree of crystallinity (X_c) was calculated from DSC curves as follows:

$$X_c = \frac{\Delta H_m}{\Delta H_0 w_{starch}} 100 \quad (5)$$

where: ΔH_m is the heat of fusion for the blend; ΔH_0 is the heat of fusion for 100% crystalline PVA; and w_{starch} is the weight fraction of polymer matrix. The heat, required for melting of 100% crystalline PVA, is 138.60 J/g (PEPPAS & MERRILL, 1976 [32]).

(d) Optical properties

Each film specimen was cut into a rectangular piece and placed directly in a UV/Vis HELIOS ALPHA spectrophotometer (Thermo Spectronic), at wavelengths from 200 to 800 nm. Measurements were performed using air as the reference. The results have been expressed as percentage transmittance. The measurements were done in triplicate and the average of three spectra was calculated. The transparency at 600 nm (T600) was obtained using the following equation (KANATT & al., 2012 [33]).

$$T600 = -\log \%T/b \quad (6)$$

where:

% T is percentage transmittance and b is the film thickness (mm).

The opacity of the films was calculated by the following equation:

$$\text{Opacity} = \text{absorbance at } 500 \text{ nm} \times \text{film thickness (mm)} \quad (7)$$

(e) Water vapour permeability

The permeability of the samples was determined with PBI-Dansensor L 80-5000. A dry room with a specified relative humidity is separated by a wet room, where the atmosphere is saturated with water vapour at a known temperature, through a sheet of material to be tested. Changing humidity in the dry chamber is achieved by water vapour passing through the tested material and it is detected by a humidity sensor that is able to provide an electrical signal that is measuring relative humidity in the dry room. The time required to increase humidity to a certain amount is measured and converted into a transmission rate of water vapour. The

permeability of the samples was measured at 23 °C.

3. Results and discussion

(a) Processing Characteristics

Figure 1 shows the torque as a function of the mixing time for PVA/Starch blends.

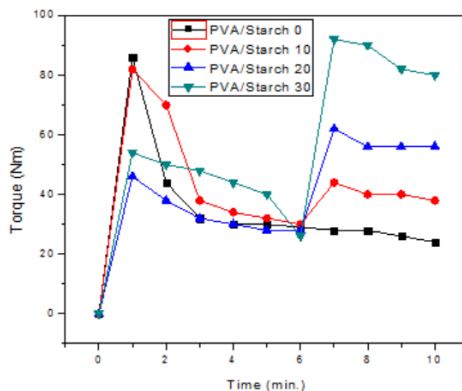


Figure 1. Torque time curve of the PVA/Starch blends at 170°C and 40 rpm

First, the premixed PVA was loaded until the torque reached a more constant value (about 30 Nm), indicating complete melting of PVA and full homogenization of the glycerol into PVA matrix. When different contents of starch have been incorporated in a plastified PVA, it is observed a general increase of torque due to increase in the viscosity of the starch phase.

An important increase is recorded for the starch 30 %. Comparing the values obtained for blends, it is observed that with increasing of the starch, the melt processing characteristics decrease.

Melt viscosity of polymers is a significant factor with respect to processing operations involving melt flow such as compression molding, extrusion and injection molding (MENON, 1999 [31]). The effect of starch content on melt viscosity index is shown in Figure 2.

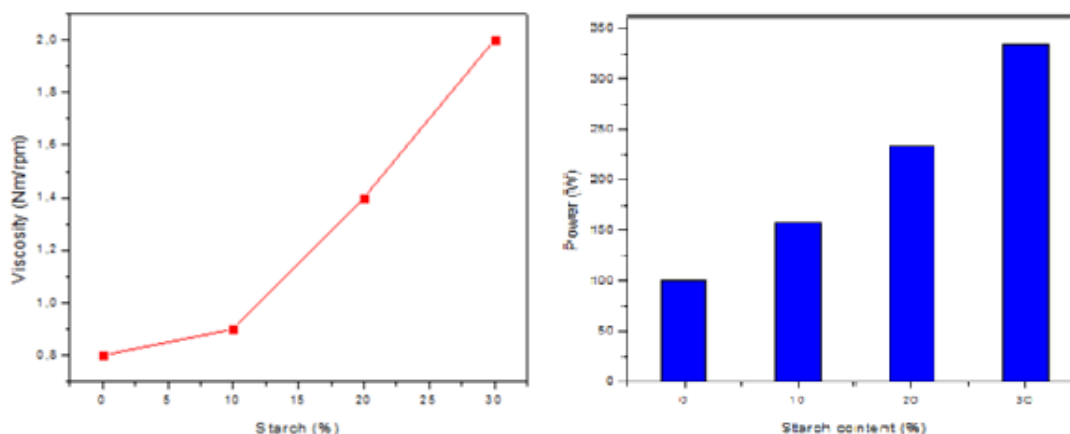


Figure 2. The graphical representation of the effect of starch content on melt viscosity index (left) and the effect of starch content on power consumption of PVA blends (right)

From Figure 2 it is observed an increase in the melt viscosity of PVA/Starch blends with the increase of starch content. The increase in melt viscosity of PVA blends indicates a hard processability during mixing.

Power consumption during processing of PVA blends is almost often a factor of major significance. It is essential that the blends should process smoothly with minimum power consumption (MENON, 1999 [31]). Figure 2 also shows the power consumption of PVA blends during processing. The blend containing 30% starch shows high power consumption for mixing in comparison with blends containing 20% and respectively 10 % of starch. This again indicates the better processability of PVA with small content of starch.

(b) Fourier-transform infrared (FT-IR) spectroscopy

FT-IR spectra of the PVA/starch blends are shown in Figure 3.

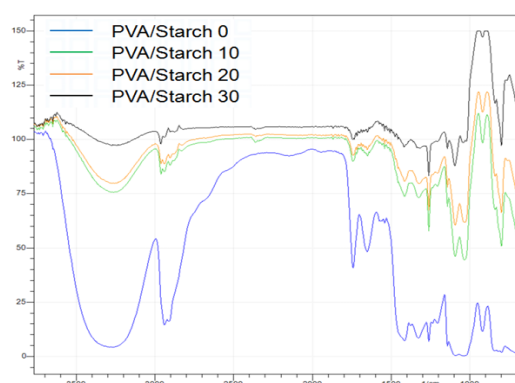


Figure 3. The FT-IR spectra of PVA blends

When two components are mixed, the physical blends and chemical interactions presents changes in the characteristic spectra peaks (SRINIVASA & al., 2003 [22]).

The stretching and bending vibration of the hydrogen bonding -OH group of PVA/starch blends occurred at 3600-3000 cm^{-1} and around 1653 cm^{-1} , respectively. The bending vibration of the hydrogen bonding -OH group is shifted to 1636 cm^{-1} for PVA/Starch 20 blend and to 1699 cm^{-1} for PVA/Starch 30 blend. The stretching vibration of C-O bond in C-O-C group in the anhydrous glucose ring appeared at 798 cm^{-1} . The absorption corresponding to the -C-O stretching occurs at 1090 cm^{-1} . The C-H rocking mode assigned to PVA was appeared at 920 cm^{-1} for all blends. The absorption corresponding to C-H wagging occurs at 1142 cm^{-1} . Absorption of C=O stretching appears at 1742 cm^{-1} , since the C-H stretching from alkyl groups is identified at 2941 cm^{-1} . The vibrational peaks are assigned to O-H stretching, C-H stretching, C=O stretching, C-H bend of CH_2 , and C-H wagging of PVA and they existed in the FTIR spectra of PVA/starch blends, indicating the success of blending of PVA with starch. The major peaks of PVA blends were similar to those described in literature (PARPARITA & al., 2012 [21]; JUBY & al., 2012 [34]).

(c) Differential Scanning Calorimetry (DSC)

The differential scanning calorimetry (DSC) test was conducted to determine the enthalpy of melting (ΔH_m) of the polymer film. DSC thermograms for ELVANOL 75-15 sample and its blends exposed to first and second heating runs are shown in Figure 4.

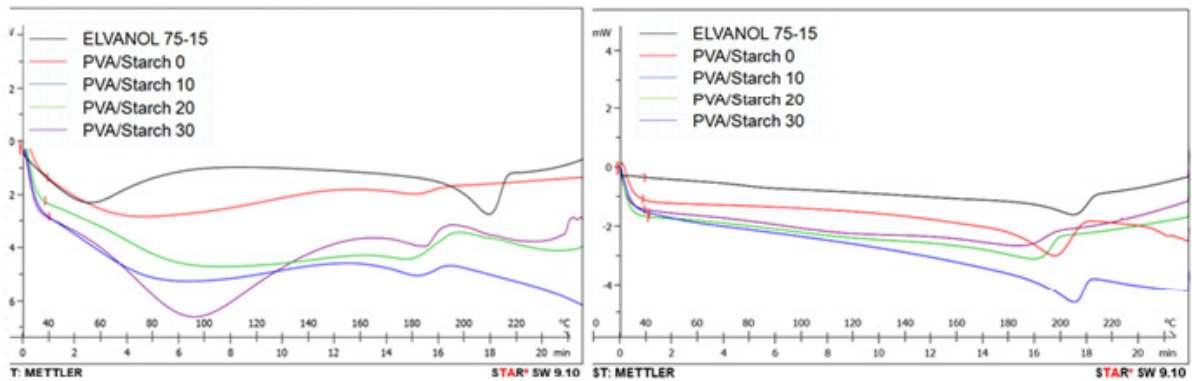


Figure 4. DSC spectra, first heating run (left) and DSC spectra, second heating run (right)

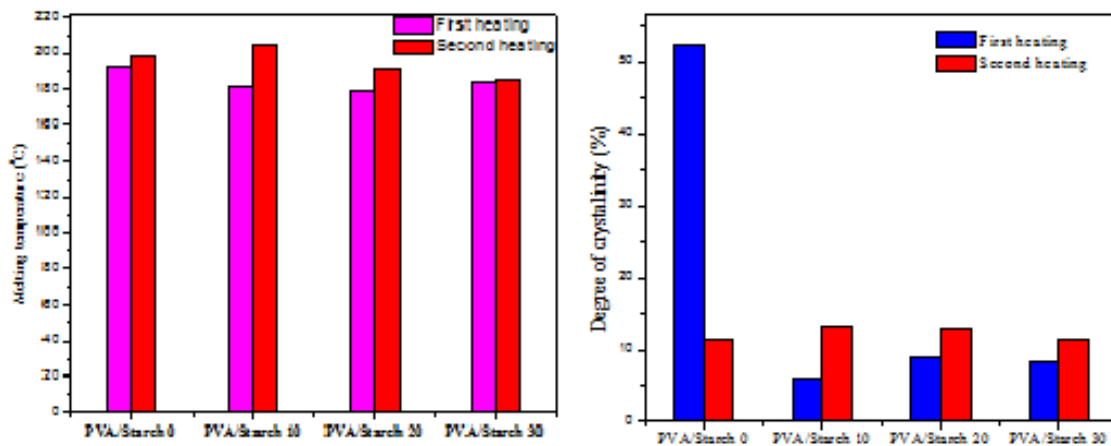


Figure 5. The graphical representation of the melting temperature of PVA blends (left) and the degree of crystallinity for PVA blends

The broad peak at approximately 100 °C represents the evaporation of residual water existing in the samples.

It is known that PVA consists of crystalline and amorphous phases. This results in quite a complex behaviour when the polymer is heated. From the second melting of PVA (Figure 5), a transition at about 96.62 °C is observed which is attributed to the glass transition (T_g) relaxation process resulting from micro-Brownian motion of the main chain backbone. The endothermic peak at 205.08 °C was attributed to the melting point of PVA.

In comparison with neat PVA, blends with starch do not show T_g . This suggests that the segmental mobility of amorphous pure PVA increases due to the addition of plasticizer and starch and become less rigid segments. Until 250°C there is not observed the thermal degradation of samples.

It was stated by HOURSTON & SONG, 2006, that the change in enthalpy of melting was used to determine the reactive interactions of polymer blends. It was clearly shown that the enthalpy of melting obtained in second melting process, ΔH_m , decreased as the amount of starch increased. This is due to the fact that the intermolecular interaction in the compound has decreased (HOURSTON & SONG, 2006 [35]). Higher ΔH_m values from second melting step of PVA/Starch 10 sample(16.43J/g) compared to PVA/Starch 30 sample (11.00 J/g) proved that the intermolecular interactions present in first blend was stronger. Thus, larger amount of energy was essential to break the bonds and free the polymer chains from the rigid and crystal structures (LIU & al., 1999 [36]). This intermolecular interaction is due to the presence of hydrogen bonds between PVA and starch. Conversely, blends with higher

percentage of starch had lower ΔH_m . Blends with less crystalline region or more amorphous nature does not require high amount of energy to break the bonds due to the relatively weak intermolecular forces.

The strong difference in crystallinity between first and second scan is due to the high crystallization rate of PVA/starch blends upon cooling. High crystalline content of PVA/starch blends is correlated with high melting temperature recorded during second melting process.

(d) Optical properties and (e) Permeability

One of the desired characteristics of a packaging material is that it should protect food from the effects of light, especially UV radiation (KANATT & al., 2012 [33]). To determine the light transmission properties of the films, they were scanned at wavelengths ranging from 200 to 800 nm and the percentage light transmittance was recorded (Figure 8).

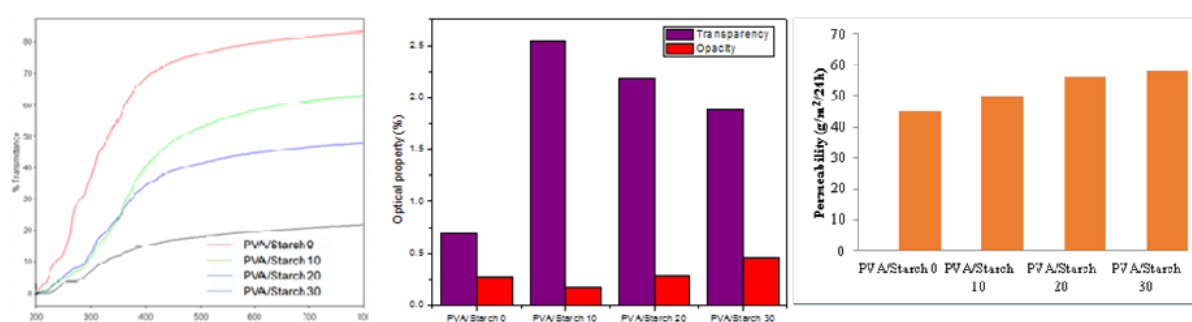


Figure 8. The graphical representation of (from left to right): light transmission properties of the films; transparency and opacity of PVA/starch films and the effect of starch on the permeability of the tested samples

Film samples exhibited low light transmission in UV light, especially at wavelengths of 280 nm. Films with starch show lower percent transmittance compared with PVA/Glycerol sample suggesting that PVA/starch films have good barrier to ultraviolet light, a powerful lipid-oxidizing agent in food systems. At 400 nm, the PVA/Glycerol film has a transmittance value of around 75 %, whereas, in PVA/starch films the transmittance values is further reduced, suggesting that films with starch improved the light barrier properties. The loss of transmittance is registered in the sample with 30 % starch.

The effects of starch content on film opacity and transparency are shown in Figure 8. PVA/Starch 0 film was more transparent (lower opacity value). Incorporation of 20% and 30 % starch increased the opacity.

The permeability of tested samples (Figure 8) has increased proportionally with the addition of starch. Also the results obtained from permeability tests are correlated with the crystallinity samples. When the permeability is high, the crystallinity of samples is low.

4. Conclusions

First the PVA with glycerol were loaded until the torque reached a constant value, indicating full homogenization of the glycerol into PVA matrix. Studies on the processability characteristics and melt rheology of PVA blends on a Brabender Plastograph show that once the starch was incorporated into the matrix, the torque of the physical blends highly increased, due to increase in the viscosity of the starch phase. This issue lead to increase in melt viscosity and power consumption during processing of PVA blends.

The strong difference in crystallinity between first and second scan is due to the high

crystallization rate of PVA/starch blends upon cooling. High crystalline content of PVA/starch blends is correlated with high melting temperature recorded during second melting process.

Films with starch show lower percent transmittance compared with PVA/Glycerol sample suggesting that PVA/starch films have good barrier to ultraviolet light, a powerful lipid-oxidizing agent in food systems. The film of PVA/Glycerol was more transparent (lower opacity value). Incorporation of 20% and 30 % starch increased the opacity.

The permeability of tested samples has increased proportionally with the addition of starch. Also the results obtained from permeability tests are correlated with the crystallinity samples.

The results obtained during this work show that the polymeric material based on polyvinyl alcohol and starch have good physical - mechanical characteristics, being suitable from this point of view for packaging industry. However, more specific further research will be conducted in order to determine if they can be used in certain field of food packaging.

5. Acknowledgements

This paper was published under the frame of European Social Fund, Human Resources Development Operational Programme 2007-2013, project no. POSDRU/159/1.5/S/132765.

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