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Thermal and Mechanical Properties of Thermoplastic Starch and Poly(Vinyl Alcohol-Co-Ethylene) Blends

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Abstract: The interest in thermoplastic starch (TPS) as a substitute material to replace conventional thermoplastics continues especially due its biodegradability, availability, low cost and because it is obtained from renewable sources. However, its poor mechanical properties and its high sensitivity to humidity have limited its use in several applications. Here, the copolymer poly (ethylene-co-vinyl alcohol) (EVOH), with two different ethylene contents, 27 and 44 mol% were blended with TPS by extrusion in order to overcome these limitations. The obtained blends were characterized by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), mechanical tensile testing, Scanning Electron Microscopy (SEM) and moisture absorption test. The addition of EVOH copolymer did not significantly changed the thermal stability of TPS, however it increased the tensile strength in 65% when compared to TPS. The morphology of the blends did not showed two distinct phases, an indication of miscibility or partial miscibility of the components. A decrease of moisture absorption was obtained by the addition of EVOH and is more pronounced for the EVOH with 44% of ethylene.

Keywords: Thermoplastic starch; EVOH; polymer blends; thermal properties of polymers; mechanical properties of polymers

1 Introduction

The development of polymer blends from polymers derived from renewable sources is of great interest to increases the potential of application of biobased materials such as starch. Even if the added material has limited biodegradability and is derived from nonrenewable sources, its use in low proportions can be considered an interesting alternative to improves the properties of biobased materials [1].

Cellulose, chitin and starch are the most abundant natural polymers and more likely to replace materials from petroleum sources. Starch has some advantages over the other two, such as its solubility, low cost, high availability, easy isolation and the possibility of being processed as a thermoplastic material [2].

Thermoplastic starch (TPS) is a semi-crystalline polymer obtained from the processing of starch in the presence of a plasticizer under the action of temperature and shear. Its application is still very limited due to its mechanical and thermal properties that are inferior when compared with other synthetic polymers already in commercial utilization. Therefore, an alternative to improve the properties of TPS and to improve its application is its combination with other polymers, as polymer blends [2]. A challenge in the development of blends containing TPS is its incompatibility with most existing synthetic polymers [3-5]. Thereby, polyvinyl alcohol-co-ethylene (EVOH), a semi-crystalline copolymer stands out as a good candidate to compose blends with TPS, since the presence of vinyl alcohol group in its backbone can improves the compatibility with starch [6-8]. The EVOH copolymer has good mechanical properties, thermal stability and is less hydrophilic than starch. Previous studies have shown that EVOH was able to

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improve TPS properties, but high concentrations of the copolymer were used in the blend (30-50 wt%) which, depending on the application, may be economically impracticable due its high cost [9-11].

Here melt blends of TPS/EVOH were prepared using EVOH with 27 and 44 mol% of ethylene. The materials were characterized by scanning electron microscopy, mechanical tensile tests, differential scanning calorimetry and moisture absorption tests.

2 Experimental

2.1 Materials

Cornstarch containing 70% amylose and 30% amylopectin (Amidex ®) was supplied by Ingredion-Brazil. Glycerol PA was supplied by Synth-Brazil. EVOH copolymers were Sigma-Aldrich, USA with two ethylene content: $EVOH_{27\%}$ and $EVOH_{44\%}$, containing respectively, 27% and 44% of ethylene.

2.2 Preparation of TPS

Glycerol was mixed to natural corn starch (11 wt% moisture) to give starch/glycerol at a proportion in dry bases of 70:30 (wt/wt). The mixture was homogenized manually and sieved to give a homogeneous powder that was stored at room temperature for at least 12 hours to promote diffusion of glycerol into starch granule before processing.

2.3 Preparation of TPS/EVOH Blends

Three concentrations of each EVOH were used, 5, 10 and 15 wt% in the final blend. EVOH pellets were grinded using liquid nitrogen in a high speed grinder and added to starch/glycerol mixture prepared as previously described and mixed in plastic bags before processing. The blend composition is detailed in Tab. 1. The mixtures were then processed in a bench single-screw extruder (AX Plasticos - Brazil) with screw diameter of 16 mm and length/screw ratio (L/D) of 26. The screw was equipped with a mixing element Maddock at its end and was operated at 30 rpm. The temperature profile from feed to die was 110°C, 120°C and 110°C. The produced material (3 mm spaghetti) was hot pressed at 140°C in plates with 2.5 mm thickness.

Table 1: Composition of the TPS and TPS/EVOH blends

	Starch (% w/w)	Glycerol (% w/w)	EVOH (% w/w)
TPS	70	30	-
$5EVOH_{27\%}$	66,5	28.5	5
$10EVOH_{27\%}$	63	27	10
$15EVOH_{27\%}$	59,5	25.5	15
$5EVOH_{44\%}$	66.5	28.5	5
$10EVOH_{44\%}$	63	27	10
$15EVOH_{44\%}$	59.5	25.5	15

2.4 Characterization

Thermogravimetric analysis (TGA) were performed to evaluate the thermal stability of TPS/EVOH blends and to determine the best processing conditions. TGA were carried out in a Pyris 1 TGA-Perkin-Elmer from room temperature up to 650°C with a platinum crucible. The analyses were performed under nitrogen atmosphere at a heating rate of 10 °C/min. The samples weight was around 20 mg.

Differential Scanning Calorimetry (DSC) analysis were performed to obtain data on thermal transitions, glass transition temperature (T_g), crystallization temperature (T_c) and melt temperature (T_m). The analyses were conducted in a DSC 8000-Perkin-Elmer, USA under nitrogen atmosphere with a flow rate of 50 ml / min. The temperature range was from -50 to 160°C for TPS sample and from -50 to 220°C for the blends and copolymers. Three heating rates were employed, 10, 20 and 30°C/min in order to determined the best condition for T_g detection.

The tensile tests were performed with an Instron 5969 Universal Testing Machine, according to the STM D-638. To prepare the samples, the materials were hot-pressed in the form of plates and cut in dumbbell shape. Before tests, all samples were conditioned at 53% relative humidity and 24ºC. Relative humidity was obtained through saturated salt solution of magnesium nitrate $(M_gNO_3)_2$. The test was carried out at 24ºC, in tensile mode using crosshead speed of 50 mm/min. At least 5 samples of each composition were tested.

Scanning Electron Microscopy (SEM). Samples were fragile fractured in liquid nitrogen and the fractured surface coated with platinum thin films by sputtering. The images were collected in a FEI scanning electron microscopy (Inspect F-50).

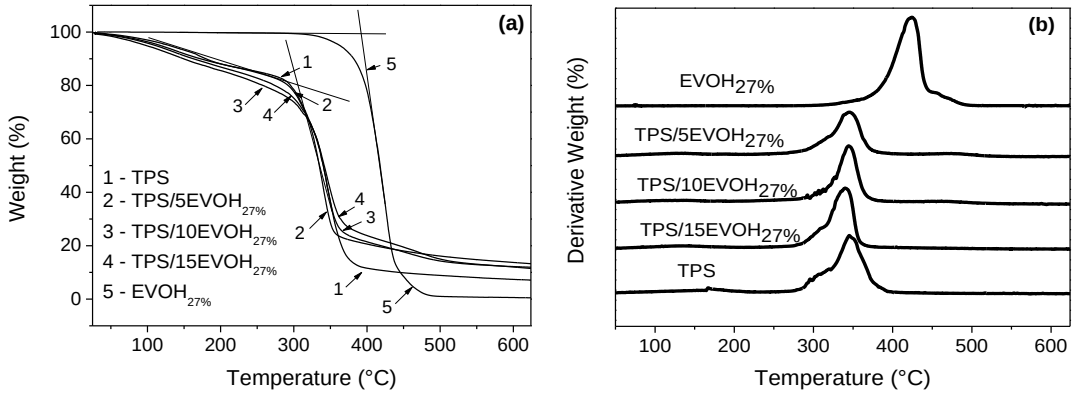
Moisture Absorption Test. The moisture absorption tests were performed in three different relative humidity, 53, 75 and 90%, obtained with saturated salt solutions of magnesium nitrate, sodium chloride and barium chloride, respectively. The specimens were cut with cylindrical shape with 11mm diameter and 1 mm thickness.

All specimens were previously dried at 105°C for 24 hours, weighed and then placed in the sealed containers with the saturated salt solutions for humidity control. At determined time intervals the specimens were removed from the container and weighed.

3 Results and Discussion

3.1 Thermogravimetric Analysis

TGA curves for TPS and for its blends with TPS/EVOH are shown in Figs. 1(a-b) and 1(c-d) respectively. EVOH copolymers showed initial decomposition temperature T_{id} = 325 and 340°C for EVOH with 27% and 44% of ethylene, respectively. It can be seen that even for 15 wt% of EVOH in the mixture, the thermal behavior of the blends was similar to TPS, meaning that the addition of copolymer did not affect its thermal stability. The peak of decomposition taken by DTG was around 400°C for EVOH and 340°C for the blends and for TPS.



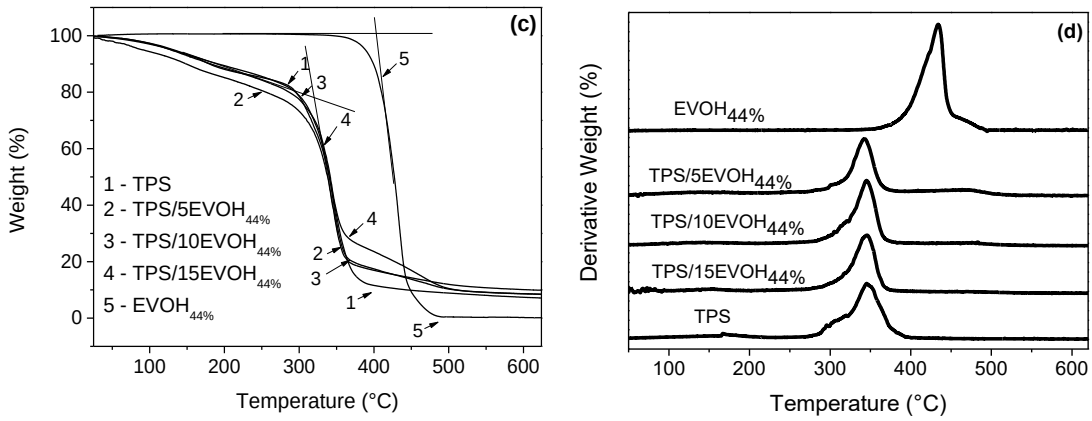
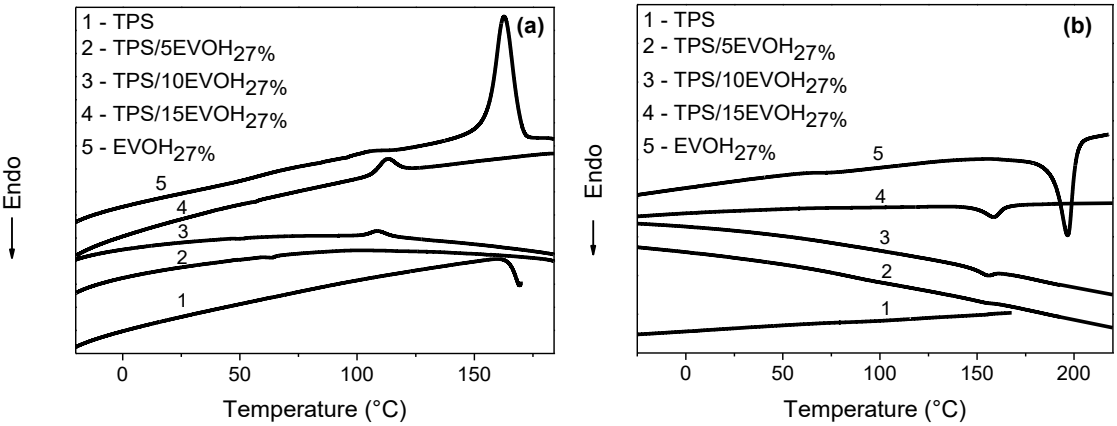


Figure 1: Thermogravimetric and corresponding derivatives curves for (a-b) $EVOH_{27\%}$ and its blends and (c-d) $EVOH_{44\%}$ and its blends

3.2 Differential Scanning Calorimetry

Fig. 2 shows the first cooling and 2nd heating curves of DSC for TPS, EVOH and their blends. For TPS no thermal transition was observed, however for the blends TPS/EVOH three transitions were observed due to EVOH (T_g, T_m and T_c). Glass transition of TPS is not easy to be observed; by other side crystallization is easier to be observed for samples stored in conditions that favor crystallization. While for neat $EVOH_{27\%}$ and $EVOH_{44\%}$ it were observed glass transition temperature of about 70°C and 54°C, respectively, for blends it was not observed, probably due to the low concentration of EVOH used (5, 10 and 15 wt%) and due to a certain degree of miscibility between EVOH and TPS. On the other hand, for higher concentrations of EVOH in blends with TPS (1:1 TPS/EVOH blends) Stenhouse et al. (1996) observed a clear glass transition temperature. The melting and crystallization peaks of EVOH in the blends decreased drastically as the EVOH content decreases from 15 to 5 wt%. Tab. 2 shows melting temperature (T_m) and melting enthalpy ($\Delta \boldsymbol{H}$) normalized to the EVOH content. The decrease of T_m and $\Delta \boldsymbol{H}$ in relation to pure EVOH indicates that probably the interactions between TPS and EVOH decreases the crystallization of the copolymer. The values for melting and crystallization temperatures of EVOH are in accordance with literature [9].



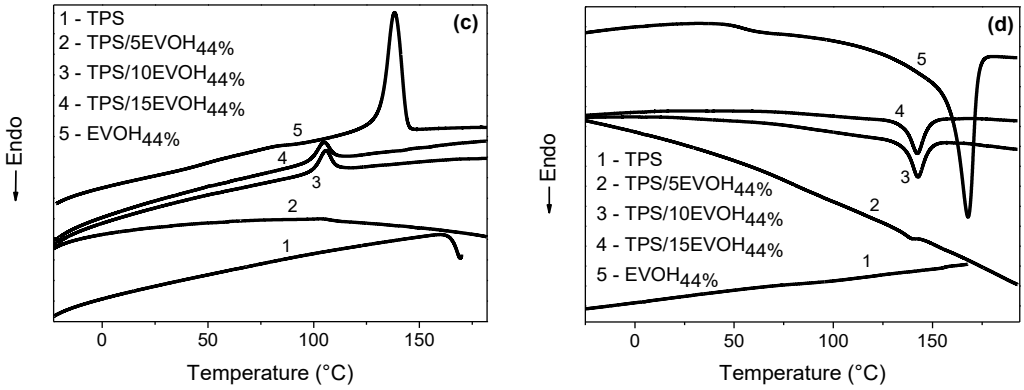


Figure 2: DSC curves of TPS, EVOH and its blends (a and c) for the first cooling cycles and; (b and d) for the 2nd heating cycles

Table 2: Melting temperature and melting enthalpy obtained by DSC curves. The data was normalized considering the EVOH content

Sample	T_m (°C)	ΔH (J/g)
TPS	None	None
$EVOH_{27\%}$	197	59,8
$TPS/5EVOH_{27\%}$	155	1,14
$TPS/10EVOH_{27\%}$	156	15,6
$TPS/15EVOH_{27\%}$	159	32,2
$EVOH_{44\%}$	168	50,7
$TPS/5EVOH_{44\%}$	139	2,6
$TPS/10EVOH_{44\%}$	142	43,8
$TPS/15EVOH_{44\%}$	143	28,8

3.3 Tensile Tests

Fig. 3 shows a representative curve for the results of tensile tests. The values for tensile strength, young's modulus and strain at break are given in Tab. 3.

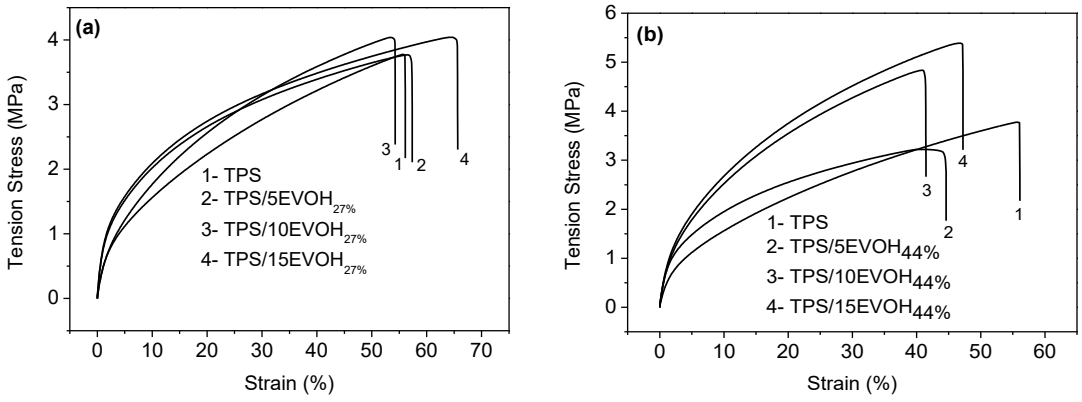


Figure 3: Stress-strain curves of TPS and TPS/EVOH blends (a) with $EVOH_{27\%}$ and (b) with $EVOH_{44\%}$

Table 3: Data for tensile strength, Young's modulus and strain at break for TPS and its blends with EVOH

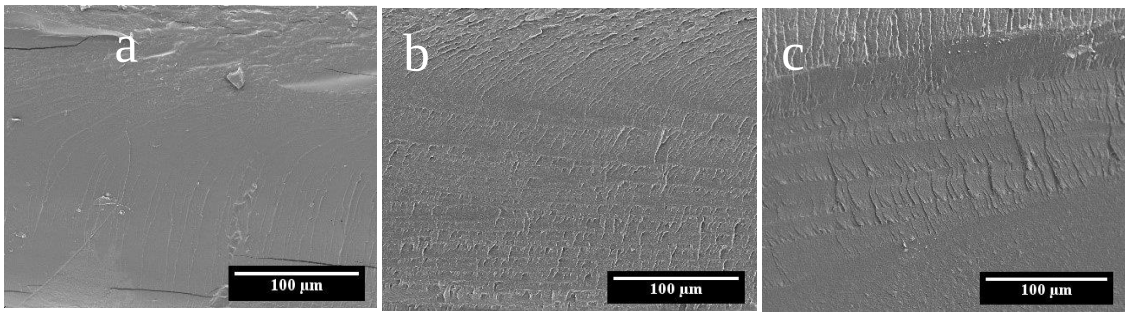
	Tensile strength (MPa)	Strain at break (%)	Young's Modulus (MPa)
TPS	3.4 ± 0.5	61 ± 13	93 ± 5
$EVOH_{27\%}$	59 ± 7.0	24 ± 9	2,800 ± 220
$TPS/5EVOH_{27\%}$	3.8 ± 0.5	48 ± 12	57 ± 2
$TPS/10EVOH_{27\%}$	3.9 ± 0.1	59 ± 6	50 ± 3
$TPS/15EVOH_{27\%}$	4.8 ± 0.2	61 ± 2	60 ± 2
$EVOH_{44\%}$	61 ± 1.0	17 ± 6	3,600 ± 150
$TPS/5EVOH_{44\%}$	3.2 ± 0.2	32 ± 4	62 ± 4
$TPS/10EVOH_{44\%}$	4.3 ± 0.3	38 ± 5	88 ± 2
$TPS/15EVOH_{44\%}$	5.2 ± 0.3	47 ± 5	91 ± 5

The tensile curves are shown in Fig. 3. The general behavior for all blends and TPS are similar showing an almost linear portion with low deformation and a plastic behavior up to rupture. The increase in tensile strength for the blend with 15 wt% of EVOH is of about 65% with respect to TPS being the highest values observed for the blends with $EVOH_{44\%}$. The modulus and elongation was almost the same for TPS and its blends with EVOH.

3.4 Scanning Electron Microscopy (SEM)

SEM micrographs of fractured surfaces of TPS, $EVOH_{27\%}$ and $EVOH_{44\%}$ are shown in Figs. 4(a), 4(b) and 4(c), respectively.TPS shows a flat and uniform fracture surface characterizing an amorphous or very low crystalline materials. On the other hand, EVOH copolymers exhibited a rough surface, typical of semi-crystalline materials.

The brittle fragile fracture surface of blends is shown in Figs. 4(d-f) for $TPS/EVOH_{27\%}$ with 5%, 10% and 15% of EVOH, respectively and in Figs. 4(g-i) for $TPS/EVOH_{44\%}$ with 5, 10 and 15 wt% of EVOH, respectively. For all blends it is possible to observe a rough surface without evidences of domains of TPS or EVOH indicating that the system is formed by a single phase, an indicative of miscibility between the components. It is interesting to observe that even with low addition of EVOH the brittle fractured surface of the blends are more close to EVOH than to TPS.



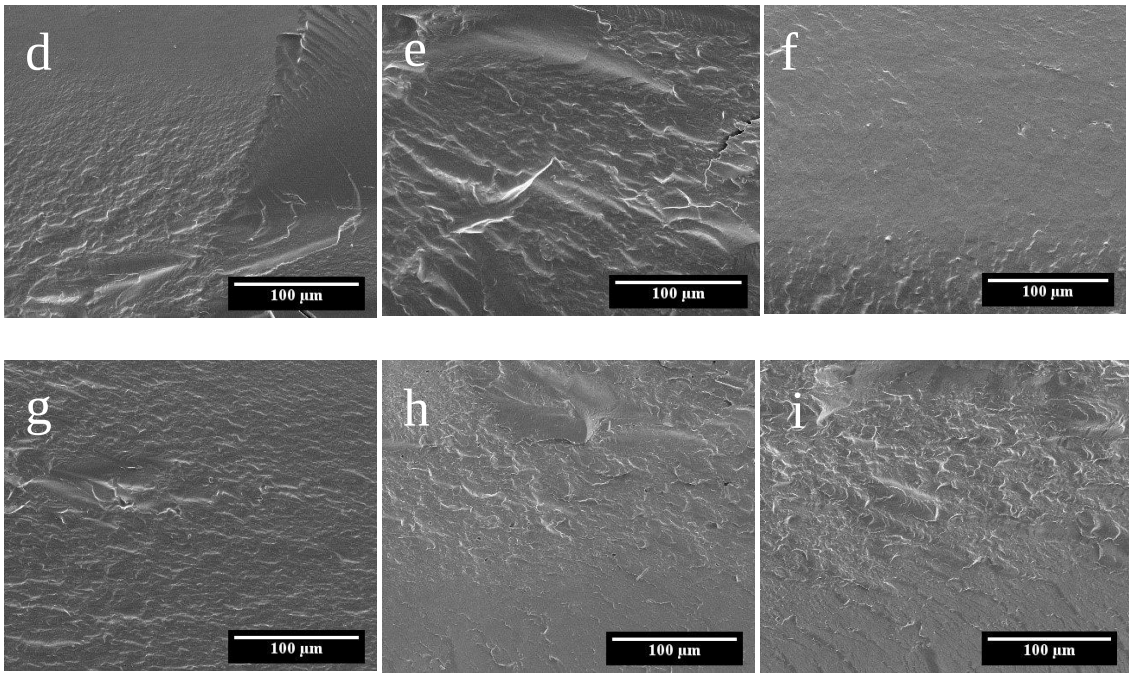


Figure 4: SEM micrographs of brittle fracture surfaces of: (a) TPS, (b) $EVOH_{27\%,}$ (c) $EVOH_{44\%,}$ (d) $TPS/5EVOH_{27\%,}$ (e) $TPS/10EVOH_{27\%,}$ (f) TPS,/$15EVOH_{27\%,}$ (g) $TPS/5EVOH_{44\%,}$ (h) $TPS/10EVOH_{44\%}$ and (i) $TPS/15EVOH_{44\%}$

3.5 Moisture Absorption Test

Moisture absorption results are shown in Fig. 5. It is observed that water uptake of samples was reduced with the increasing addition of EVOH and with the increase in the ethylene content in EVOH. The highest decrease in water absorption was observed for the samples conditioned in 90% relative humidity environment.

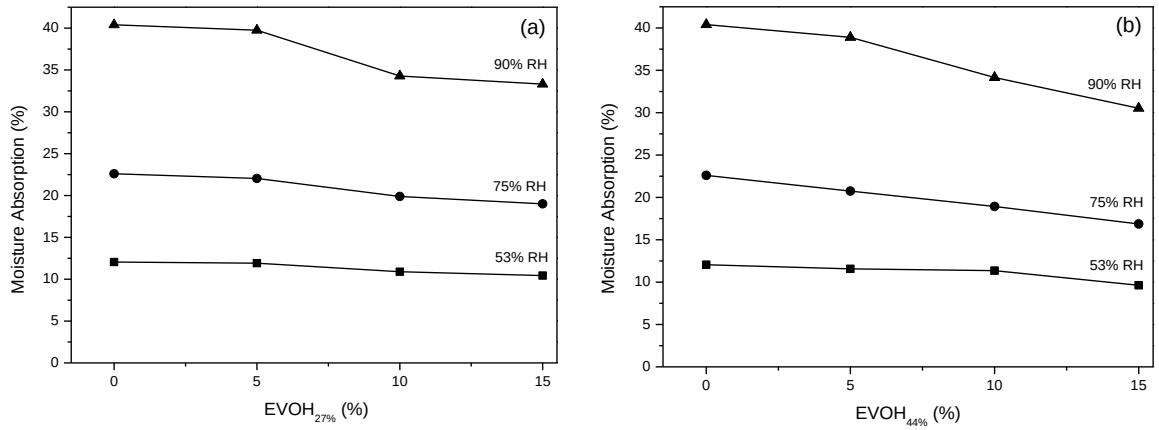


Figure 5: Moisture absorption of the materials according to copolymer content: (a) $TPS/EVOH_{27\%}$ blends and (b) $TPS/EVOH_{44\%}$ blends

4 Conclusions

Blends of TPS and EVOH with 275% and 44% of ethylene were successfully prepared. TPS/EVOH blends showed a thermal stability of about 290°C when measured by TGA. The addition of EVOH causes an increase in the tensile strength and in the Young's modulus of about 50%. Differential scanning calorimetry suggests a good interaction between starch and EVOH since the melting temperature and mainly the melting enthalpy of EVOH decreases in the blends when compared with the neat EVOH polymers. This result was also corroborated by SEM analysis showing an indicative of miscibility whereas the SEM images of the blends did not show distinct phases of EVOH or TPS. The moisture absorption test showed that the addition of EVOH and the increase of ethylene content decrease the water uptake.

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