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Bio–based blends of achira starch and polyvinyl alcohol: mechanical and thermal approach

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ABSTRACT

This work aimed to study thermo-mechanical behavior of blends based on polyvinyl alcohol (PVA), achira starch and glycerol as plasticizer. Several formulations were prepared using an experimental mixture design. Initially, raw materials were mixed in a roll mill at 60°C. Afterwards, these blends were molded at 110°C and 38 MPa to obtain translucent and flexible films. Tensile, scanning electronic microscopy (SEM), differential scanning calorimetry, thermo gravimetric and Fourier transform infrared (FTIR) analysis were conducted to evaluate the interaction among components. Mechanical results indicated that deformation mechanism of studied blends is probably ascribed not only to rearrangement of PVA microstructure, but also to starch granules characteristics. Besides, SEM micrographs corroborated the strong influence of shape and size range granules on the fracture mechanism. Moreover, the addition of starch, PVA and plasticizer increased Young's modulus, tensile strength and elongation at break, respectively. Thermal evaluation suggested a slightly influence of starch gelatinization on enthalpy of endothermal process as well as a correlation between mass loss fraction and second order interactions. Likewise, FTIR data let take more certain about the presence of inter- and intra-molecular hydrogen bonds among components of the blend.

Keywords*—PVA/starch blend, thermoplastic starch, polyvinyl alcohol, glycerol*

I. INTRODUCTION

During the last decade, there have been intensive attempts to develop bio-based/nonbiodegradable and biodegradable polymers with synthetic and natural raw materials. The growth in the use of biopolymers includes especially packaging (flexible & rigid) and textile market segments. Thus, international projections estimate that the global production capacity of those materials will rise around 2.4 million tons in 2022 [1].

Starch, a naturally occurring polymer, has been considered as a viable alternative in developing biodegradable polymers due to its relative abundant availability and low cost. The approaches toward promising starch-based biopolymers entail to overcome disadvantages mainly related to its strong hydrophilic nature and poor mechanical integrity [2]. It was found a progressive development of those materials through chemical modifications of starch, thermoplastic starch [3] and blends of starch with other biopolymers such as polylactic acid, polybutylene succinate, poly(3-hydroxibutirate) and polyvinyl alcohol (PVA) [4][5].

In particular, the hydrophilic nature of PVA promotes compatibility with other biodegradable materials by providing a stable supporting surroundings to the formulation of thermoplastic materials [6]. Additionally, PVA is a biodegradable material wide use due to its versatility, barrier properties and low toxicity [7]. In this sense, PVA/starch blend is well suited to develop biopolymers with applications in both packaging and agricultural sectors [8].

The plasticizers are strongly necessary to obtain moldable thermoplastic films of PVA/starch blend; therefore, several substances have been studied such as sorbitol, polyethylene glycol, 1,4-butanediol, pentaerythritol, 1,2,6-hexanetriol, xylitol, mannitol, sucrose, urea, ascorbic acid, citric acid, succinic acid, malic acid, tartaric acid and so on [2][9]. Nevertheless, glycerol (1,2,3-propanetriol) is a suitable plasticizer to attain homogeneity, flexibility and workability of the films [10][11].

Although PVA and traditional starches blends have been extensively investigated, further comprehensive analysis of using alternative starches is still needed. Based on this perspective, this work aims to use the achira (*Canna edulis*) starch as a raw material to formulate PVA/starch blends with glycerol as plasticizer. The effect of different concentrations of components on the mechanical and thermal behavior were investigated.

II. MATERIALS AND METHODS

A. Materials

Native achira starch (food grade) was purchased from CAMARI-FONDO ECUATORIANO POPULORUM PROGRESSIO (Quito, Ecuador). PVA 88% hydrolysis degree was supplied by SEKISUI CHEMICAL CO., LTD (Osaka, Japan). Zinc stearate was acquired from SIGMA-ALDRICH (Darmstadt, Germany). Glycerol (99% purity) was provided by LOBA CHEMIE PVT. LTD (Mumbai, India); this plasticizer was used without further purification.

B. Blends preparation

PVA and achira starch were dried in an oven MMM Group VENTICELL, model LSIS-B2V/VC 55 (Munich, Germany) for 48 hours at 50°C to remove moisture. In order to formulate blends based on starch, PVA and glycerol, several formulations were prepared using an experimental mixture design with lineal constraints. On the upper and lower limits PVA:starch ratios were 70:30 and 50:50, respectively. The percentage range selected for plasticizer was 15 wt. % to 35 wt. %. The Minitab 1.7 software was used to obtain several formulations statistically representative. In consequence, thirteen formulations were prepared according to the composition shown in Table I and plotted in Figure 1. The codification GXPY was used to identify each formulation, according to the following description: G (glycerol), X (glycerol wt. % over the formulation), P (ratio PVA:starch) and Y (PVA wt. %/ starch wt. %).

TABLE I. COMPOSITION OF BLENDS*

Sample	Glycerol	PVA	Starch
G15P1	0.150	0.423	0.423
G15P1.5	0.150	0.507	0.338
G15P2.3	0.150	0.592	0.254
G20P1.2	0.200	0.435	0.360
G20P1.9	0.200	0.519	0.276
G25P1	0.250	0.373	0.373
G25P1.5	0.250	0.447	0.298
G25P2.3	0.250	0.522	0.224
G30P1.2	0.300	0.385	0.310
G30P1.8	0.300	0.449	0.246
G35P1	0.350	0.323	0.323
G35P1.5	0.350	0.387	0.258
G35P2.3	0.350	0.452	0.194

*Remaining fraction corresponds to zinc stearate

To process each formulation, raw materials were mixed in a bench-type roll mill COLLIN model W 100 T (Ebersberg, Germany) at 60°C and 80 rpm. Afterwards, these blends were molded using a laboratory hydraulic press CARVER, model 2112 (Menomonee, USA) for 7 min at 110°C under constant pressure of 38MPa.

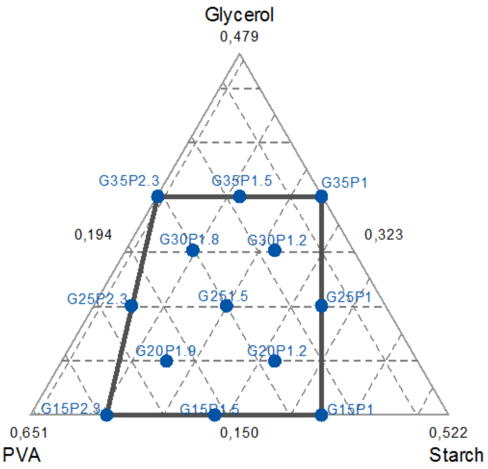


Fig. 1. Ternary plot of studied blends

C. *Mechanical assessment*

Young modulus, tensile strength and elongation at break of thirteen formulations were determined by using universal testing machine INSTRON model 3365 (Norwood, USA) at room temperature according to ASTM D638-14 standard. The test was carried out at a crosshead speed of 50 mm/min. At least five samples were tested for each formulation.

Detailed inspection of fracture surfaces on broken specimens was performed by means of scanning electron microscope TESCAN model VEGA II LMU (Brno, Czech Republic) at an accelerating voltage of 15 kV.

D. *Thermal evaluation*

Differential scanning calorimetry (DSC) evaluation was recorded using a calorimeter NETZSCH 204, model F1 Phoenix (Munich, Germany). Samples were evaluated according to standard method ASTM D3418-15 from -20°C to 250°C at 20°C/min.

In addition, thermogravimetric analysis (TGA) was performed by a thermo-balance SHIMADZU, model 50 (Kyoto, Japan). The analysis was conducted according to ASTM E1131-8(2014) standard. Measurements were tested from 23°C to 650°C at 3°C/min, under nitrogen atmosphere with the flow rate of 50 cm3/min.

E. *FTIR analysis*

Infrared spectra of pristine materials and PVA/starch films were accomplished in attenuated total reflectance mode on a spectrophotometer PERKIN ELMER, model spectrum one (Beaconsfield, United Kingdom). The spectra were obtained from 650 cm^{-1} to 4000 cm^{-1} at a resolution of 4 cm^{-1}.

III. RESULTS AND DISCUSSION

A. *Mechanical behavior*

From Figure 2 can be observed that PVA/starch blends are translucent and homogeneous on a macroscopic scale. Nevertheless, specimens evidence optical differences after tensile test which are associated to deformation mechanisms in the plastic flow regime. In particular, under uniaxial stretching PVA probably undergo a chain-folded spherulite rearrangement through a crystallographic slip mechanism within the lamellae [12].

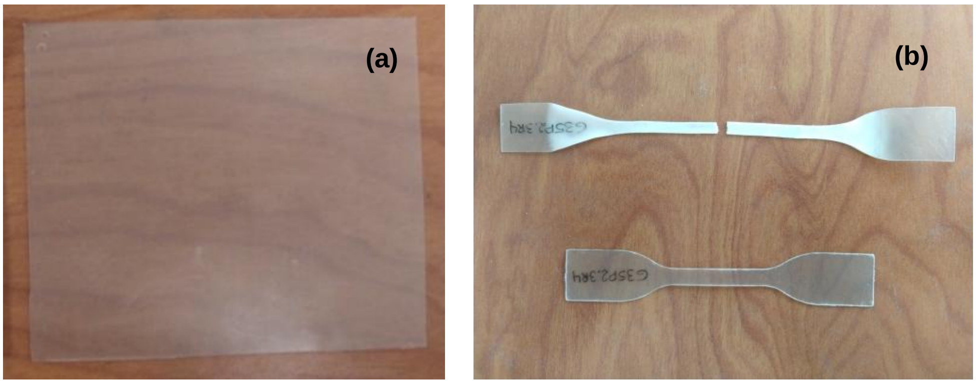


Fig. 2. Visual aspect of (a) PVA/starch film and (b) specimen before and after the tensile test

Figure 3 presents the stress-strain curves obtained for different contents of raw materials. All samples exhibit elastic regime at low deformations and plastic area at large strain values. Mechanical behavior of PVA/starch films is characterized by the absence of an overshoot typical of yield-stress semicrystalline polymers. However, curves suggest that elastic zone is followed by a deformation of crystalline domains of PVA. Moreover, high values of elongation indicate that recrystallization process are also possible.

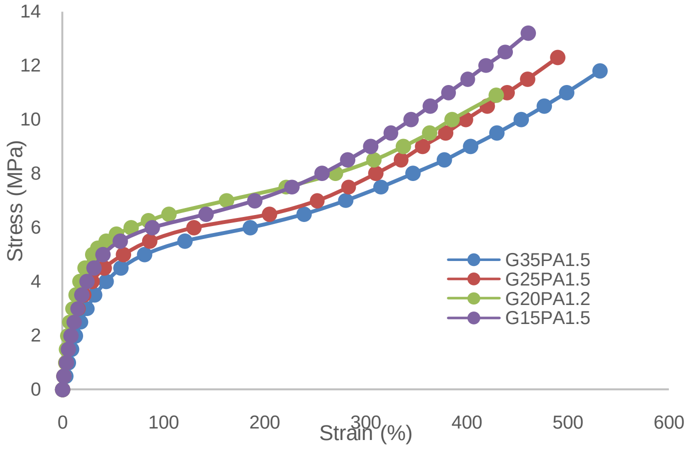


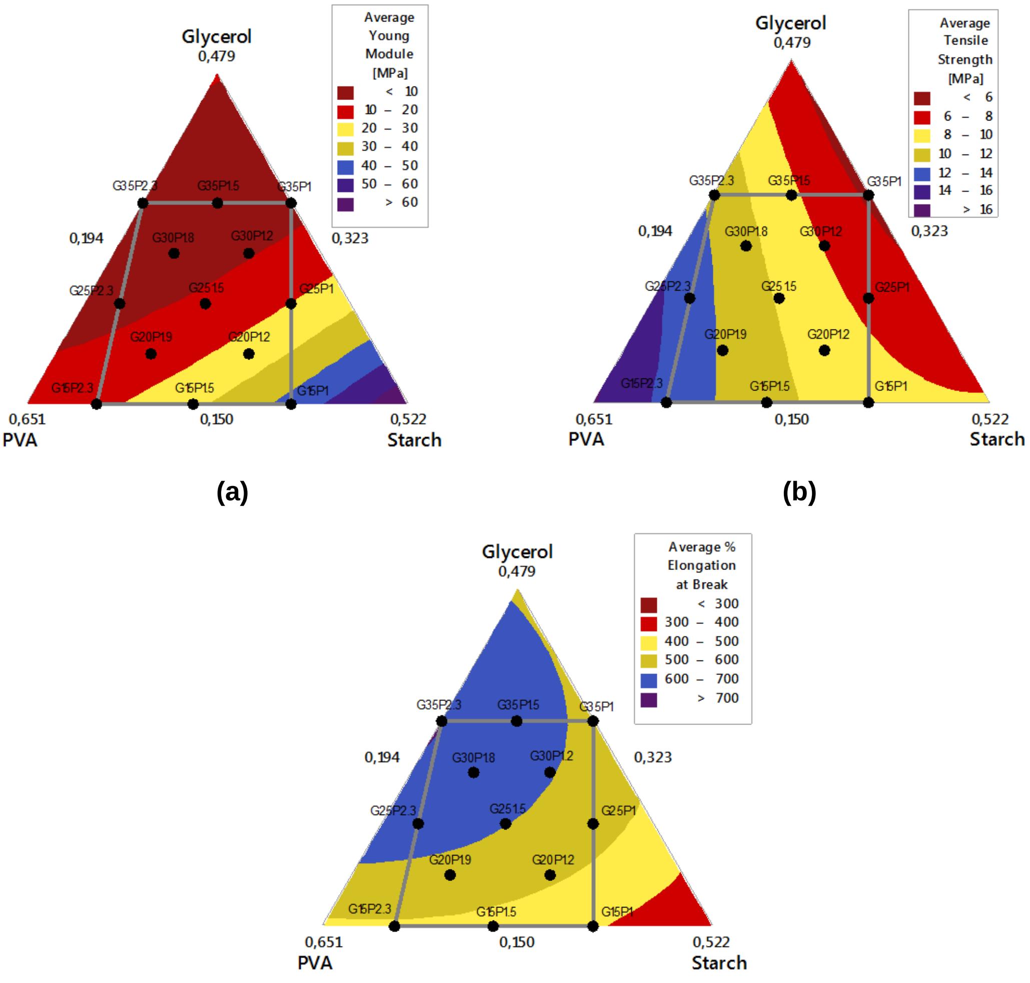
Fig. 3. Tensile curves of PVA/starch blends

Tensile properties of evaluated specimens are shown in Table II. Initially, it is noticed that samples with high proportion of starch exhibit dispersion values higher than the other formulations. This variability is possibly correlated not only with starch granule size but also with differences in the cohesion forces among components. The strong interchain interactions of blend components, through hydrogen bonds, produce some difficulty in the shift of polymer chains during the mechanical test.

The influence of component contents is presented in Figure 4. From contour plots patterns, it can be observed a directly proportional relation between Young modulus and achira starch; therefore, the contribution of starch to elastic behavior of blends is minimal, in accordance with similar observations for PVA/starch blends [13]. Furthermore, the addition of PVA and glycerol increase tensile strength and elongation at the break, respectively.

TABLE II. MECHANICAL PROPERTIES OF PVA/STARCH BLEND FILMS UNDER TENSILE EVALUATION

Sample	Young modulus (MPa)	Tensile strength(MPa)	Elongation at the break (%)
G15P1	45,76 ± 0,93	8,66 ± 0,59	416 ± 14
G15P1.5	26,86 ± 0,88	11,06 ± 0,48	472 ± 27
G15P2.3	17,62 ± 0,72	13,24 ± 0,41	483 ± 25
G20P1.2	21,20 ± 0,91	9,25 ± 0,58	516 ± 29
G20P1.9	16,64 ± 0,70	11,90 ± 0,78	558 ± 17
G25P1	19,10 ± 0,54	7,61 ± 0,59	518 ± 22
G25P1.5	12,92 ± 0,64	9,48 ± 0,48	607 ± 19
G25P2.3	7,45 ± 0,19	13,24 ± 0,43	654 ± 23
G30P1.2	10,55 ± 0,27	8,03 ± 0,44	602 ± 15
G30P1.8	7,67 ± 0,51	10,16 ± 0,33	678 ± 22
G35P1	7,34 ± 0,41	5,83 ± 0,72	588 ± 25
G35P1.5	5,28 ± 0,91	8,10 ± 0,27	631 ± 18
G35P2.3	4,94 ± 0,20	11,76 ± 0,39	695 ± 20



(a) (b)

(c)

Fig. 4. Contour plot of (a) Young modulus (b) tensile strength and (c) elongation at break

SEM micrographs of Figure 5 show numerous undestroyed starch granules on fracture surface suggesting that mixing and molding process did not affect the totality of granules. Microstructural surface describes a dimple like geometry which is a characteristic of ductile fracture mechanism. An analysis within a mechanical fracture context suggests that critical defects are related with starch microstructure. Moreover, micro-voids were apparently originated not only for oval-shaped but also due to the size range of granules. In terms of granules distributions of achira starch, previous investigations reported a wide range of granule size [14], [15]; that disparity leads to numerous stress concentration sites which affect the fracture behavior of studied blends. From the perspective of fracture energy on the defect’s presence, fracture probably has occurred by stress values lower than theoretical cohesive resistance.

It is worth noting that, mechanical behavior is not exclusively associated with starch granules characteristics. Elastic and plastic deformation as well as final fracture surface are also influenced by the reorientation of crystalline zones in the direction of applied remote tensile and destruction of some of the largest crystalline domains [12].

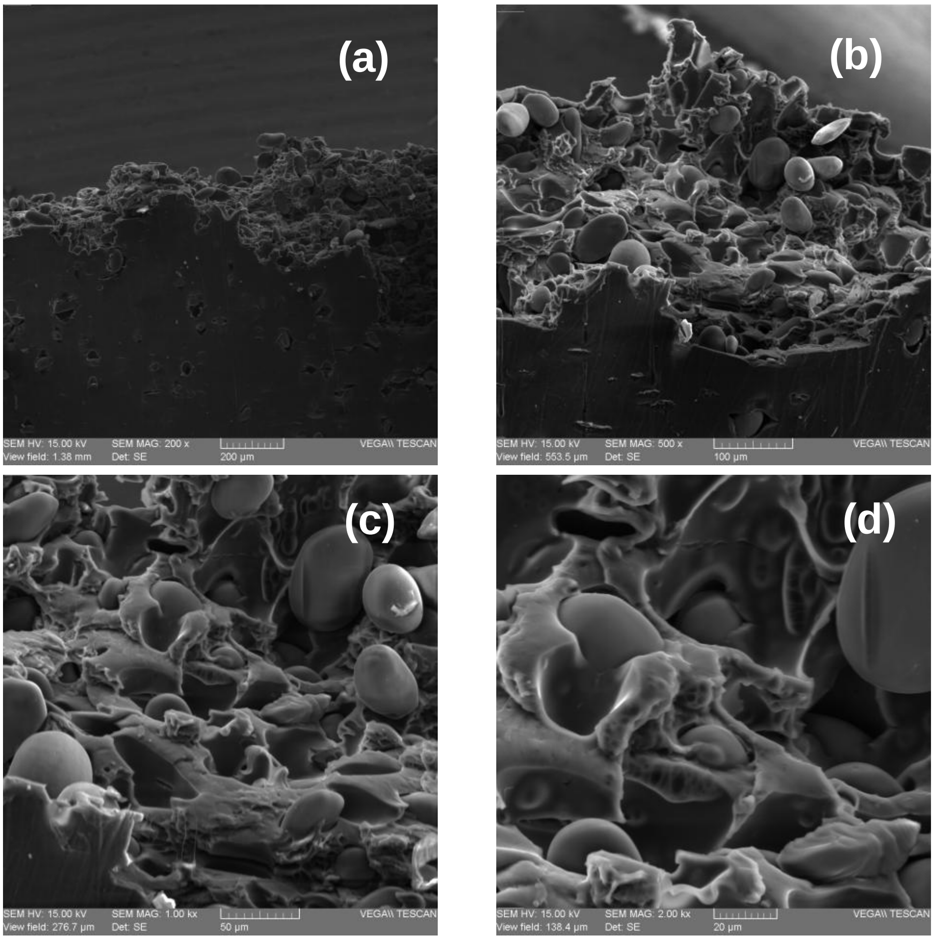


Fig. 5. SEM images showing fractographic features of PVA/starch blend films (a) 200X (b) 500X (c) 1000X and (d) 2000X

B. DSC evaluation

DSC measurements summary of PVA/starch blend films are presented in Figure 6. The enthalpy of melting process was extracted from thermograms and plotted in Figure 7. It can be observed in Figure 6 that there are no discernible changes of the thermal behavior of samples. DSC traces of all specimens show an overlap of some events spread over a large temperature range (20–140ºC). These endothermal transitions have been discussed extensively; however, thermal behavior of PVA/starch blends in this range is not well understood. Thermal events shown in the present study may hide glass transition temperature (Tg) due to partially crystalline starch microstructure, amorphous chains surrounded by crystalline zones and water release, in agreement with other authors [2][16][17]. Additionally, hydrogen bonding produced not only between hydroxyl groups of PVA and starch but also among functional groups of PVA, starch and plasticizer suppose a higher chain rigidity. Therefore, these strong interactions through inter- and intra-molecular hydrogen bonds may influence on the water release and consequently on identification of thermal transitions patterns corresponding to Tg.

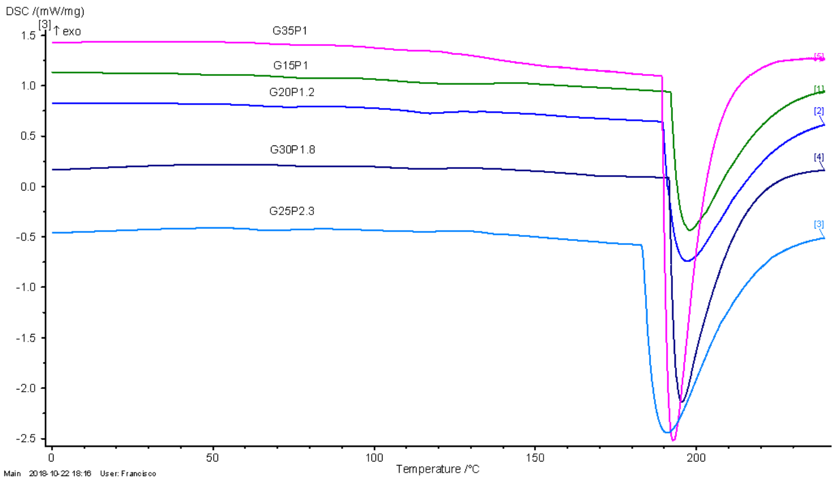


Fig. 6. DSC scans for PVA/starch blends

On the other hand, a broad endothermal peak was detected from 180ºC to 250ºC, which is attributed to the melting of the crystal of PVA. In this case, the variations of enthalpy of this thermal event are presumably related to the effect of plasticizer on the formation of PVA crystallites due to hydrogen bonds. Glycerol molecules size avoid an easily accommodation in the crystal lattice of PVA leading to smaller crystallites and defectives in the lamellar morphology [17]. In addition, undestroyed granules observed on SEM micrographs suggest that enthalpy of endothermal peak is slightly affected by starch gelatinization. Thus, the probability of stronger hydrogen bonding resulting from starch gelatinized with PVA is reduced [11].

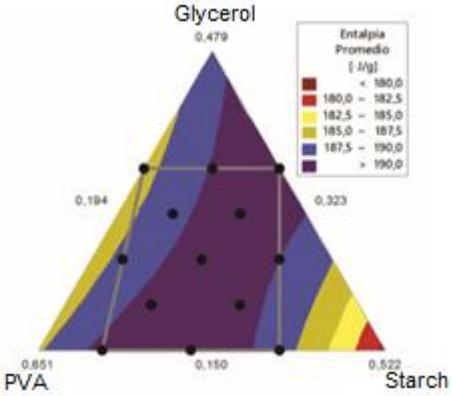


Fig. 7. Contour plot of endothermal enthalpy in the range of 180 ºC to 250ºC

C. *Thermal stability*

Thermogravimetric data listed in Table III indicate four decomposition stages in the tested range. The first step is associated to evaporation of free water and to the beginning of volatiles loss. Second thermal decomposition is related to the evaporation process of glycerol and bounds water. However, during this step it is also produced the evaporation of water which is generated by the detachment of hydroxyl groups of PVA and their reaction with the hydrogen of the PVA main chain [10][18][19]. The third stage, with the highest degradation rate, is probably ascribed to the PVA and starch nonoxidative processes generating carbon monoxide, carbon dioxide, acetaldehyde and acetic acid [17]. Last phase is attributed to decomposition of low molecular weight structures which were produced by PVA in previous stages. It should be noted that all formulations exhibit similar thermogravimetric behavior in terms of total mass loss. Likewise, the greatest thermal decomposition takes place above 245ºC. This pointed out a possible correlation between mass loss fraction and interaction among components through hydrogen bonds [20][17].

TABLE III. THERMOGRAVIMETRIC CHARACTERISTICS OF PRISTINE COMPONENTS AND PVA/STARCH BLENDS

Sample	**Mass loss in each decomposition stage (%)**				**Total mass loss (%)**
	First	***Second***	***Third***	***Fourth***	
	23–170ºC	***170–245ºC***	***245–390ºC***	***390–800ºC***	
PVA	4.55	59.07		28.77	92.39
Starch	15.65	53.60		-	69.25
Glycerol	32.49	-	-	-	32.49
G15P1	9.06	11.75	47.97	10.04	78.82
G15P1.5	9.14	11.76	47.93	10.25	79.08
G15P2.3	9.13	11.77	47.25	10.01	78.16
G20P1.2	9.97	13.04	45.10	10.37	78.48
G20P1.9	10.25	11.73	45.15	11.23	78.36
G25P1	9.86	15.57	43.68	9.52	78.63
G25P1.5	10.87	13.69	41.78	9.75	76.09
G25P2.3	10.18	14.54	43.79	10.31	78.82
G30P1.2	10.55	12.82	38.86	10.58	72.81
G30P1.8	11.87	14.98	38.20	7.69	72.74
G35P1	11.74	17.25	37.18	8.26	74.43
G35P1.5	11.12	13.54	37.58	9.66	71.90
G35P2.3	11.71	18.26	36.15	10.76	76.88

D. FTIR analysis

Figure 8 shows a summary of FTIR spectra of studied materials whereas Table IV presents main changes among spectra of raw materials and PVA/starch blends, in terms of frequencies of relevant functional groups. In general terms, it has been identified a number of different changes in all analyzed vibrational groups.

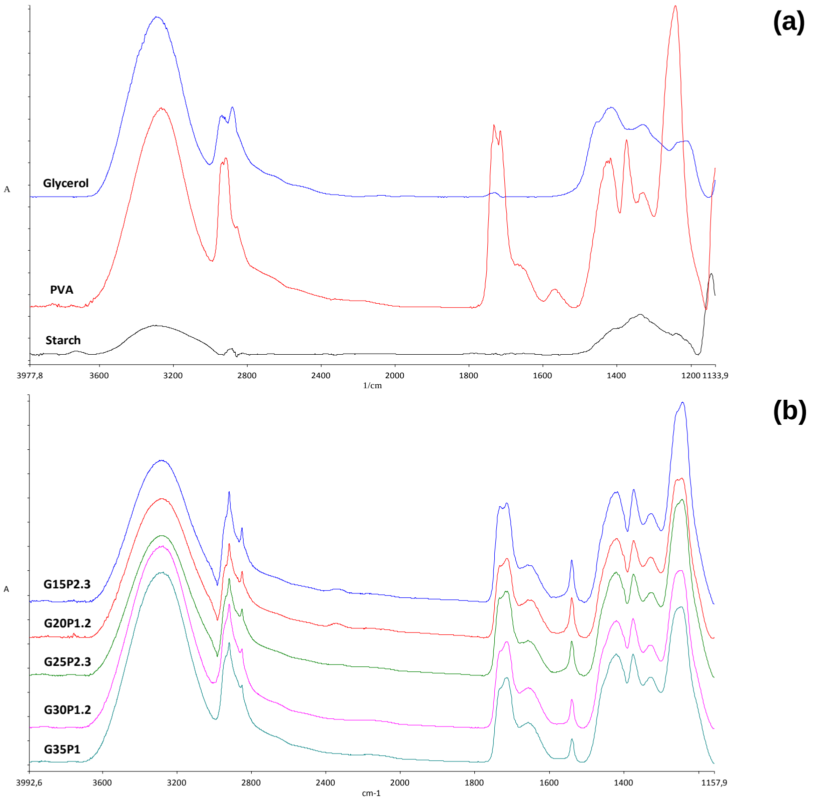


Fig. 8. FTIR spectra of (a) pristine componentsand (b) PVA/starch blends

TABLE IV. SUMMARY OF FTIR RESULTS

Sample	**Functional group**			
	OH stretching	***Bound water***	***C–O stretching of C–O–H***	***C–O stretching of C–O–C***
PVA	3265	1650	-	1086
Starch	3310	-	1144	1077
Glycerol	3294	-	1107	-
G15P1	3292	1657	1141	1026
G15P1.5				
G15P2.3				
G20P1.2	3279	1655	1142	1089
G20P1.9				
G25P1	3279	1655	1141	1090
G25P1.5				
G25P2.3				
G30P1.2	3273	1655	1141	1092
G30P1.8				
G35P1	3272	1655	1141	1094
G35P1.5				
G35P2.3				

PVA exhibit a band at 3265 cm^{-1} which is ascribed to stretching vibration of free and bonded OH groups. Blends show absorption bands in the range of 3272 cm^{-1} to 3292 cm^{-1} showing an evident shift to higher wave number [21]; this behavior implies an increase of intermolecular hydrogen bonding. Based on the starch OH stretching point of view, a substantial movement to lower frequencies is also observed [22].

The band in 1660 cm^{-1} corresponding to deformation vibration of the OH groups increase to a higher frequency region by around 5-7 cm−1 suggesting a strong hydrogen bond among components. In addition, C–O stretching of C–O–H functional group, detected in 1144 cm^{-1} in starch, slightly shift to lower frequencies (1141-1142 cm^{-1}) which is probably related to variation of hydrogen bonding ratio in the PVA/starch blends. In addition, changes in C–O stretching of C–O–C band suggest a possible transform into double peaks due to the effect of glycerol in starch microstructure [2]. Therefore, FTIR changes of vibrational functional groups corroborate the presence of inter- and intra-molecular hydrogen bonds among blend components argued in mechanical and thermal analysis.

IV. CONCLUSION

PVA/starch blends, based on an experimental mixture design, were formulated successfully. Mechanical results indicated that deformation mechanism of studied blends is probably associated to chain-folded spherulite rearrangement of PVA as well as to starch granules characteristics. The fracture surface corroborates the strong influence of shape and size range granules on the formation of critical defects which in turn lead to numerous stress concentration sites. From the perspective of mechanical properties, the addition of starch, PVA and plasticizer increase Young modulus, tensile strength and elongation at the break, respectively.

Both SEM and DSC evaluation evidenced a slightly influence of starch gelatinization on enthalpy of endothermal process. According to thermogravimetric analysis, the greatest thermal decomposition took place above 245ºC suggesting a correlation between mass loss fraction and second order interaction among components. Reported FTIR data, indicate the presence of inter- and intra-molecular hydrogen bonds which could promote the compatibility among blend components and consequently improve mechanical and thermal integrity.

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