

Starch / Polyvinyl Alcohol Blends Containing Polyurethane as Plasticizer

Lucía del Sol González-Forte¹, Oscar R. Pardini^{1,2} and Javier I. Amalvy^{1,2,3,*}

¹*Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), (CCT La Plata CONICET-UNLP), Diag. 113 y 64. La Plata, Argentina*

²*Comisión de Investigaciones Científicas de La Provincia de Buenos Aires (CICPBA), Argentina*

³*Centro de Investigación y Desarrollo en Ciencia y Tecnología de Materiales (CITEMA), Facultad Regional La Plata (Universidad Tecnológica Nacional) 60 y 124. La Plata, Argentina*

Abstract: Starch-based films containing 70wt% of starch and a combination of poly(vinyl alcohol) and a low glass transition temperature polyurethane as plasticizer were prepared. The effect of PVA/PU ratio content on the morphology and physical properties was investigated by infrared spectroscopy (FTIR), X-ray diffraction, differential scanning calorimetry, thermogravimetric analysis, scanning electron microscopy and measurements of mechanical properties and water vapor permeability. A relative small amount of PU (less than 15 wt%), significantly changes the properties of the blend due to intermolecular hydrogen bonding interactions between the three components. FTIR and XRD results indicate that blends containing PU are more amorphous than the pure starch/PVA blend and SEM images show a homogeneous matrix due to the good compatibility between starch and PU. Incorporation of PU to the starch/PVA blend shifts the glass transition temperature to lower values and reduce the elastic modulus, indicating a successful plasticization effect. The resulting blends produce films with improved physical properties.

Keywords: Coatings, hydrogen bonding, barrier properties.

1. INTRODUCTION

There is an increasing tendency to use natural biopolymers due to their renewable, biocompatible and biodegradable characteristics. Natural biopolymers including starch, cellulose, and chitosan have been tested, alone or combined with synthetic polymers, to explore the possibility of forming a fully or partially biodegradable film [1]. Of these three materials, starch is the most attractive candidate because of its low cost, easy availability, potential mass production from renewable resources [2].

However, the low water resistance and high brittleness of starch films have limited their application. Therefore, many attempts have been made to overcome these problems by blending starch with other biodegradable synthetic polymers for several applications [3, 4]. Starch/polyvinyl alcohol (PVA) polymer combination is one of the most common biodegradable blends [5, 6]. PVA is a biodegradable synthetic polymer which has the advantages of excellent film forming capacity, adhesive properties, and high thermal stability increasing their role in the material industry. However, the physical properties such as the mechanical properties and water

resistance of the starch/PVA-blended systems are still lower than those of conventional polymers and huge amounts of PVA, as high as 50wt%, sometimes is necessary to achieve the desired film properties. Plasticization of starch by external plasticizers is also a common way of modifying properties. Typical substances include glycerol, sorbitol, xylitol and natural oils [7]. In particular Sreekumar *et al.* [8] studied starch/polyvinyl alcohol blends using glycerol as plasticizer. They found that the crystallinity of the blend decreases, the maximum degradation temperature increases and the tensile property decreases when the starch content is increased. The stronger the hydrogen bonds between starch and the plasticizer, the more difficulty for starch to recrystallizes during storage [9].

External plasticizers are low molecular weight molecules that interact with polymer chains, but because they are not chemically attached to the polymer they can be lost by evaporation, migration or extraction (temporary additives).

Others high molecular weight polymers can also act as plasticizers [10-12] and owing to the lower mobility the migration process is reduced [13].

In order to obtain films containing starch as the major component, an effective plasticization or compatibilizer compound is required. Wu and Zang [14] mixed a thermoplastic starch with waterborne polyester-type polyurethane based on 2,4-toluene

*Address correspondence to this author at the Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), (CCT La Plata CONICET-UNLP), Diag. 113 y 64. La Plata, Argentina; Tel: ++ 54-221-4257291/4257430 (Ext: 154); Fax: ++ 54-221-4254642; E-mail: jamalvy@inifta.unlp.edu.ar

diisocyanate (TDI) and using compression molding prepared sheets of the blended materials. They found that mechanical properties and water resistance were all higher than that of starch when PU content was in the range from 5 to 30wt%. Lu *et al.* [15] proposed to use an isophorone diisocyanate-based PU to modify a glycerol plasticized starch. They found that when PU content is lower than 20wt%, plasticized starch can be miscible with PU and the properties of the plasticized starch/PU blend can be attributed to intermolecular hydrogen bonding interactions between starch and polyurethane.

Karagoz and Ozkoc [16] used poly(lactic acid) as plasticizer and 1,4-phenylene diisocyanate as compatibilizer. In this case by using the compatibilizer the homogeneity of the blends and the interfacial interactions between the two phases were improved. More recently Yu *et al.* [17] found that the compatibility between starch and PVA is improved when the starch is treated at 55°C, which modifies the bonds strength.

In this work we proposed a new strategy based in the combination of PVA with functional polyurethane (PU) of low glass transition temperature (T_g). Hydrogen-bonding interactions between the urethane and ether groups of polyurethane chains, and the hydroxyl groups of starch and PVA chains are expected. Therefore this functional polyurethane is expected to act as an effective plasticizer and compatibilizer, disrupting hydrogen bonds between starch chains and forming new hydrogen bonds between PVA and starch chains and, because of the effectiveness, it will be used in low quantity in order to obtain starch-based films containing no less than 70wt% of starch. In this work, the following weight ratios: starch/PVA/PU 70/25/05; 70/20/10 and 70/15/15 were selected and the results are presented and discussed.

2. MATERIALS AND METHODS

2.1. Materials

Commercial corn starch (Maizena Duryea[®], Unilever Argentina S. A.), containing 0.11g water, 0.006g lipids, 0.003g ash, 0.003g proteins/g starch, and an amylose/amylopectin ratio of 25/75 (dry basis) was used [18]. Poly (vinyl alcohol) (PVA) was a laboratory grade reagent in the form of powder, hydrolyzed 98% and with a range of molecular weight (M_w) from 13,000 to 23,000 (Sigma Aldrich, USA). The polyurethane (PU) was prepared from dicyclohexylmethane-4,4'-diisocyanate (H_{12} MDI, Desmodur

W, Bayer) and polypropylene glycol, M_n 2,000 (PPG 2000, Voranol 2120, Dow) following a prepolymer process. Ethylene diamine (EDA, Sigma Aldrich, USA), dibutyltindilaurate (DBTDL, Sigma Aldrich, USA) and 2-hydroxy ethylmethacrylate (HEMA, Sigma Aldrich, USA) were of analytical grade and were used as received. Triethylamine (TEA) was provided by ADELFA S. A. and it was also used as received. Dimethylol propionic acid (DMPA, Sigma Aldrich, USA) was dried at 100°C for 2h in an oven.

2.2. Processing

2.2.1. Aqueous Dispersions Preparation

Starch-gelatinized dispersion was prepared by heating 3wt% of starch in water at 90°C for 1 hour with magnetic stirring. PVA was dissolved in water at 90°C with magnetic stirring for 24 hours.

2.2.2. Synthesis of the Polyurethane Dispersion

A 1000ml six-neck separable flask with a mechanical stirrer, thermocouple, condenser, sampling tube, inlet system for gases and pump feed inlet was used as a reactor. PPG2000 and DMPA were charged into the dried flask. While stirring, the mixture was heated to 90°C, homogenized and bubbled dried N_2 for approximately 60min, followed by increasing the temperature to 98°C and adding a mixture of H_{12} MDI and DBTDL catalyst. The mixture was allowed to remain at this temperature for approximately 2h. The prepolymer was cooled to 45°C and HEMA dissolved in acetone was added slowly and allowed to react for approximately 90min. Then, the temperature was raised to 60°C and kept constant until the isocyanate (NCO) content reached the desired value (approximately for 90min). The free isocyanate content was determined using the conventional dibutylamine back-titration method [19]. Upon obtaining the theoretical NCO value (ca. 4.7%) the mixture was cooled to 55°C and TEA (in acetone) was fed in slowly over 50min. After neutralization the temperature was lowered to room temperature. An aqueous dispersion of PU was obtained by adding the PU prepolymer to water containing the appropriate amount of EDA to perform the chain extension reaction. The dispersion was performed at about 300rpm in an ordinary glass reactor at 30°C during 45min. The resulting product was a stable dispersion with solid content of about 30wt% [20].

2.2.3. Blend and Film Preparation

Blends of starch/PVA/PU were prepared by adding drop wise the PVA aqueous solution and the starch

dispersion to the PU dispersion, allowing stirring for 30min. The composite films were prepared by casting the required amount of dispersion on a Teflon[®] substrate and evaporating the water at room temperature. The ratios of starch, PVA and PU were selected based on the optical quality of films (good transparency), fixing the starch composition to 70wt%. The remaining 30wt% was completed with PVA and PU. After preliminary test the following ratios starch/PVA/PU 70/25/05; 70/20/10 and 70/15/15 were selected.

2.3. Characterization

2.3.1. FTIR Spectroscopy

The FTIR spectra were measured in transmission and ATR mode using a FTIR Nicolet 380 spectrometer, Thermo Scientific, USA. The samples were in free standing films or they were powdered mixed with KBr and formed disks by pressing.

The FTIR spectra were obtained by recording 64 transmission scans between 4000 and 400cm⁻¹ or between 4000–650cm⁻¹ (ATR, ZnSe IRE) with a resolution of 4cm⁻¹. Spectra processing was performed using the software EZ Omnic (Thermo Electron Corporation, USA).

2.3.2. Modulated Differential Scanning Calorimetry (MDSC)

The glass-transition temperature, T_g of the polymeric materials was measured with a modulated differential scanning calorimeter (Modulated DSC Q 200, TA Instruments, USA). Nitrogen was used as a purge gas at a flow rate of 30ml/min. An empty hermetic aluminum pan was used as a reference and the heating/cooling rate was 2.5°C/min, modulated by a sinusoid with amplitude 1°C and period 60s. The temperature range was from room temperature to 150°C. All glass-transition temperatures were determined from the inflection point in the reversing-heat-flow signal (RHF) with the TA Instrument Analyzer Software. The derivative reversing heat-flow (DRHF) curves were calculated using a smoothing region width of 5°C by Universal Analysis 2000 software.

2.3.3. X-ray Diffraction Analysis (XRD)

X-ray diffraction analysis of blends was performed using a PANalytical, model X'Pert PRO instrument. Samples were irradiated with Cu K α radiation 1.5403 Å using 40mA and 40kV. The diffractograms were obtained in the range of 3–40°/2 θ with a scan speed 0.0044°/s.

2.3.4. Thermogravimetric Analyses (TGA)

The thermogravimetric analyses (TGA) were carried out with a Shimadzu TGA-50 instrument (Japan) at a heating rate of 30°C/min in a nitrogen atmosphere at 30ml/min, from room temperature to 550°C using 4mg of sample in aluminum pans [21]. A convenient way of expressing thermal stability is using the initial decomposition temperature (IDT) and the temperatures corresponding to a 5% and to 50% of weight loss, i.e. the thermal indexes T_5 and T_{50} respectively [20]. The residual water content of films was determined from the first weight loss in the TGA curve. The residual mass at 540°C was also determined.

2.3.5. Film Stress-Strain Tests by Dynamic Mechanical Analysis (DMA)

Probes of 6mm × 30mm were used to analyze the tensile stress–strain behavior of the composite films using a dynamic mechanical analyzer DMA TA Instruments-Q 800 (New Castle, DE, USA), equipped with tension clamps. One end of the strand was attached to a superior mobile clamp and the other end fixed to a lower clamp. For quasi-static test in uniaxial condition, a preload force of 2N and a constant force ramp rate 0.9N min⁻¹ were applied to record the stress–strain curves until the film rupture. Tests were carried out at 25°C. At least five replicates of each condition were obtained. According to Mancini *et al.* [22] and Del Nobile *et al.* [23] a mathematical model able to describe the entire stress–strain curve is:

$$\sigma_T = E_C \varepsilon_T e^{\varepsilon_T K} \quad (1)$$

where ε_T and σ_T (MPa) are the true strain and the true stress, respectively, E_C (MPa) is the elastic modulus (the tangent to the stress–strain curve at the origin), and K is a constant considered as a fitting parameter.

2.3.6. Water Vapor Permeability

Water vapor permeability (WVP) of different coating formulations was determined following the guidelines of the ASTM E96-95 (Standard Test Methods for Water Vapor Transmission of Materials), using circle samples with a free surface area of 18.85cm². Silica gel was used as desiccant. Samples were placed in individual test cups and equilibrated for 24h in a desiccator cabinet maintained at 13°C and 80% of relative humidity (RH) with an ammonium chloride saturated aqueous solution. Samples were weighed daily to calculate weight loss with time for seven days.

2.3.7. Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) of the surface and cryo-fractured surfaces of the starch/PVA/PU composites were performed using a FEI-Quanta 200 (The Netherlands) microscope in the low vacuum mode operated at 20kV acceleration voltage and current of 100 μ A. Samples were prepared by breaking them in liquid nitrogen and coated using gold sputtering prior to inspection to prevent sample-charging effects.

3. RESULTS AND DISCUSSION

Optical appearance of films depends on the composition. Pure starch films are opaque and brittle. Starch/PVA 70/30 has good transparency and those containing PU have a very good transparency and flexibility.

Starch is characterized by the ability to retain water. This residual water contributes to the structure and there are several studies about the influence on properties. Pure starch films prepared in this work have a residual water of 8.6wt%. This level of water is enough for a crystalline organization of the starch in crystalline and amorphous regions [24].

3.1. FTIR Spectroscopy

The way the FTIR spectrum is affected may give information about the presence of specific interactions between the functional groups of the polymers. Before discussion of starch, PVA and PU interactions in the ternary blends, we will discuss first the FTIR spectra of the starch/PVA 70/30 blend. Figure 1 shows the FTIR spectra of starch, PVA and starch/PVA 70/30 in the 1500–700 cm^{-1} region.

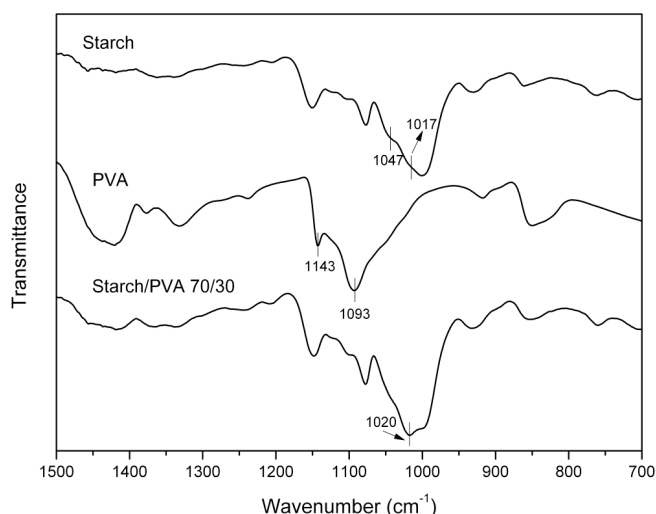


Figure 1: FTIR spectra of starch, PVA and starch/PVA 70/30 in the 1500–700 cm^{-1} region.

The spectrum of starch shows typical bands below 1500 cm^{-1} , where the vibrations of glucose molecules dominate [25]. These bands are attributed to contribution of three main vibrational modes, C-O stretching, C-O-H deformation and bending. The absorption of the $-\text{CH}_2\text{OH}$ along with the coupling modes of C-O and C-C stretching are responsible for other bands [24]. The relevant band for the discussion in our case is the one located at 1000 cm^{-1} . Capron *et al.* [24] have used FTIR to study starch in rubbery and glass states. They have identified amorphous starch by a FTIR band around 1022 cm^{-1} and the crystalline state by a band at 1047 cm^{-1} . The corresponding peaks in this study are observed as shoulders at 1017 and 1047 cm^{-1} , respectively (see Figure 1).

The FTIR spectrum of pure PVA sample in Figure 1, shows an absorption peak at 1143 cm^{-1} attributed to the crystalline part of the PVA and related to carbonyl stretching band (C=O) [27] and at 1093 cm^{-1} also due to the carbonyl stretching band (C=O) [28].

The FTIR spectrum of the starch/PVA 70/30 blend shows important changes in the 1000 cm^{-1} band assigned to starch. Starch and PVA are polar substances having hydroxyl groups in their chemical structure, these highly polar hydroxyl groups tend to form intermolecular and intramolecular hydrogen bonds, improving the integrity of starch/PVA blends accordingly [29, 30]. An increase of the intensity of the amorphous C-O band is observed in the FTIR spectrum indicating that the PVA increases the amount of the amorphous region of starch [31].

The OH region of the FTIR spectrum of starch/PVA also shows the typical disruption of the crystallinity of the starch due to the disruption of intermolecular H-bonding of the starch molecules themselves and the introduction of H-bonding between PVA and starch chains [32]. This interaction was confirmed in our case *via* FTIR (not shown here) in which the O-H stretching band from the glucose ring at 3315 cm^{-1} for the pure starch shifted to a lower wave number (3286 cm^{-1}) when including PVA.

Figure 2 show the FTIR spectra of films starch/PVA 70/30, starch/PVA/PU 70/15/15 and starch/PVA/PU 70/25/5 in the vibrational modes of the O-H, C=O and C-O groups. The FTIR spectra of pure PU is also included for comparison purposes. The typical carbonyl stretching band at 1716 cm^{-1} is clearly observed in the 70/15/15 blend.

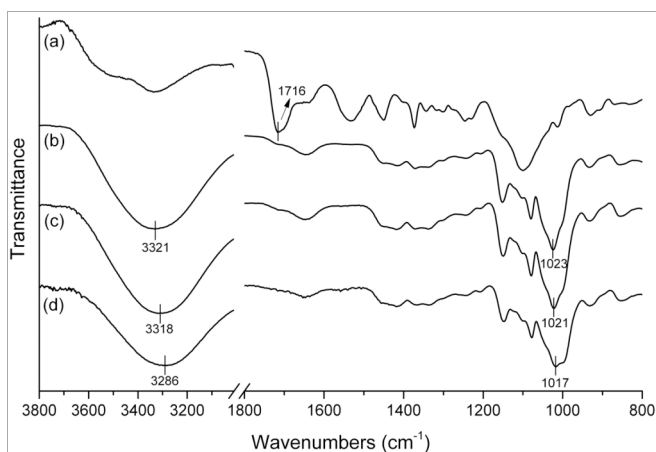


Figure 2: FTIR spectra of pure PU film, (a) starch/PVA/PU 70/15/15, (b) starch/PVA/PU 70/25/5, (c) and starch/PVA/PU 70/30 film, (d) in the -OH and CO vibrational regions.

By including 5 wt% of PU the OH band of the starch/PVA at 3286cm^{-1} shift to 3318cm^{-1} and with 15 wt% to 3321cm^{-1} , indicating that the PU chain interferes with H-bond formation of the starch-PVA, probably because the formation of H-bonds with ether groups of the polyol or by hydrogen bonding interactions between the urethane groups of PU and the hydroxyl groups on starch.

In the C-O region an increase of the intensity of band at 1022cm^{-1} indicate a more amorphous characteristics and plasticization of blends when including PU in the blend, indicating again that the PU chains modify the hydrogen-bonds properties.

In conclusion, changes observed in the intensities and positions of bands of FTIR spectra suggest interactions of the PU chains with the -OH groups of starch and PVA, which contribute to the miscibility of the three components in the blend [33, 34].

3.2. Modulated Differential Scanning Calorimetry (MDSC)

Differential scanning calorimetry technique is one of the convenient methods for investigating the compatibility of polymer blend. It is used to investigate the effect of blending starch, PVA and PU on the glass transitions. The use of modulated DSC allows separating the total heat flow into reversing and non-reversing components and the differential of heat capacity signal with temperature, dC_p/dT , over the glass transition region, makes easier the T_g determination [35].

In this work we use the reversing heat flow (RHF) and the derivative of reversing heat flow (DRHF) to study the miscibility of blends. The RHF curves of the

pure components and the starch/PVA/PU blends in the relevant region (from 20 to 100°C) are shown in Figure 3 and detailed in Table 1.

Table 1: Thermal Transitions of Pure Components and Starch/PVA/PU Blends

Film Composition	Thermal Transition ($^\circ\text{C}$)
Pure Starch	79
PVA	---
Starch/PVA 70/30	79
Starch/PVA/PU 70/25/5	77
Starch/PVA/PU 70/20/10	70
Starch/PVA/PU 70/15/15	52
PU H_{12} MDI	82

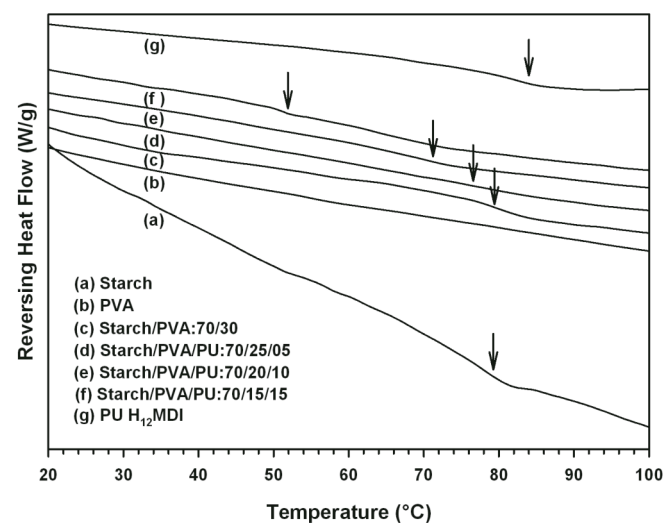


Figure 3: Reversing heat flow of pure starch, pure PVA, pure PU H_{12} MDI, starch/PVA 70/30 and starch/PVA/PU with compositions: 70/25/5, 70/20/10 and 70/15/15.

The RHF curve for pure PVA did not show any transition in the studied region. For pure PU H_{12} MDI, the RHF curve showed a transition at 85°C associated to the hard segments of the polymer [36]. For pure starch, a glass transition centered at 79°C is observed, corresponding to the starch containing about 10% water content [37].

The RHF curve of the starch/PVA blend shows a glass transition at 79°C (arrow in Figure 3 curve "c"), corresponding to the starch. The thermal behavior of different compositions of unplasticized corn starch/PVA blends was described by Moneam *et al.* [38] using conventional DSC. They found for the blends only one glass transition temperatures close to the starch T_g value and they suggested the occurrence of compatibility.

The RHF curve for starch/PVA/PU 70/25/5 shows a very weak signal at about 77°C related to the starch glass transition and no signal associated to PVA is observed. The PU chains could lead to disruption of bonding between starch and PVA and formation of new bonds leading to a better compatibility between the starch and PVA phases due to the high mobility of PU chains. By adding 10wt% of PU a glass transition centered at 70°C was observed. The 70/15/15 curve shows also a transition centered at 52°C. These results indicate that the PU chains are modifying the interactions, plasticizing the blends and only one transition is observed indicating a better miscibility.

3.3. X-ray Diffraction Analysis (XRD)

The XRD patterns of blends prepared in this work are shown in Figure 4.

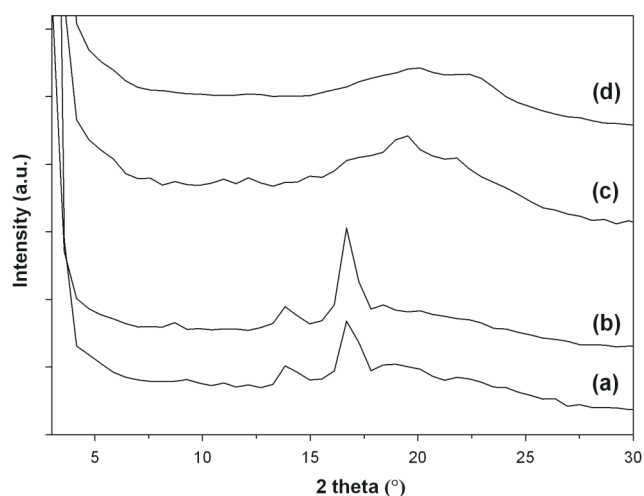


Figure 4: X-ray diffraction patterns of starch/PVA/PU blends (a) 70/30; (b) 70/25/5; (c) 70/20/10; (d) 70/15/15.

In gelatinized starch the glucosidic chains are predominant in an amorphous state (low crystallinity) and starch X-ray patterns are quite noisy [39]. According to *Wu et al.* [40], XRD of corn starch presents peaks at 14.88, 17.08, 17.98, 19.98, and

22.78°. The X-ray patterns of starch/PVA: 70/30 and starch/PVA/PU: 70/25/5 blends show the starch peaks at about 14° and 17° but in the starch/PVA/PU: 70/20/10 and starch/PVA/PU: 70/15/15 were not seen indicating changes after increasing the PU content and a decreasing crystallinity. A similar behavior was reported by *Ran et al.* [11] using a polyester as plasticizer. They also claim that by reducing the crystallinity the processing properties (blending modification, pelleting and blow molding) are improved.

3.4. Thermogravimetric Analysis (TGA)

Table 2 shows the residual water, initial decomposition temperature (IDT), thermal indexes T_5 , T_{50} and final residue at 540°C.

For the pure starch films, the residual water is 8.6wt% and for the starch/PVA films it increases to 10.1wt% due to the PVA's hydrophilicity. By replacing some PVA for PU, a slight decrease in the residual water is observed, due to the lower hydrophilicity of PU. A similar behavior was observed by *Lu et al.* [15]. The PU addition to the starch/PVA blend did not modify the IDT and residue at 540°C.

The T_5 and T_{50} of pure starch are 105°C and 345°C respectively. By including PVA the temperatures are almost the same (Table 1). However, by including PU the T_5 decreases, being the lowest value for the starch/PVA/PU 70/20/10 blend. These values are within the loss of water range of temperature (60 – 170°C) indicating that the hydrophobic nature of PU facilitates the loss of water. The same is observed for the T_{50} for starch/PVA/PU 70/20/10 blend, indicating a decrease of stability. For the other two blends no discernible trend is detectable regarding the amount of PVA/PU, T_5 temperatures decreases in all cases when PU is incorporated to the starch/PVA blend, but a slightly increase in T_{50} is observed, indicating in these cases a stabilizing effect of PU.

Table 2: Residual Water, Initial Decomposition Temperature (IDT), T_5 , T_{50} and Final Residue at 540°C of Systems Prepared in this Work

Film Composition	Residual Water (wt%)	IDT (°C)*	T_5 (°C)	T_{50} (°C)	Residue# (wt%)
Pure Starch	8.6	270	105	345	13.0
Starch/PVA 70/30	10.1	235.5	103.5	346.3	14.5
Starch/PVA/PU 70/25/5	9.8	240.0	84	348.9	17.2
Starch/PVA/PU 70/20/10	8.7	236.0	78.5	340.5	15.3
Starch/PVA/PU 70/15/15	8.5	236.5	89.8	347.2	15.4

*IDT: after water loss.

#Residue at 540°C.

3.5. Stress-Strain Behavior

The relationship between stress and strain, which corresponds to elastic modulus, was here affected by an exponential term acting as a damping factor [23]. The E_c parameter could be estimated, which allowed characterizing the elastic region of the curves, meaning that the points immediately before rupture were not considered to obtain a better fitting of the experimental points at initial and intermediate deformations. The mechanical behavior of starch/PVA/PU films at 25°C exhibited values of stress and strain of about 20MPa. The incorporation of PU decreases slightly the maximum stress as expected.

Figure 5 exhibits the elastic modulus obtained from (1) for all samples assayed at 25°C; as it was expected, the incorporation of PU lowers the elastic modulus, indicating that PU is an effective plasticizer.

3.6. Water Vapor Permeability (WVP)

The WVP of starch/PVA 70/30 and starch/PVA/PU with different PVA/PU ratios is about 0.08 (± 0.02). $10^{-11} \text{gs}^{-1} \text{m}^{-1} \text{Pa}^{-1}$. This value is much lower than gelatinized starch ($17.66 (\pm 2.97) \cdot 10^{-11} \text{gs}^{-1} \text{m}^{-1} \text{Pa}^{-1}$ [41]. The addition of PVA (and PU) introduces a tortuous path for water molecules to pass through as reported in other work [42]. As starch is the main component of blends (70wt%), by changing the remaining 30wt% of the blend by PVA or combination of PVA and PU no

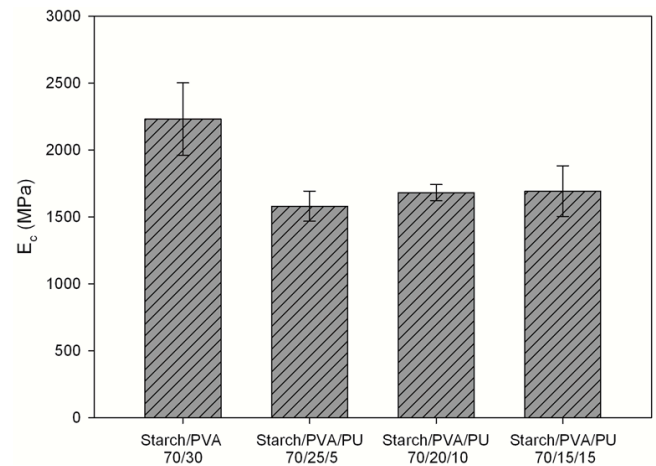


Figure 5: Elastic modulus, E_c , of starch/PVA 70/30 and starch/PVA/PU with compositions: 70/25/5, 70/20/10 and 70/15/15.

important changes in the overall hydrophilicity is expected and similar WVP values are observed.

3.7. Scanning Electron Microscopy (SEM)

Scanning electron microscopy of cryo-fracture sections of samples are shown in Figure 6.

Smooth surfaces and no voids are observed in all cases. The SEM micrographs of starch/PVA 70/30 blend illustrate that starch structure is completely disrupted and a continuous phase is obtained due to the high compatibility between the starch and PVA, which contributed to the formation of less structured matrix, with less starch-starch interaction [43]. Blends

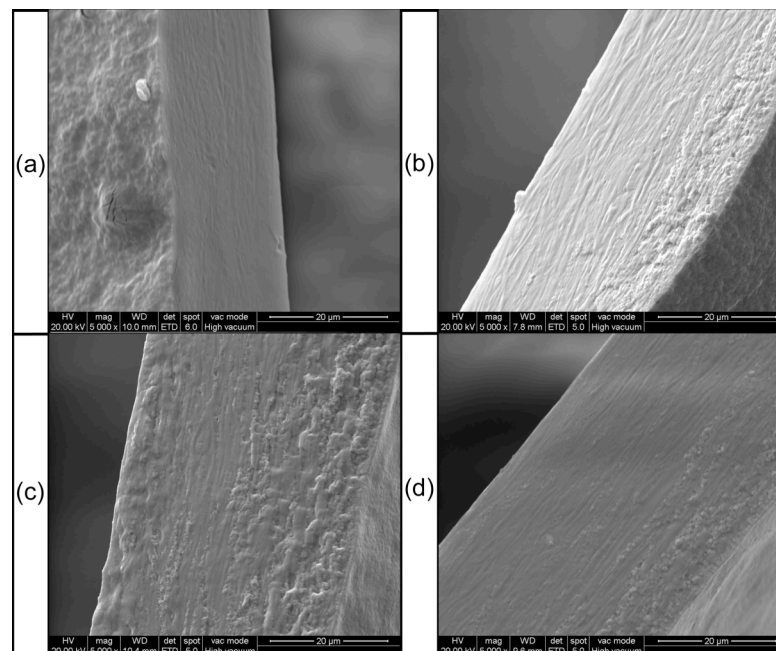


Figure 6: SEM (5000x) images of transversal cutting of films of starch/PVA 70/30 (a) and starch/PVA/PU 70/25/5 (b) 70/20/10 (c) and 70/15/15 (d). Scale: 20µm.

starch/PVA/PU exhibit an almost smooth fractured surface, with no evidence of phase separation. This is attributed to the good compatibility between starch and PU because of hydrogen bonding interactions between the urethane groups of PU and the hydroxyl groups on starch and the hydrogen bonding interactions existing in the interface between PVA, starch and PU [15]. The uniform distribution of the polymers in the matrix plays an important role in improving the mechanical performance of the resulting composite films.

CONCLUSIONS

Blends of starch-based films containing 70wt% of starch were prepared using PVA and a low T_g polyurethane. Plasticization was achieved by using a low amount of PU (less than 15wt%), which significantly changes the properties of the resulting blend films. Elastic modulus of ternary blend decreases by 23% compared to the starch/PVA blend. XRD studies show that the crystallinity decreases after incorporation 10wt% of PU. The key factor determining the better properties of the ternary blend can be attributed to intermolecular hydrogen bonding interactions between starch, PVA and polyurethane. The PU prepared with the polyol of M_n 2000 interacts with the -OH groups of the PVA and the starch chains, promoting a more homogeneous system. So, incorporating PU to the starch/PVA blends at around 15 wt% represents a good strategy for improving the properties of the films.

ACKNOWLEDGEMENTS

Contract grant sponsors: CICPBA and ANPCyT (PICT 2014–1785). The authors thank to ITPN (UBA) for performing the TGA measurements and Centro de Investigaciones Geológicas (La Plata) for the XRD analysis.

SUPPLEMENTAL MATERIALS

The supplemental materials can be downloaded from the journal website along with the article.

REFERENCES

- Jiang L and Zhang J. Biodegradable polymers and polymer blends. In: Ebnesajjad S, Ed. Handbook of biopolymers and biodegradable plastics: properties, processing applications. Kidlington, Oxford: Elsevier 2013; pp. 109-128. <http://dx.doi.org/10.1016/B978-1-4557-2834-3.00006-9>
- Zhang Y, Rempel C and Liu Q. Thermoplastic Starch Processing and Characteristics - A Review. Crit Rev Food Sci Nutr 2014; 54(10): 1353-1370. <http://dx.doi.org/10.1080/10408398.2011.636156>
- Brassoulis D. An overview on the mechanical behaviour of biodegradable agricultural films. J Polym Environ 2004; 12(2): 65-81. <http://dx.doi.org/10.1023/B:JOOE.000010052.86786.ef>
- Santayanan R and Wootthikanokkhan J. Modification of cassava starch by using propionic anhydride and properties of the starch-blend polyester polyurethane. Carbohydr Polym 2003; 51: 1724. [http://dx.doi.org/10.1016/S0144-8617\(02\)00109-1](http://dx.doi.org/10.1016/S0144-8617(02)00109-1)
- Jayasekara R, Harding I, Bowater I, Christie GBY and Lonergan GT. Preparation, surface modification and characterisation of solution cast starch PVA blended films. Polym Test 2004; 23: 17-27. [http://dx.doi.org/10.1016/S0142-9418\(03\)00049-7](http://dx.doi.org/10.1016/S0142-9418(03)00049-7)
- Khan MA, Bhattacharia SK, Kader MA and Bahari K. Preparation and characterization of ultra violet (UV) radiation cured bio-degradable films of sago starch/PVA blend. Carbohydr Polym 2006; 63: 500-506. <http://dx.doi.org/10.1016/j.carbpol.2005.10.019>
- Gurgel Adeodato Vieira M, Altenhofen da Silva M, Oliveira dos Santos L and Masumi Beppu M. Natural-based plasticizers and biopolymer films: A review. Eur Polym J 2011; 47: 254-263. <http://dx.doi.org/10.1016/j.eurpolymj.2010.12.011>
- Sreekumar A, Al-Harhi MA and De SK. Studies on compatibility of biodegradable starch/polyvinyl alcohol blends. Polym Eng Sci 2012; 52: 2167-2172. <http://dx.doi.org/10.1002/pen.23178>
- Spychaj T, Wilpiszewska K and Spychaj S. Starch-urethane polymers: physicochemical aspects, properties, application. In: Bhattacharyya D, Ed. Handbook of engineering biopolymers: homopolymers, blends, and composites 2007; pp. 155-165. <http://dx.doi.org/10.3139/9783446442504.005>
- Dong A, Xie J, Liu Q, Li D and Hu P. rheological and thermal behavior of pvc/starch blends modified by acrylic acid. Polym Eng Sci 2013; 54: 2449-2454. <http://dx.doi.org/10.1002/pen.23825>
- Ran X, Deng P, Zhuang Y, Dong L, Gao G, Zhao C, et al. Characterization of full-biodegradable starch-PVA-polyester film. Chem Res Chin Univ 2003; 19(2): 249-252.
- Kaseem M, Hamad K and Deri F. Thermoplastic starch blends: a review of recent works. Polym Sci 2012; 54(2): 165-176. <http://dx.doi.org/10.1134/s0965545x1202006x>
- Pedersen GA, Jensen LK, Fankhauser A, Biedermann S, Petersen JH and Fabech B. Migration of epoxidized soybean oil (ESBO) and phthalates from twist closures into food and enforcement of the overall migration limit. Food Addit Contam 2008; 25(4): 503-510. <http://dx.doi.org/10.1080/02652030701519088>
- Wu Q and Zhang L. Preparation and characterization of thermoplastic starch mixed with waterborne polyurethane. Macromol Rapid Commun 2001; 40: 558-564. <http://dx.doi.org/10.1021/ie000582t>
- Lu Y, Tighzert L, Berzin F and Rondot S. Innovative plasticized starch films modified with waterborne polyurethane from renewable resources. Carbohydr Polym 2005; 61: 174-182. <http://dx.doi.org/10.1016/j.carbpol.2005.04.013>
- Karagoz S and Ozkoc G. Effects of a Diisocyanate Compatibilizer on the Properties of Citric Acid Modified Thermoplastic Starch/Poly(lactic acid) Blends. Polym Eng Sci 2013; 53: 2183-2193. <http://dx.doi.org/10.1002/pen.23478>
- Yu H, Cao Y and Fang Q. Effects of Treatment Temperature on Properties of Starch-based Adhesives. BioResources 2015; 10: 3520-3530. <http://dx.doi.org/10.15376/biores.10.2.3520-3530>
- Ferrero C, Martino MN and Zaritzky NE. Effect of hydrocolloids on starch thermal transitions, as measured by DSC. J Therm Anal 1996; 47: 1247-1266. <http://dx.doi.org/10.1007/BF01992826>

- [19] Hepburn C. Analysis and characterization of polyurethane elastomers. In: Polyurethane elastomers. London: Elsevier Science 1991; pp. 292-337.
- [20] Pardini OR and Amalvy JI. FTIR, ¹H-NMR spectra, and thermal characterization of water-based polyurethane/acrylic hybrids. *J Appl Polym Sci* 2008; 107: 1207-1214. <http://dx.doi.org/10.1002/app.27188>
- [21] Barrera JE, Rodríguez JA, Perilla JE and Algecira NA. Estudio de la degradación térmica de poli (alcohol vinílico) mediante termogravimetría y termogravimetría diferencial. *Ingeniería e Investigación* 2007; 2: 100-105.
- [22] Mancini M, Moresi M and Rancini R. Mechanical properties of alginate gels: empirical characterisation. *J Food Eng* 1999; 39: 369-378. [http://dx.doi.org/10.1016/S0260-8774\(99\)00022-9](http://dx.doi.org/10.1016/S0260-8774(99)00022-9)
- [23] Del Nobile MA, Chillo S, Mentana A and Baiano A. Use of the generalized Maxwell model for describing the stress relaxation behavior of solid-like foods. *J Food Eng* 2007; 78: 978-983. <http://dx.doi.org/10.1016/j.foodeng.2005.12.011>
- [24] Capron I, Robert P, Colonna P, Brogly M and Planchot V. Starch in rubbery and glassy states by FTIR spectroscopy. *Carbohydr Polym* 2007; 68: 249-259. <http://dx.doi.org/10.1016/j.carbpol.2006.12.015>
- [25] Kizil R, Irudayaraj J and Seetharaman K. Characterization of irradiated starches by using FT-Raman and FTIR spectroscopy. *J Agric Food Chem* 2002; 50: 3912-3918. <http://dx.doi.org/10.1021/jf011652p>
- [26] Cael JJ, Koenig JL and Blackwell J. Infrared and Raman Spectroscopy of carbohydrates. Part VI: Normal coordinate analysis of V-amylose. *Biopolym* 1975; 14: 1885-1903. <http://dx.doi.org/10.1002/bip.1975.360140909>
- [27] Mallapragada SK and Peppas NA. Dissolution mechanism of semicrystalline poly(vinyl alcohol) in water. *J Polym Sci B Polym Phys* 1996; 34: 13397. [http://dx.doi.org/10.1002/\(SICI\)1099-0488\(199605\)34:7<1339::AID-POLB15>3.0.CO;2-B](http://dx.doi.org/10.1002/(SICI)1099-0488(199605)34:7<1339::AID-POLB15>3.0.CO;2-B)
- [28] Ilcin M, Hola O, Bakajova B and Kucerik J. FT-IR study of gamma-radiation induced degradation of polyvinyl alcohol (PVA) and PVA/humic acids blends. *J Radioanal Nucl Chem* 2010; 283(1): 9-13. <http://dx.doi.org/10.1007/s10967-009-0321-2>
- [29] Sin LT, Rahman WAWA, Rahmat AR and Khan MI. Detection of synergistic interactions of polyvinyl alcohol–cassava starch blends through DSC. *Carbohydr Polym* 2010; 79: 224-226. <http://dx.doi.org/10.1016/j.carbpol.2009.08.003>
- [30] Sin LT, Rahman WAWA, Rahmat AR and Mokhtar M. Determination of thermal stability and activation energy of polyvinyl alcohol–cassava starch blends. *Carbohydr Polym* 2011; 83: 303-305. <http://dx.doi.org/10.1016/j.carbpol.2010.07.049>
- [31] Luo X, Li J and Lin X. Effect of gelatinization and additives on morphology and thermal behavior of corn starch/PVA blend films. *Carbohydr Polym* 2012; 90: 1595-1600. <http://dx.doi.org/10.1016/j.carbpol.2012.07.036>
- [32] Dean KM, Do MD, Petinakis E and Yu L. Key interactions in biodegradable thermoplastic starch/poly(vinyl alcohol)/montmorillonite micro- and nanocomposites. *Compos Sci Technol* 2008; 68: 1453-1462. <http://dx.doi.org/10.1016/j.compscitech.2007.10.037>
- [33] Benmerad MF, Djadoun S, Alothman ZA and Aouak T. Miscibility study of poly(vinyl chloride)/poly(methyl methacrylate-co-4-vinylpyridine) by viscosimetry, DSC, and FTIR. *J Appl Polym Sci* 2011; 119: 173-182. <http://dx.doi.org/10.1002/app.32443>
- [34] Icoz DZ and Kokini JL. Probing the boundaries of miscibility in model carbohydrates consisting of chemically derivatized dextrans using DSC and FTIR spectroscopy. *Carbohydr Polym* 2007; 68: 68-76. <http://dx.doi.org/10.1016/j.carbpol.2006.07.011>
- [35] Hourston DJ and Mo Song M. Applications of modulated temperature differential scanning calorimetry to polymer blends and related systems. In: Reading M, Hourston DJ, Eds. Modulated temperature differential scanning calorimetry. theoretical and practical applications in polymer characterisation. Dordrecht, Netherlands: Springer 2006; pp. 161-215. http://dx.doi.org/10.1007/1-4020-3750-3_3
- [36] Adhikari R, Gunatillake PA, Meijs GF and McCarthy SJ. The effect of diisocyanate isomer composition on properties and morphology of polyurethanes based on 4,4'-dicyclohexyl methane diisocyanate and mixed macrodiols (PDMS–PHMO). *J Appl Polym Sci* 1999; 73: 573-582. [http://dx.doi.org/10.1002/\(SICI\)1097-4628\(19990725\)73:4<573::AID-APP13>3.0.CO;2-N](http://dx.doi.org/10.1002/(SICI)1097-4628(19990725)73:4<573::AID-APP13>3.0.CO;2-N)
- [37] Zhong Z and Sun SX. Thermal characterization and phase behavior of cornstarch studied by differential scanning calorimetry. *J Food Eng* 2005; 69: 453-459. <http://dx.doi.org/10.1016/j.foodeng.2004.07.023>
- [38] Moneam YKA, Sakr HAA, Ali HE, Khalil SA and El-Naggar AWM. Characterization and Antimicrobial Properties of Gamma Synthesized Plasticized Starch/Poly(vinyl alcohol)/ZnO Composites as Protective Coating for papers. *Int J ChemTech Res* 2014; 6(4): 2583-2597.
- [39] Frost K, Kaminski D, Kirwan G, Lascaris E and Shanks R. Crystallinity and structure of starch using wide angle X-ray scattering. *Carbohydr Polym* 2009; 78: 543-548. <http://dx.doi.org/10.1016/j.carbpol.2009.05.018>
- [40] Wu YP, Ji MQ, Qi Q, Wang YQ and Zhang LQ. Preparation, structure, and properties of starch/rubber composites prepared by co-coagulating rubber latex and starch paste. *Macromolecular Rapid Communications* 2004; 25: 565-570. <http://dx.doi.org/10.1002/marc.200300125>
- [41] García MA, Pinotti A, Martino MN and Zaritzky NE. Characterization of starch and composite edible films and coatings. In: Embuscado ME, Huber KC, Eds. Edible Films and Coatings for Food Applications. New York: Springer 2009; pp. 169-209. http://dx.doi.org/10.1007/978-0-387-92824-1_6
- [42] Ghanbarzadeh B, Almasi H and Entezami AA. Improving the barrier and mechanical properties of corn starch-based edible films: Effect of citric acid and carboxymethylcellulose. *Ind Crops Prod* 2010; 33(1): 229-235. <http://dx.doi.org/10.1016/j.indcrop.2010.10.016>
- [43] Cinelli P, Chiellini E, Lawton JW and Imam SH. Foamed articles based on potato starch, corn fibers and poly(vinyl alcohol). *Polym Degrad Stab* 2006; 91: 1147-1155. <http://dx.doi.org/10.1016/j.polymdegradstab.2005.07.001>

Received on 06-04-2016

Accepted on 17-04-2016

Published on 30-06-2016

DOI: <http://dx.doi.org/10.12974/2311-8717.2016.04.01.1>

© 2016 Gonzalez-Forte et al.; Licensee Savvy Science Publisher.

This is an open access article licensed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0/>) which permits unrestricted, non-commercial use, distribution and reproduction in any medium, provided the work is properly cited.