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Original Article

The effect of molecular weight and hydrolysis degree of poly(vinyl alcohol) (PVA) on the thermal and mechanical properties of poly(lactic acid)/PVA blends

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Abstract: The effect of molecular weights and hydrolysis degrees (HD) of polyvinyl alcohol (PVA) on thermal and mechanical properties and crystallinity of polylactic acid (PLA)/PVA blends was investigated. Blends were prepared by the melt blending method using PLA/PVA ratios: 80/20, 90/10 and 97/3 wt. %. A single glass transition temperatures was observed for all PLA/PVA blends, suggesting the formation of binary compatible blends at concentration range studied. Thermogravimetric analysis results showed a better thermal stability for PLA/PVA blends containing PVA of higher Mw and HD. According to mechanical properties, low quantities of PVA (3 wt. %) do not affect the tensile strength of blends (irrespective of Mw and HD). However, as the PVA content increases, tensile strength tends to lower values, especially for blends with 20 wt. % of PVA, with 98% of HD.

Keywords: material testing, melt blending, polylactic acid, polyvinyl alcohol, polymer blend.

1. Introduction

Polylactic acid (PLA) is a linear aliphatic polyester obtained from renewable sources such as starch and sugar. It is one of the most widely used bioplastics due to its optical, mechanical and barrier properties, and good processability by conventional transformation techniques of thermoplastics[1]. The worldwide production capacity of PLA in 2021 is estimated around 297.000 tons, 40% more than that produced in 2016[2]. PLA is classified by the American food and drug administration

as generally recognized as safe and hence it is very common in the food packaging industry. Its barrier, thermal and mechanical properties are in fact similar to those of synthetic polymers such as polystyrene[3-6].

PLA can be biodegraded under compost conditions; it takes up to a year to degrade in real and simulated soil burial conditions. This slow degradation compared to other polymers such as for example poly (hydroxy alkanoates), is due to the fact that PLA must be hydrolyzed before microorganisms can use it as a source of nutrients[7,8]. Adding small quantities of compatible hydrophilic polymers such as PVA, which is biodegradable, hydrophilic and flexible[9] is a way to enhance the biodegradability of PLA. For example, it has been reported that polyvinyl alcohol (PVA) has the ability to accelerate the degradation of PLA, by increasing the hydrophilicity of the blend and breaking the crystallinity of PLA[10]. Furthermore, the hydroxyl groups in PVA readily form hydrogen bonds with the ester groups of PLA, which favors the compatibility of their blends. Yeh et al., (2008) [11] found that a compatible blend PLA: PVA (80: 20 wt. %: wt. %) prepared by melt blending method using PLA Mw = 37 kg/mol and PVA with HD = 97-98.5% and Mw = 75 kg/mol. Similar results were reported by Shuai et al., 2001[12] for blends PLA/ PVA 10 to 90 wt. % of PVA with polymerization degree of 2000 and HD=99%. They report the formation of interpolymer hydrogen bonds in the amorphous region of PLA/PVA blends (PVA content higher than 50 wt. %), which contributes to compatibility of these blends. However, PVA and PLA crystallized as isolated phases, for that tensile strength and elongation at break first declines for PVA content from 0 to 50 wt. % and then increases with increasing when the PVA content.

Several authors have reported the effect of PVA content with different HD and Mw on mechanical properties of PLA/PVA blends. For example, Lipsa et al. (2008)[13] prepared films by these blends using PVA with HD = 98% and Mw = 18 kg/mol. They found that the blends are partially compatible for PVA content from 70 to 90 wt. %, and slight reduction of mechanical properties, such as lower tensile strength were observed in blends.

Tsuji and Muramatsu (2001)[14] found that the Young's modulus, tensile strength and percent elongation at break of the blends increase with increasing PVA content from 50 to 90 wt. % (HD=99.5%). Hoai N. et al. (2014)[15] prepared nanofibrillary structures from PLA/PVA blends, varying content of PVA from 0 to 100 wt. %. They found that increasing the amount of PVA results the thermal degradation of blends more stable.

However, a systematic study that show the influence of content, molecular weight and hydrolysis degree of PVA on compatibility, and therefore on the thermal and mechanical properties and crystallinity of PLA has not found. In this work, PLA/PVA blends prepared by the melt blending method was studied.

2. Materials and Methods

2.1 Materials

The commercial PLA grade 3251D, Mw of 55.4 kg/mol and isomer D lactic acid content of 1.2% [16] was purchased from Nature Works®, United States. Four different types of PVA with different hydrolysis degree and molecular weight were provided by Sigma Aldrich®. The main specifications of PVA are summarized in Table 1 . The pure PLA processed under similar conditions was studied as reference material.

Table 1.
Nomenclature of blends.

PVA Code	PVA		Sample code for PLA/PVA blends		
	Range of Mw (g/mol)	HD (%)	80/20 wt.%	90/10 wt.%	97/3 wt.%
1PVA	13000-23000	87-89	1PVA 80/20	1PVA 90/10	1PVA 97/3
2PVA	13000-23000	98	2PVA 80/20	2PVA 90/10	2PVA 97/3
3PVA	31000-50000	87-89	3PVA 80/20	3PVA 90/10	3PVA 97/3
4PVA	31000-50000	98	4PVA 80/20	4PVA 90/10	4PVA 97/3

2.2 Processing

The PLA/PVA blends, ratios of 80/20, 90/10 and 97/3 wt. % for each type of PVA (Table 1), were prepared via melt blending in a Brabender mixer (Plastograph ® EC plus, Mixer 50EHT32, Germany) at 60 rpm for 8 min. The temperature was set at 190 °C. The PLA was previously dried at 40 °C overnight in a vacuum oven. After blending, the samples were pressure-molded at 30 bar and 10 min in order to obtain plates for XRD and impulse excitation technique (IET) tests. The temperature was set between 170 and 210 °C, depending on the type of PVA used in the preparation of the sample.

2.3 Blend characterization

2.3.1 DSC

The thermal properties of PLA/PVA blends were evaluated using a differential scanning calorimetry (DSC) analyzer (Netzsch DSC 204 F1 Phoenix), Germany. DSC curves were scanned at 10 °C/min under nitrogen atmosphere (20 mL/min). The DSC scans were performed from room temperature to 250 °C. Then, the samples were cooled to 25 °C and a second heating scans were made up to 250 °C. Glass transition temperature (Tg), cold crystallization temperature (Tcc), cold crystallization enthalpy (ΔHcc), melting temperature (Tm), melting enthalpy (ΔHm), and degree of crystallinity (X_C) were determined from the second heating scans. X_C of PLA in the blends was calculated by the Equation (1) :

where ΔH_m is the melting enthalpy of the blends, W is the weight fraction of PLA and ΔH°_m is the melting enthalpy of 100% crystalline PLA (93 J/g)[17,18].

2.3.2 TGA

Thermal stability of pure PLA, PVA's and their blends was evaluated using a thermogravimetric analyzer Netzsch TGA 209 F3 (Tarsus, Selb, Germany). TGA scans were carried out at 10 °C/min under nitrogen atmosphere (20 ml/min), from 35 to 600 °C.

The following parameters were reported: (*i*) temperature at maximum decomposition rate for each step of decomposition (T_{max}), (*ii*) weight loss associated with T_{max} (WL T_{max}), (*iii*) the onset temperature (T_{onset}) corresponding to each decomposition step and (*iv*) the temperature corresponding to 5% weight loss ($T_{5\%}$).

2.3.3 XRD

The XRD measurements were recorded on a Bruker diffractometer Endeavor model D4/MAX-B (United States) operated at 40 kV, 20 mA, at room temperature, using a CuKα source and λ= 1.5405 Å. The diffraction spectra were taken in the range 3°<2θ<45° at 0.02° steps and a scanning rate of 1°/min. The pure PLA and PLA/PVA blends were previously annealed for 20 min at 120 °C under vacuum conditions.

2.3.4 Tensile test

The mechanical properties of PLA/PVA blends were evaluated using tensile test performed on a Karg Industrietechnik machine (Germany) according to ASTM D638 standards. Samples type V were fabricated using a mini injection equipment type Haake Minijet II, and injection

conditions were 350 bar of pressure and injection temperature of 180 °C. Prior testing, specimens were conditioned under 25°C and 50% relative humidity (R.H) for 7 days. The crosshead speed was set at 10 mm/min. The Young's modulus, strength and elongation percentage at break were obtained from the stress–strain curves. At least 5 individual measurements were carried out for each formulation and mean values and standard deviations were reported. Collected data were evaluated with a one-way analysis of variance at the 95% confidence level.

For comparison purpose, elastic modulus of PLA/PVA blends were evaluated by Impulse excitation technique (IET). The rectangular samples were suspended by soft and tiny tape sticks to simulate a "free-free" boundary condition and were excited by an impact hammer. The samples have an aspect ratio of a/b=1.5, where a, b are the plate's length and width dimensions, respectively. The vibration of the samples is captured by a microphone which was connected to a data acquisition system. A signal processing software computed the frequency content of the measured signals from which the experimental resonant frequencies were identified. Once the experimental resonant frequencies were identified, the elastic modulus was computed using the relationships presented in Equation (2)[19]:

where # = 0.4 is Poisson´s ratio, ρ is the density, E is the elastic modulus and h=0.85 and a=20 are plate's dimensions (thickness and length respectively, in millimetres). The variable ω corresponds to the second resonant frequency of the plate, which was easier to be excited and measured.

2.3.5 SEM

The morphology of cryogenic-fractured cross-sections of PLA/PVA blends was analyzed by scanning electron microscopy (JEOL JSM 6380 LV, Tokyo-Japan), operated at 20 and 5 kV. The samples were fractured under liquid nitrogen and sputtered with a gold coating of ca. 50 nm. The magnifications were 100x and 500x.

3. Results and Discussion

3.1 DSC Analysis

DSC thermograms of PLA, PVA's and PLA/PVA blends are shown in Figure 1 . The thermograms for pure PLA and PLA/PVA blends display successive peaks corresponding to the glass transition, cold crystallization and melting. The Tg, Tcc and Tm are resumed in Table 2 . The only one peak of Tg is observed for PLA/PVA blends, which is ranged from 42 to 55 °C, intermediate between the Tg values of pure PLA and PVA. This behavior is characteristic of compatible blends. Shuai et al., 2001[12] found by ^{13}C solid-state nuclear magnetic resonance spectroscopy, the presence of hydrogen bonds between hydroxyl groups of PVA and carbonyl groups

of PLA in the amorphous region of blends with PVA content of 30 wt. %. A single Tg of PLA/PVA blends with PVA content lower than 20 wt. % is attributed to this kind of interpolymer interaction. Tg peak is shifted to lower temperatures with increasing PVA content in the blends.

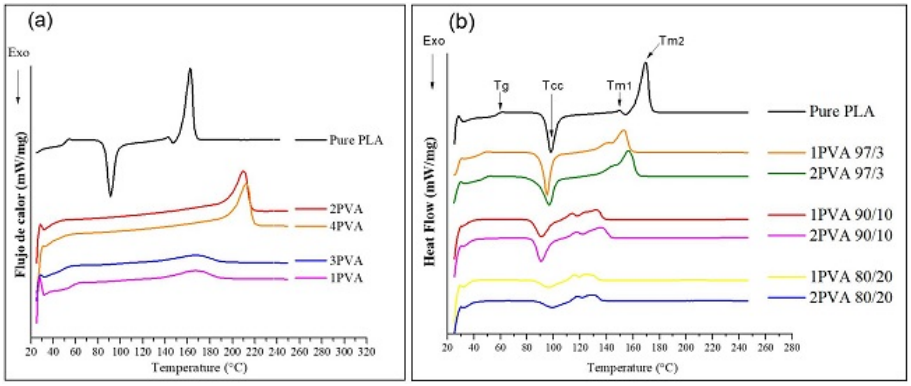

Figure 1.
Second heating run DSC thermograms for: (a) Pure PLA and PVA's; (b) PLA/PVA blends.

Table 2.
Thermal characteristics of pure PLA, PVA's and PLA/PVA blends.

Sample code	Tg (°C)	Tcc (°C)	Tm1 (°C)	Tm2 (°C)	ΔHcc (J.g^{-1})	ΔHm (J.g^{-1})	Xc (%)
Pure PLA	61	98	150	169	38	54	58
1PVA	37	___	167	___	___	20	___
1PVA 80/20	42	96	116	124	13	14	19
1PVA 90/10	43	91	114	133	24	22	26
1PVA 97/3	50	95	142	153	39	41	45
2PVA	40	___	210	___	___	66	___
2PVA 80/20	44	99	118	130	13	14	19
2PVA 90/10	42	91	118	136	28	25	30
2PVA 97/3	53	97	143	157	41	49	54
3PVA	44	___	167	___	___	21	___
3PVA 80/20	55	89	111	132	16	15	20
3PVA 90/10	43	92	121	138	27	23	27
3PVA 97/3	50	94	143	157	45	52	57
4PVA	42	___	212	___	___	61	
4PVA 80/20	51	91	112	130	14	16	22
4PVA 90/10	42	88	117	136	32	27	32
4PVA 97/3	54	94	149	159	40	47	53

The blends and pure PLA exhibited two endothermic peaks of melting characteristic of the formation of two PLA crystal structures during its cold crystallization, known as α and β forms with melting temperatures Tm2 and Tm1 respectively. The melting temperature of the α-form is higher because of the better quality and higher size of its crystals [20,21]. The melting temperatures of the blends are also shifted toward lower temperatures, with increasing the PVA content irrespective of Mw and HD.

The *Xc* values for PLA in blends decrease, especially when 20 wt. % of PVA was added. Thus, the crystallization of PLA in presence of PVA is affected due to the formation of imperfect crystals in PLA by considering that the presence of the PVA can cause a dilution of the PLA nuclei, combined with the possible interference between the chains

of PLA and PVA due to partial compatibility between them. Opposite results were obtained by Yeh et al., (2008) [11] who found that highest PLA crystallinity, appears in PLA/PVA blends containing 20 wt. % of PVA (MW: 75KDa, HD: 98%), attributed to the interactions between PLA and PVA that promote the crystallization. However, Tsuji and Muramatsu (2001)[14] report a zero *Xc* value of PLA for all PLA/PVA blends (ratio 90:10 to 50:50 wt. %) indicating that PLA is amorphous in the blend. On the other hand, Shuai et al., (2001)[12] reported a decrease in *Xc* values of PLA when PVA is added in contents more than 70 wt.%, result of some depression of the PLA crystallinity upon blending with a large amount of PVA.

Variations in values of Tcc, Tm, and *Xc* in PLA/PVA blends are usually attributed to interactions between the components. In general, the decrease in PLA crystallinity is related to the partially compatible nature of the blends[11,22].

3.2 TGA Analysis

Thermal stability of pure PLA, PVA's and PLA/PVA blends was evaluated by TGA analysis. Table 3 summarizes the thermal parameters. The TGA curve for pure PLA showed one-step degradation with a weight loss of 99%, associated with the loss of ester groups by unzipping depolymerization [23,24]. T_{max} for pure PLA was 364 °C. In contrast, pure PVA's displayed three degradation steps. The first one, between 31 and 188 °C and a weight loss below 5 wt. %, is associated with the loss of absorbed moisture. The second step, between 190 and 388 °C and a weight loss ranged from 65 to 77%, is related to the loss of low molecular weight substances, such as residual acetate groups, non-conjugated polyenes, acetic acid and H_2O. The third step, between 351 and 426 °C, is associated to the breakdown of polymer backbone[25]. The main product of thermal degradation of PVA is water, which is formed by the elimination of hydroxyl side-groups[26].

Table 3.
TGA and DTG parameters for pure PLA, PVA and PLA/PVA blends.

Sample code	TGA	DTG					
	$T_{5\%}$	$T_{onset-1}$ (°C)	T_{max-1} (°C)	WL-1 (%)	$T_{Onset-2}$ (°C)	T_{max-2} (°C)	WL-2 (%)
Pure PLA	334	284	364	99			
1PVA	241	216	306	77	391	426	12
1PVA 80/20	268	191	301	90	381	425	7
1PVA 90/10	280	232	312	92	392	427	5
1PVA 97/3	301	256	353	97	411	420	1
2PVA	186	216	261	69	351	421	15
2PVA 80/20	272	188	305	93	383	428	4
2PVA 90/10	286	231	330	95	406	419	2
2PVA 97/3	301	251	348	97	411	421	1
3PVA	261	221	314	75	391	426	16
3PVA 80/20	275	218	305	88	388	432	7
3PVA 90/10	285	225	322	93	395	422	3
3PVA 97/3	301	241	345	97	406	427	1
4PVA	215	206	260	71	351	416	14
4PVA 80/20	270	220	380	87	390	435	4
4PVA 90/10	288	240	331	94	393	427	3
4PVA 97/3	311	261	356	98	421	431	1

For the same Mw, PVA with higher HD (98%) showed the lowest values of T_{max-1} in the second step of degradation with values around 260 °C and weight loss associated with this T_{max-1} was 69–71% (see Table 3). Therefore, PVA with HD of 87-89%, present better thermal stability. Acetate groups present in PVA with lower HD, confer higher thermal decomposition temperatures to PVA, favoring its thermal stability[27].

Two degradation steps were observed for PLA/PVA blends, (see Figure 2) suggesting that thermal decomposition of PVA and PLA happens as a combined process [25]. The first step of decomposition was between 188 and 386 °C with a weight loss of 75–98 wt.%. The second one was between 381 and 507 °C with a weight loss 0.2-2.2 wt. %. With increasing PVA content in the blends, the main degradation step is shifted significantly to lower temperatures. Water absorbed by PVA, could be favoring hydrolytic degradation of PLA.

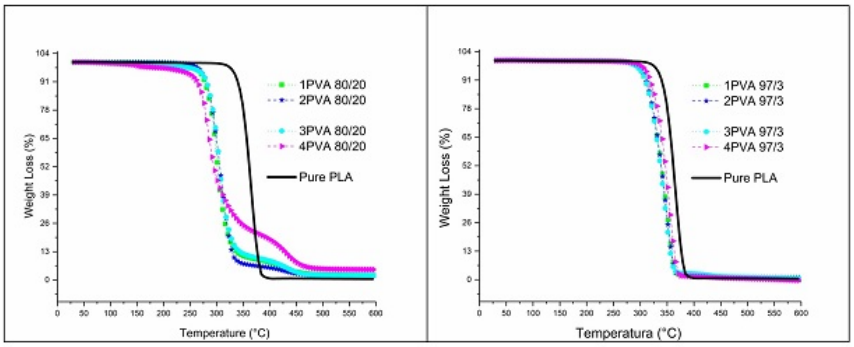

Figure 2.
TGA diagrams for (a) Pure PLA, PVA's; (b) blends PLA/ PVA: 80/20 wt. % blends; (c) blends PLA/PVA: 97/3 wt. %.

The Tmax-1 shifts to higher values for those blends with PVA's of higher Mw and higher HD. With increasing Mw of PVA, the entanglement along the chains of PLA and PVA is favored. These results are in agreement with some literature reports[28-30] for higher Mw of PVA, which favors intramolecular entanglement between PVA and PLA, primarily by virtue of esterification of PVA hydroxylic groups and PLA carboxylic groups, improving the thermal stability of PVA in the blend.

3.3 XRD analysis

The XRD diffraction patterns for pure PLA, PVA and selected PLA/PVA blends are shown in Figure 3 . The results are shown only for two types of blends, considering that the diffraction patterns for all PLA/PVA blends and pure PLA were very similar.

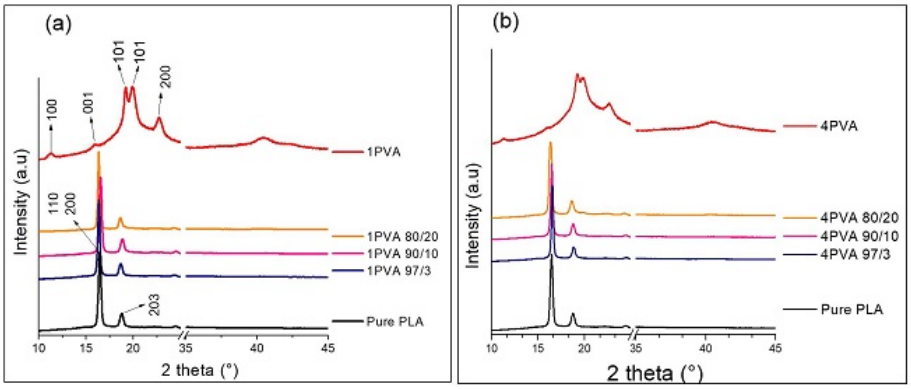

Figure 3.
Diffractions patterns for: (a) PLA/1PVA blends and (b) PLA/4PVA blends.

The most intense peaks for PVA's appeared around 2θ=19.3°, 20° and 22.7°, related to reflections of planes 10#1, 101, and 200, respectively, associated with a monoclinic unit cell[14]. Assender and Windle, 1998[31] reported that PVA chains are lying along the b-axis of the unit cell. Two characteristic peaks of pseudo orthorhombic α–phase crystallites structure (Space group $P3_2$) were observed for pure PLA, around 16.5 and 18.8° (2θ), corresponding to the reflection of 110/200 and 203 planes with two chains in a helical conformation [11,32,33].

The absence of characteristic PVA peaks in blends is attributed to the absence of PVA crystallization in the presence of PLA suggesting that PVA molecules was trapped in an amorphous state in the PLA phase and/or PLA molecules reduce the nucleus density of PVA crystallites[14]. In this context, Shuai et al. (2001)[12] reported the presence of two isolated crystalline phases (called co-crystalline phase) coexisting in PLA/PVA blends (ratio 1:1), that have the same crystal structure without inter-polymer interactions between them. Furthermore, with the addition of PVA in PLA, all of the blends show no shift in characteristic diffraction peaks of PLA, implying that, there is no significant effect of PVA on the crystal structure of PLA[11].

3.4 Mechanical analysis

Tensile strength of pure PLA and PLA/PVA blends are shown in Figure 4 . Compared with pure PLA, the tensile strength of blends containing 3 wt. % of PVA, is very similar (irrespective of Mw and HD). However, as the PVA content increases, tensile strength tends to lower values, especially for blends with 20 wt.% of PVA, with 98% of HD.

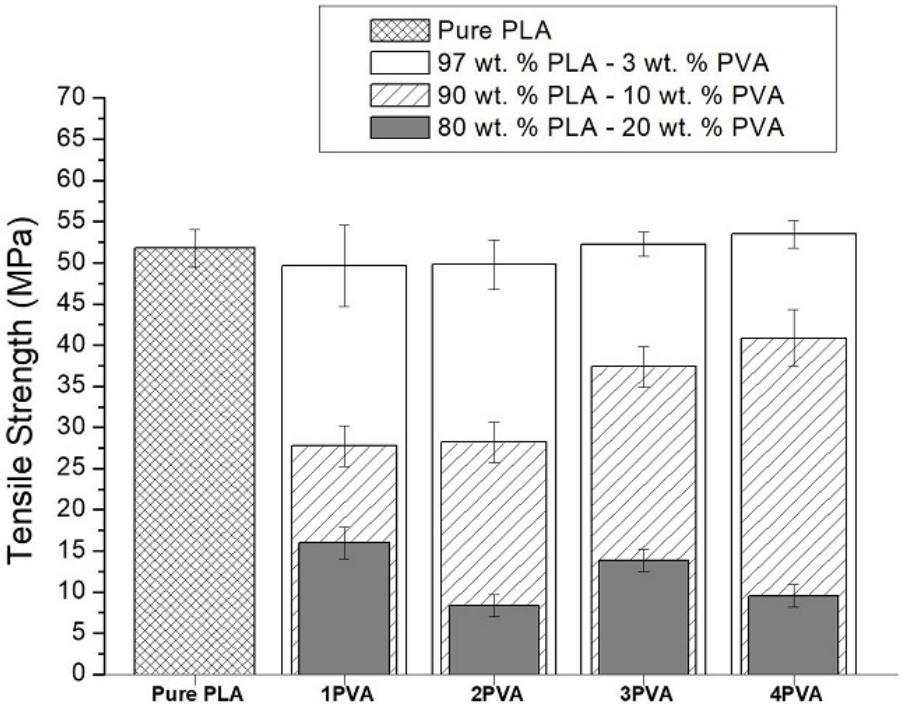

Figure 4.
Tensile strength for pure PLA and PLA/PVA blends.

Influence of Mw is observed for blends with 10 wt.% of PVA. Thereby, blends containing PVA with higher Mw showed higher values in the tensile strength, irrespective of the HD.

Young's modulus results from tensile test analysis for pure PLA and PLA/PVA blends are presented in Figure 5 . As compared with pure PLA, it is observed a decrease in Young′s modulus with increasing the content of PVA, particularly for blends with 20 wt.% of PVA (HD: 98%), indicating that presence of PVA affect the rigidity of PLA.

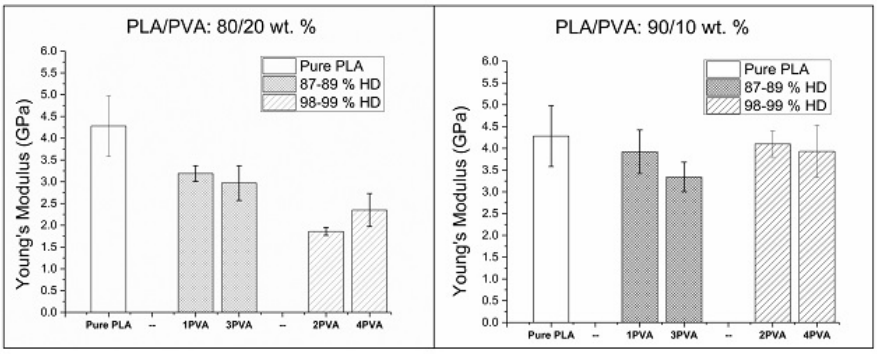

Figure 5.
Young's modulus from tensile test for pure PLA and PLA/PVA blends.

Influence of HD of PVA is clearer in Young´s modulus values obtained by IET analysis presented in Table 4 . For higher HD, increasing content of PVA from 10 to 20 wt.%, decrease Young´s modulus values, and for the same Mw, samples containing 20 wt.% PVA with higher HD, present lower young´s modulus. PVA present flexible characteristic, in this way is expected a decrease of rigidity in PLA/PVA blends, suggesting that acetate groups present in PVA with lower HD influence the mobility of polymeric chains in the blends. In this context, according to DSC results, the lowering of crystallinity of PLA in presence of PVA can lead a decrease in mechanical properties of PLA/PVA blends.

Table 4.
Young´s modulus from IET for pure PLA and PLA/PVA blends.

Sample code	Young's Modulus (GPa)		
	80/20 wt.%	90/10 wt.%	100 wt.%
Pure PLA			4.7
PLA/1PVA	4.3	4.1	
PLA/2PVA	2.1	4.0	
PLA/3PVA	4.1	4.0	
PLA/4PVA	3.0	4.2	

Results reported for Shuai et al., 2001 and H. Tsuji, 2001[12,14], pointing out that the lowering of mechanical properties with increasing PVA content was attributed to the partial compatibility of the blends, due to the weak interfacial adhesion between the two phases in PLA/PVA blends. However, PVA with higher Mw conferring more resistance to PLA/PVA blends acts like a cross-linked component between molecules of PVA and PLA.

3.5 SEM Analysis

Figure 6 shows cross-section SEM images of selected PLA/PVA blends. In general, is observed a porous morphology for all blends, related to the partially compatible nature of PLA/PVA blends.

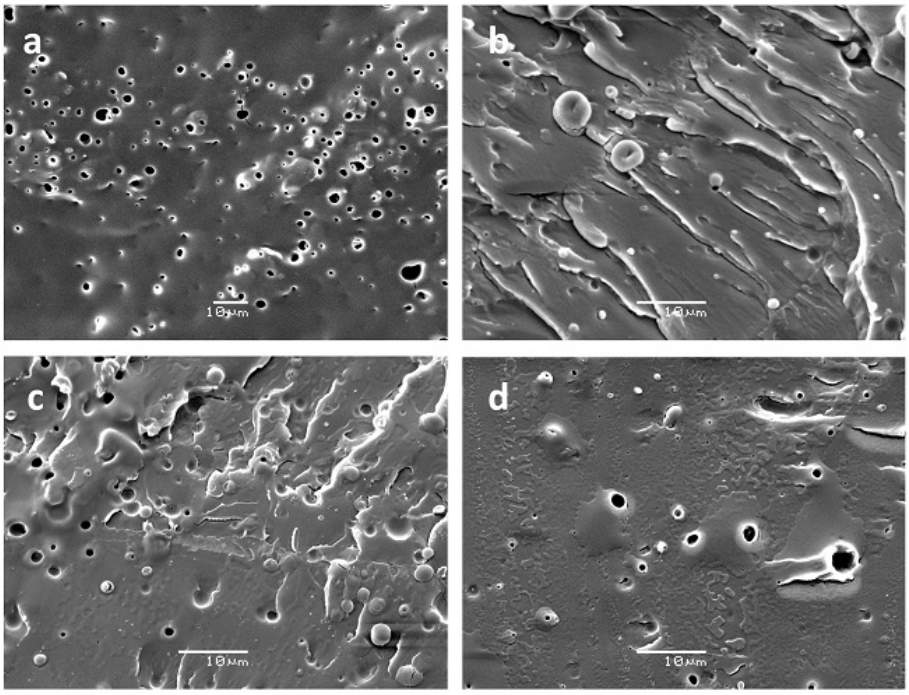

Figura 6.
SEM images of selected PLA/PVA blends: (a) 3PVA 80/20; (b) 4PVA 80/20; (c) 3PVA 97/3; (d) 4PVA 97/3.

However, the content of PVA had a remarkable influence on blends morphology, as evidenced in the characteristics of the observed pores. In this context, blends with higher content of PVA have higher density of pores, indicating a greater phase separation, unlike blends containing less PVA (particularly with high Mw and independent of the HD), which have smaller pores, suggesting that the compatibility of PVA and PLA was improved on addition of low quantities of PVA with higher Mw.

In this context, Zhang et al., (2012)[34] reported that increasing the PVA content (polymerization degree:1700, HD:88%) from 10 to 80 wt. % in PLA/PVA blends produced a less smooth surface. This was attributed to an excessive PVA content that led to strong and extensive intermolecular hydrogen bonding, which in turn resulted in PLA aggregation. Other reports showed development of pores with an average size of 5 μm for 50/50 PLA/PVA blends, suggesting the formation of two separate phases; a PLA-rich phase forming domains leading to porosity and a continuous PVA-rich phase [14].

4. Conclusions

The partially compatible nature of PLA/PVA blends were evidenced from thermal and mechanical results. In this context, were observed one peak of Tg for PLA/PVA blends, intermediate between the Tg values of pure PLA and PVA, characteristic behavior of compatible blends. Additionally, for a higher content of PVA, decrease crystallinity of PLA, thus, PLA/PVA blends with 20 wt.% of PVA tend to reduce mechanical properties of PLA, particularly for those with 98% HD. However, the addition of low quantities of PVA (3 wt. %) do not reduce the tensile strength in PLA/PVA blends, because of better compatibility between PLA and PVA. PVA's with higher Mw favors the entanglement of PVA and PLA improving the thermal stability of PLA/PVA blends. With increasing PVA content in the blends, the main degradation step is shifted significantly to lower temperatures, however PVA with HD of 87-89%, present better thermal stability due to acetate groups conferring higher thermal decomposition temperatures to PVA, favoring the thermal stability of the PLA/PVA blends.

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