Starch-PVA composite films:

towards a new generation of biodegradable packaging material

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STARCH - POLY(VINYL ALCOHOL) COMPOSITE FILMS

STARCH: polysaccharide

✓ ability to form a continuous matrix

✓ low cost

✓ low oxygen permeability

✓ odorless, colourless and transparent

Lineal, glucose linked α-(1-4)   Branched in α-(1-6)
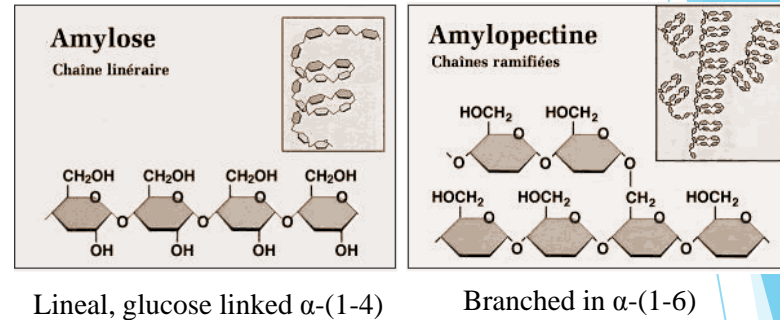
Pea Starch: Advantages: amylose content (25%), has a high-amylose content, which normally contributes to improve the mechanical strength and gas barrier properties of starch based films (Han et al.,2006).

PVA: synthetic polymer from polyvinyl acetate

✓ fully degradable

✓ high tensile strength and flexibility

✓ good aroma and oxygen barrier

✓ odorless, colourless and transparent
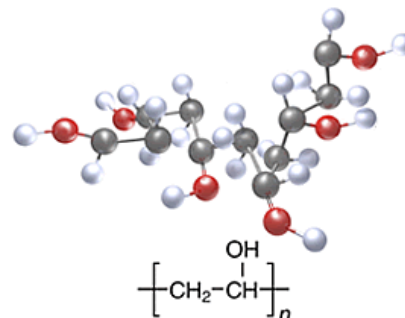
OBJECTIVE

The aim of this work was to analyze the effectiveness of mixing two biodegradable polymers, **pea starch (PS)** and **polyvinyl alcohol (PVA)**, to develop biodegradable packaging material for food application.
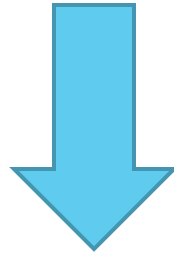
To this aim, **microstructural** and **physical properties** of **PS**, **PVA** and composite films (**PS:PVA**), stored during one and five weeks were analyzed.

MATERIALS AND METHODS

Film forming dispersion

1. PS (2% w/w) was heated in water bath at 95ºC-30 minutes.

2. PS was homogenized with rotor-stator ultraturrax D125.

3. PVA was added in a ratio PS:PVA 1:0.5 and dissolved at 90ºC-30 min on stirred plate.

4. Glycerol was introduced as a plastizicer in a ratio PS:Gly - 1:0.25 and mixed during 10 minutes with stirring.

5. Aqueous dispersion was casted into a teflon plates containing 1.5 g of solids.

6. Films were dried under controlled condition at 25ºC – 45%RH.

Films were equilibrated at **53% RH** using magnesium nitrate-6-hydrate saturated solution during 1 and 5 weeks.

Characterization of films

| EXPERIMENTAL MEASURE	EQUIPMENT	METHODOLOGY
Thickness	Micrometre	6 points by film
Moisture content	Vacuum Oven	Gravimetric at 60ºC 5 samples/formulation
Water vapour permeability (WVP)	Payne permeability cups	ASTM E96-95 modified method (Mc Hugh et al., 1994) 4 samples/formulation
Oxygen permeability	Oxtran System	Standar method D3985-95 (ASTM, 2002) 2 repetitions/formulation

Characterization of films

EXPERIMENTAL MEASURE	EQUIPMENT	METODOLOGY
Internal Transmitance (Ti)	Spectroco-lorimeter	Kubelka-Mun's Theory (Hutchings, 1999) 3 samples/formulation
Gloss	Gloss meter	Angle of incidence: 60º 3 samples/formulation
Microstructure	FESEM	Cryofractured by immersion in liquid N_2
Mechanical properties	Texture analyser TXA	Standar method 882(ASTM, 1992). Θ, TS and ϵ% at break 8 repetitions by formulation
Statistical analyses	Statgraphics Plus 5.1. Program	Variance analysis (ANOVA). Fisher least significant difference (LSD) at 95% confidence level

RESULTS

FESEM micrographs
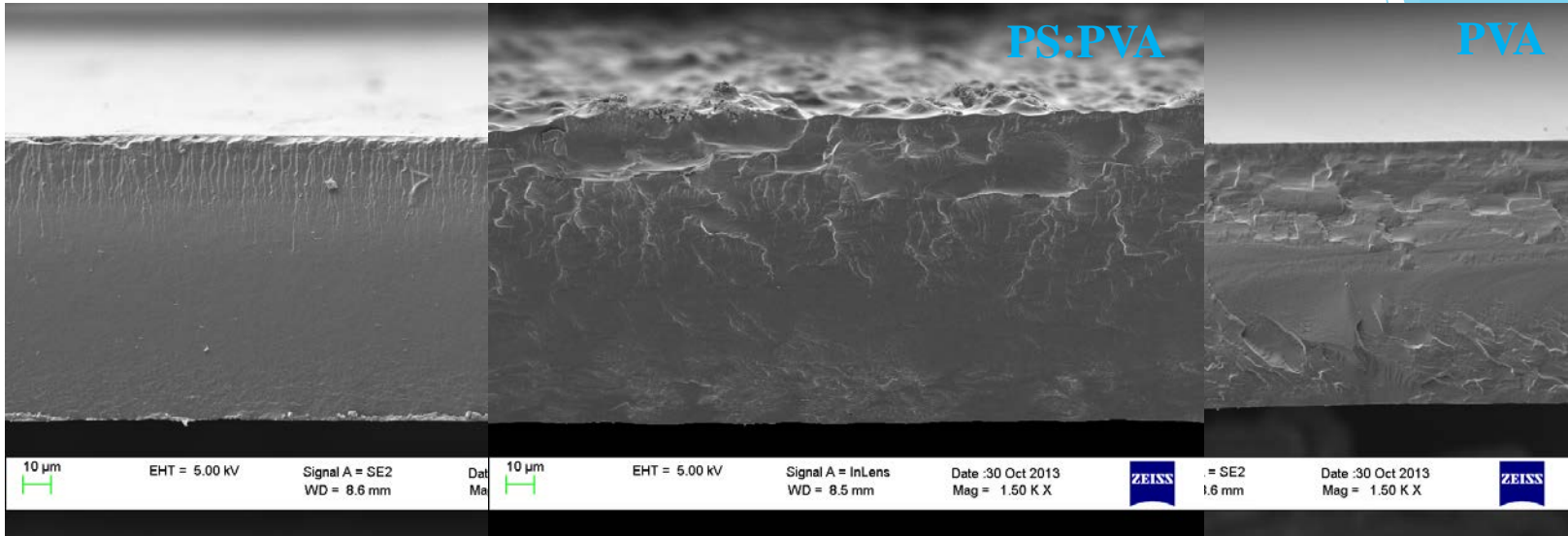
- ➢ **PS** films showed the typical homogenous and soft appearance.

- ➢ **PVA** films presented some irregularities typical from semi-crystalline structures, as a consequence of the arrangement of some segments of the polymer chain.

- ➢ **PS:PVA** films presented a structure more similar to the pure PVA (Chen et al., 2008).

Mechanical properties

Table 1: Elastic modulus (Θ), tensile strength at break (TS) and percentage of elongation at break (%$\mathcal{E}$) of PS (pea starch), PVA and PS:PVA composite films at two storage times (t_0-1 week and t_f-5 weeks). Mean values and (standard deviation).

	1 WEEK			5 WEEK		
	Θ (MPa)	TS (MPa)	%$\mathcal{E}$	Θ (MPa)	TS (MPa)	%$\mathcal{E}$
PS	417(41)[a1]	14.2(1.3)[a1]	10(2)[a1]	964(88)[a2]	24(2)[a2]	4.7(0.9)[a2]
PVA	95(22)[b1]	27(2)[b1]	69.13(0.43)[b1]	103(20)[b1]	27.2(0.9)[b1]	69.296(0.013)[b1]
PS:PVA	506(62)[c1]	26.9(1.4)[b1]	40(4)[c1]	689(44)[c2]	32.3(1.6)[c2]	41(3)[c1]

[a,b,c] different letter in the same column indicate significant differences among formulations ($p<0.05$)
[1,2] different number in the same file indicate significant differences between storage times ($p<0.05$)

- At **1W**, significant differences ($p<0.05$) between matrixes were found: **PS** films exhibited poor mechanical properties (low TS and %$\mathcal{E}$), **PVA** and **PS:PVA** films were very resistant and stretchable, similarly to the commercial plastics.

- At **5W**, **PS** films increased the rigidity and decreased significantly ($p<0.05$) the deformability due to the starch recrystallization. On the contrary, the mechanical behavior of **PVA** and **PS:PVA** films was not affected by the storage.

In the composite films: certain degree of inhibition of the retrogradation process surely occurred due to the establishment of interactions between both polymers.

Barrier properties

Table 2: Solubility, moisture content (MC), water vapour permeability (WVP) and oxygen permeability (OP) of PS (pea starch), PVA and PS:PVA composite films at two storage times (1 week and 5 weeks). Mean values and (standard deviation).

	Solubility (g film /g film)	MC(%d.b.)		WVP(gmm/KPahm^2)		OP(10^{-14}cm^3/msKPa)	
		1W	5W	1W	5W	1W	5W
PS	0.1157(0.0008)^a	11.4(0.4)^{a1}	8.7(0.4)^{a2}	6.0(0.3)^{a1}	6.7(0.7)^{a1}	2.5(1.8)	1.8(1.3)
PVA	0.208(0.019)^b	12.8(1.2)^{b1}	11.9(1.3)^{b1}	4.74(1.05)^{b1}	4.8(0.8)^{b1}		
PS:PVA	0.19(0.05)^c	8.03(0.54)^{c1}	7.06(1.69)^{a1}	5.09(1.17)^{ab1}	5.1(0.4)^{b1}	1.43(0.06)	1.65(0.005)

[a,b,c] different letter in the same column indicate significant differences among formulations ($p<0.05$)
[1,2] different number in the same file indicate significant differences between storage times ($p<0.05$)

- **At 1W, PS** films showed poor **barrier properties ($p<0.05$)** whereas **PVA** films presented greater resistance to the water vapour transfer, and **PS:PVA** films had intermediate behavior between both polymers.

- **At 5W, barrier properties** of the **PVA** and **PS:PVA** films did not change throughout storage time.

Optical properties

Table 3: Gloss (60º) and internal transmittance of PS (pea starch), PVA and PS:PVA composite films at two storage times (1 week and 5 weeks). Mean values and (standard deviation).

	Gloss 60º		Ti (450nm)	
	1W	5W	1W	5W
PS	47(17)[a1]	33(8)a[2]	85.4(1.6)[a1]	87.09(0.12)[a2]
PVA	53(23)[a1]	32(11)[a1]	88.57(0.15)[b1]	85.7(0.9)[a1]
PS:PVA	13.2(1.6)[b1]	12.9(1.2)[b1]	86.2(0.5)[a1]	85.2(0.9)[a1]

[a,b,c] different letter in the same column indicate significant differences among formulations ($p < 0.05$)
[1,2] different number in the same file indicate significant differences between storage times ($p < 0.05$)

- **At 1W, PS** and **PVA** films showed **greater gloss values ($p < 0.05$)**, thus indicating a smooth and homogeneous surface.

- **At 5W,** gloss values of **PS** films were reduced, thus becoming less glossy due to starch crystallization process, whereas **PVA** and **PS:PVA** films did not change.

Some inhibition of the retrogradation process surely occurred due to the establishment of interactions between both polymers.

- **Internal trasmittance** values (Ti) (related to transparency): similar values in the different films and storage times.

CONCLUSIONS

- The FESEM micrographs suggested that both polymer , **PS** and **PVA** are not highly incompatible and the blends were satisfactory.

- The **PS:PVA** films presented better mechanical and barrier properties than pure **PS** films.

- Properties of **PS** films were highly affected by ageing due to the recrystallization process. On the contrary, the properties of **PS:PVA** films did not change throughout storage.

- **In conclusion**, **composite films** presented very good optical and barrier properties. They behave mechanically similar to the commercial plastics and these properties were not affected by ageing. This fact is remarkable and suggests that the starch recrystallization was partially inhibited in these composite films.

Thank you for your atention!

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