

Structure and Physical Properties of EVA/Starch Precursor Materials for Foaming Applications

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ABSTRACT: The use of biodegradable materials to develop polymeric blends visioning distinct applications is desirable and nowadays is an important research field. In this work, blends of an ethylene-vinyl acetate copolymer (EVA) and 30, 50, and 70% in weight of an unmodified corn starch have been successfully fabricated. The structure of these blends have been characterized using scanning electron microscopy (SEM), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and Fourier transform infrared spectroscopy (FTIR). It was found that the original starch particles are kept in the blends forming a separate phase from EVA. The FTIR confirmed that EVA and starch comprise a physical mixture in the blends. Besides, the blends were found very homogenous and mainly amor-

phous with the EVA melting temperature being independent of the starch content. The melt flow index (MFI) decreased for higher contents of starch, revealing that starch acts as a filler in the blends. Physical properties such as density, hardness, and thermal conductivity were found to increase with the content of starch in the blends. Considering one of the goals of this research, which is producing foams using these blends as precursor materials, the structural and physical characteristics determined here are very satisfactory and open good perspectives in this sense. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 2324–2330, 2011

Key words: blends; EVA; starch; mechanical properties; thermal properties

INTRODUCTION

Starch has been used in the last years in the plastic industry with two main goals. The materials can be processed to end products having acceptable physical and chemical properties and the biodegradability of the products may open an avenue for increasing usage of farm commodities and other renewable resources.^{1–5} The biocompatibility of starch has also become a field of interest visioning medical applications.^{6–8} However, the presence of a synthetic polymer in polymer formulations based on starch is still

important to impart a higher insensitivity to moisture and to improve thermal and mechanical properties.^{9–14} Additionally, in the case of using unmodified starch, it is possible to reduce costs due to the low price of this material.

The processing by injection molding and the structure and properties of solid EVA/starch blends have been analyzed.^{15–17} High contents of starch (up to 70%) have been tested and materials have been produced using different kinds of starches (different contents of amylopectin and amylose).^{15–17} The use of additional synthetic polymers containing reactive functional groups, such as maleic anhydride, to improve the compatibility between both starch and EVA has also been analyzed in detail.^{15–17} In spite of the high amount of starch used in these materials, the samples displayed excellent physical properties. The main drawbacks of adding starch were an increase of the density and a reduction in the strain at break of the blends in comparison with the pure synthetic polymer.^{15–17} Another investigation on this topic considered the dynamic mechanical behavior of EVA/starch blends¹⁸ that was related with the granular arrangement of the starch and the adhesion between both phases.

The interest in polyolefin foams has considerably increased in the last years^{19–22} due to some

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interesting advantages, such as weight reduction, thermoplastic character, excellent flexibility, high amount of energy absorbed in impact, low level of humidity absorption, possibility of thermoforming, etc.¹⁹ On the other hand, these materials are nonbiodegradable and are produced from petrol. In addition, for several applications these materials are crosslinked. These aspects make these materials non suitable considering their disposal.¹⁹ From all the polyolefins available, ethylene-vinyl acetate copolymers with high vinyl acetate contents have a complementary character with starch.^{17,23–25} Due to this reason, the blends of these two materials could balance several important aspects, such as an adequate control of the density and cellular structure during foaming and suitable combination of stiffness and toughness. Besides, these materials will have a low price and an acceptable behavior from the environmental point of view.

The main goal of our research is to obtain foams of EVA/starch blends with suitable structure and properties using the improved compression molding technique.^{26,27} To obtain these materials, there are several aspects that the blend have to fulfill prior to the production of the foams. Some of these aspects are: a good compatibility between phases, a good dispersion of the filler and the blowing agent, density close to the theoretical one and suitable thermal and mechanical properties.

In this article a detailed characterization for blends containing EVA and 30, 50, and 70% in weight of starch designed for foaming has been carried out. The characterization was performed using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), scanning electron microscopy (SEM), Fourier transform infrared (FTIR) absorption spectroscopy, melt flow index (MFI), hardness, density, and thermal conductivity.

EXPERIMENTAL

The corn starch was supplied by Syral (Zaragoza, Spain) and used as received, i.e., powder with an average particle size of 10 μm . The EVA grade was supplied by Repsol YPF (Madrid, Spain) (PA-440) and presents a vinyl acetate (VA) content of 28% and a melt flow index of 7 g/10 min (190°C/2.16 kg). To use these blends as precursors for foaming, a commercial grade of azodicarbonamide (AZD) Uquifoam L supplied by Urquinsa (Barcelona, Spain) with an average particle size of 4.9 μm was used in the formulations. Fixed amounts of stearic acid supplied by Renichen S.L and zinc oxide (Silox Active grade) provided by Safin Alcan were also used. The stearic acid is a processing aid useful to reduce heating of the compound during blending and the zinc

TABLE I
Formulations of the EVA/Starch Blends (in Weight Percentage)

Name	100% EVA	70% EVA	50% EVA	30% EVA
EVA	94.7	66.3	47.35	28.4
Starch	0	28.4	47.35	66.3
AZD	5	5	5	5
Zinc oxide	0.1	0.1	0.1	0.1
Stearic acid	0.2	0.2	0.2	0.2

oxide is commonly used to reduce the decomposition temperature of azodicarbonamide.^{28,29}

The blending process was carried out during 10 min using a Rheodrive 5000 rheometer from Haake Fisions with the screw speed at 7 rpm and a temperature at 80°C, which is right below the decomposition temperature of the blowing agent (avoiding any premature gas formation). After blending, the material was cooled down to room temperature and cut in 5 mm portions for the fabrication of solid materials (called precursors in this article). The precursors were produced by introducing 6.0 g of each blend in a steel mold with cylindrical shape. Talc from Luzenac (Grade A-10) was used as a releasing agent. The mold was heated at 0.4°C s⁻¹ from room temperature to 80°C. As soon as the temperature reached 70°C, a pressure of 160 bar was applied using a piston that can be introduced into the mold. When the temperature reached 80°C, three consecutive pressure releases (160 bar \rightarrow 0 bar) were carried out. The time between each pressure release was 100 s and during this time the pressure was 160 bar. This process allows reducing the amount of trapped gas in the precursor material. Finally, the precursor was cooled down to 40°C under 160 bar. The precursors were cylindrical with a diameter of 22.8 and 15 mm in thickness. Precursors with four different ratios of EVA/starch (100/0%, 70/30%, 50/50%, 30/70%) and with a constant content of azodicarbonamide (5%) were prepared as shown in Table I. The produced precursors were transferred to a desiccator and stored until characterization (50% humidity and 23°C).

The TGA measurements were performed using a Mettler TGA/SDTA 851^e with a temperature program from 50 to 850°C at 10°C min⁻¹ in a N₂ atmosphere. Samples of 12.0 mg were used in these experiments. DSC experiments were carried out using a Mettler DSC 862 instrument from -40 to 200°C at 10°C min⁻¹ in a N₂ atmosphere. Samples of 5.0 mg were used. The SEM images were collected using a JEOL JSM 820. Density measurements were determined by Archimedes' principle using the density determination kit of the AT261 Mettler balance. Melt flow index was obtained following the ISO standard 1133 : 2006, with an ATS-FAAR equipment

model TWELVINDEXTM and a Mettler balance model AE260. The measurements were performed at 180°C and with a weight of 10.0 kg. Hardness measurements were obtained following the ISO standard 868: 2003, with a BAREISS U 72 equipment. The thermal conductivity was measured using a Thermal Constants Analyser type Hot Disk based on the transient plane source technique (TPS).^{30–32} The FTIR spectra were recorded using a Bruker spectrometer model Tensor 27 in the ATR mode (not polarized). The experiments were performed using 64 scans and 4 cm⁻¹ spectral resolution.

RESULTS AND DISCUSSION

Thermogravimetric analysis (TGA)

To produce foams of EVA/starch blends with adequate structure and properties using the improved compression molding technique,^{26,27} several aspects have to be considered. The first issue is related to the homogeneity of the blends and the amount of chemical blowing agent in the formulation, which was investigated by TGA. The results are shown in Figure 1 for the two main raw materials (EVA and starch) and for three different samples of the EVA/starch 50% blend. As it can be observed, the three curves for the blends overlap indicating an excellent homogeneity of these materials. Four mass losses were detected in the materials containing EVA, starch and azodicarbonamide. The first one starting at around 100°C corresponds to the humidity in the starch phase (~ 10% mass loss) and the next one at around 220°C is due to the decomposition of the blowing agent.³³ The third one at 300°C has three contributions: decomposition of residues of azodicarbonamide, starch decomposition and partial decomposition of acetic acid in EVA.³⁴ Finally, the

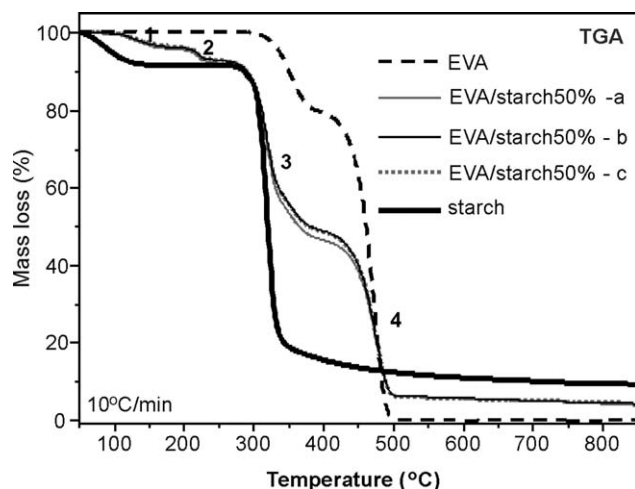


Figure 1 Thermogravimetric curves of EVA, starch and three different samples (a–c) of the EVA/starch50% blend.

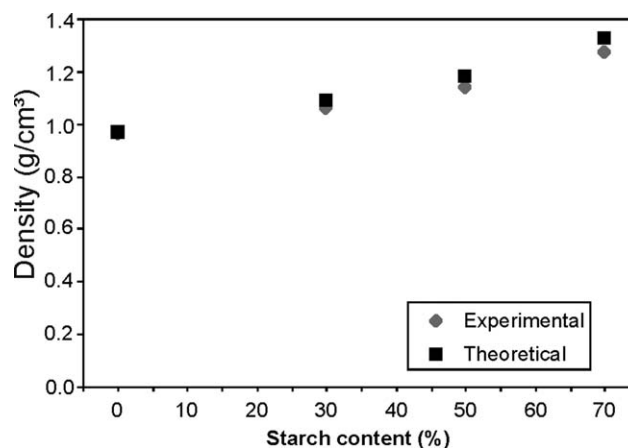


Figure 2 Experimental and theoretical density for EVA and EVA/starch blends.

fourth corresponds to decomposition of ethylene units in the EVA copolymer.³² By measuring the mass loss at 220°C (5%), it was confirmed that no decomposition of the blowing agent was produced during the initial blending of the raw materials. Therefore a content of 5% was achieved for all the produced blends.

Relative density

A second important feature for foaming is to obtain precursor materials with a reduced porosity. This guarantees that all the gas used for foaming is a result of the blowing agent decomposition. To analyze this aspect, the experimental and theoretical densities of the blends were compared. As it can be observed in Figure 2, the density increases with the starch content; this was expected considering the higher density of starch. The differences between experimental and theoretical densities are lower than 5% for all blends analyzed, which indicates a small amount of porosity in the precursors. The theoretical densities were obtained using the mixture rule utilizing the following values for the components: $\rho_{\text{EVA}} = 0.95 \text{ g cm}^{-3}$, $\rho_{\text{starch}} = 1.60 \text{ g cm}^{-3}$ and $\rho_{\text{Azo}} = 1.65 \text{ g cm}^{-3}$.³⁵

Melt flow index

A third aspect which has a significant effect on the foaming behavior is the melt flow index modification due to the incorporation of a second phase. It is well known that foaming depends on many aspects and one of them is the melt rheology of the polymeric matrix; in general reducing the melt flow index is positive from this point of view.^{19–21} As expected, the data given in Figure 3 show a strong linear reduction (40 times reduction) when starch is added, indicating that starch acts as a filler in the materials under study.

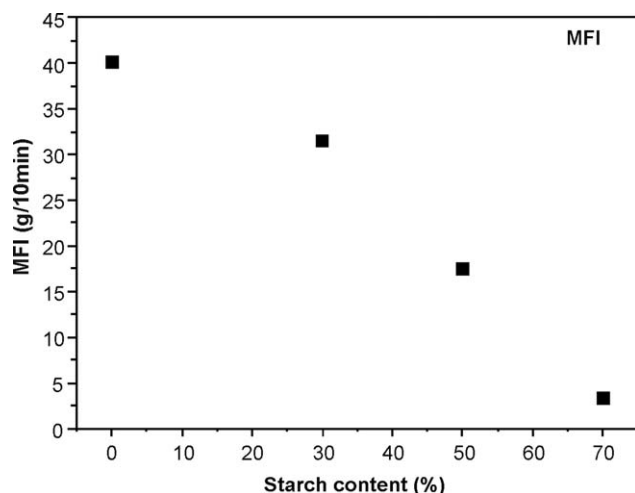


Figure 3 Melt flow index for EVA and EVA/starch blends.

Differential scanning calorimetry (DSC)

Differential scanning calorimetry was used to examine the possible influence of starch particles on the crystalline structure of the EVA/starch blends. The results of this analysis are shown in Figure 4 and Table II. The data shows that both the melting temperature and the crystallinity of the EVA phase did not change when starch was included in the formulation. The high VA content in the EVA (28%) resulted in materials with low melting temperatures (72°C) and an almost whole amorphous structure since the crystallinity was only 6%. The crystallinity was calculated from the area of the DSC peak, dividing the heat of fusion by the heat of fusion of a 100% crystalline material (288 J g⁻¹).³⁶ For the materials with starch and azodicarboamide in the composition, the

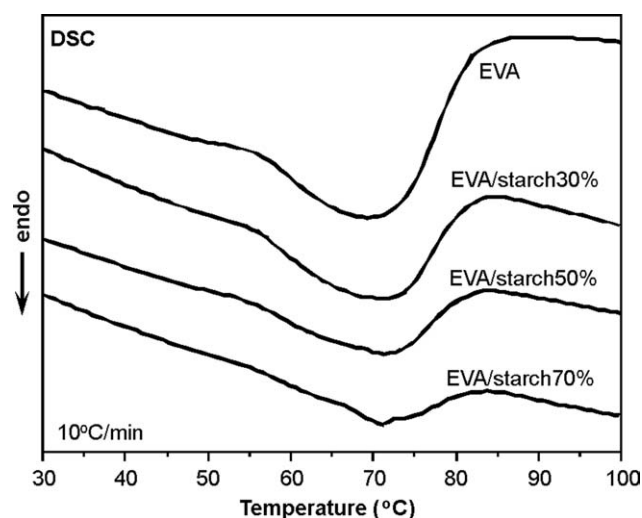


Figure 4 Differential scanning calorimetric curves of EVA and EVA/starch blends.

TABLE II Melting Temperature and Degree of Crystallinity of the EVA/Starch Blends

Blends	Melting temperature (°C)	Crystallinity (%)
100% EVA	71.1	5.8
70% EVA	72.6	6.1
50% EVA	72.1	5.5
30% EVA	72.1	6.1

crystallinity was corrected taking into account the amount of EVA in the blends.

Scanning electron microscopy (SEM)

An important aspect that has an influence on the foaming behavior and on the physical properties of these blends is the morphology of the composite material.^{15-17,37} An example (EVA/starch50%) of the morphology observed by SEM is shown in Figure 5 (similar results were found for the other

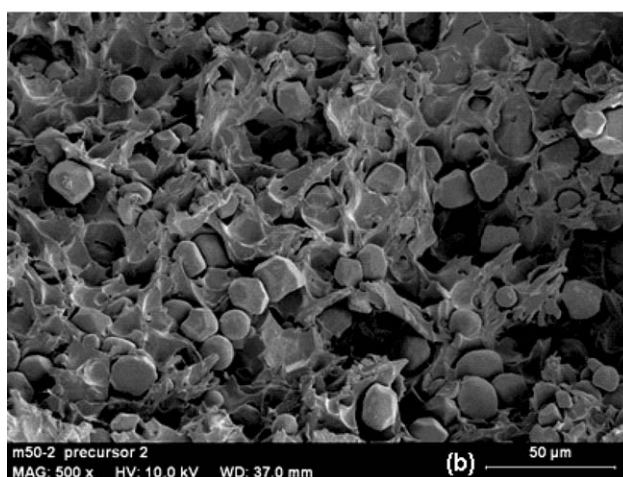
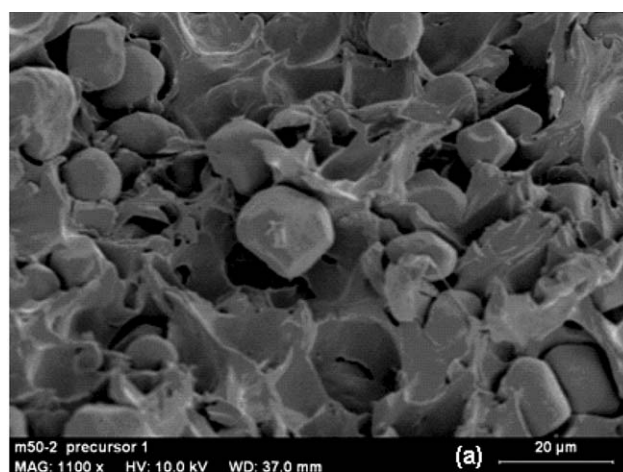


Figure 5 SEM micrographs for EVA/starch50% recorded with (a) ×1100 (bar scale: 20 µm) and (b) ×500 (bar scale: 50 µm) magnification.

formulations). As observed, starch particles can be seen in the image, indicating that the original particles were maintained during processing. As expected, gelatinization did not take place during blending. The reasons are related to the small water content during blending, very low temperature and low shearing. Therefore, and as suggested above, the starch particles should be considered as a filler for the polymeric matrix. From Figure 5, it can be seen the phase separation between both materials with the starch particles spread all over the polymer matrix.

Hardness

The mechanical properties of foams depend on the properties of the polymeric matrix and on the cellular structure.³⁸ To gain some information on the effect of starch and azodicarbonamide on the mechanical properties of the polymeric matrix, the effect of including both components on the hardness (Shore D) was studied. The results are shown in Figure 6 and reveal that adding starch and azodicarbonamide increases the hardness values in a significant way. Therefore, starch acts as a reinforcement for the EVA polymer selected. For instance, the hardness for 70% starch content was increased 1.75 times. The influence of the blowing agent particles had a similar effect, increasing the material hardness. This is an important result because the use of starch as filler for EVA increases the strength of the polymer and as a consequence would also increase the strength of the foams to be produced. In addition, it is interesting that the use of this particular chemical blowing agent (azodicarbonamide) is also beneficial from the mechanical point of view.

Thermal conductivity

Figure 7 shows the results for the thermal conductivity of the blends, which increase as a function of the starch content in the solid samples. The variation was

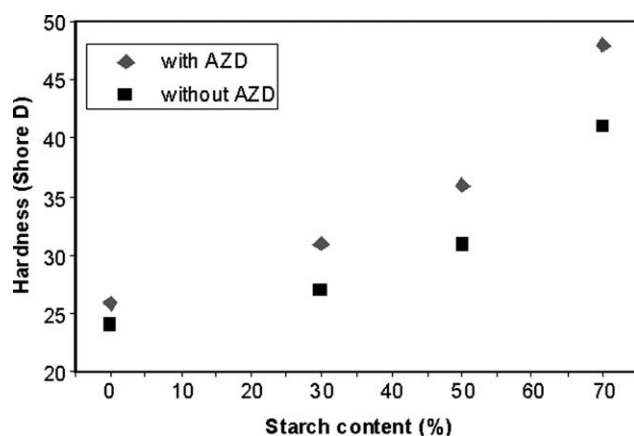


Figure 6 Hardness Shore D of EVA and EVA/starch blends with and without azodicarbonamide.

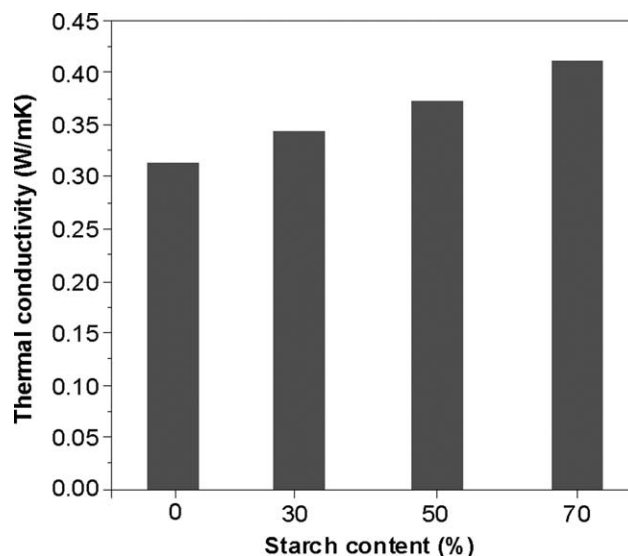


Figure 7 Thermal conductivity of EVA and EVA/starch blends.

from 0.32 W mK^{-1} for the pure EVA to 0.42 W mK^{-1} for the EVA/starch70% blend. Since the experimental and theoretical density values found for the blends are very close (i.e., the porosity is very similar for all the materials), the observed increase in thermal conductivity is due to the introduction of starch. An increase of the thermal conductivity is positive from the point of view of the foaming process. Cooling after foaming would be quicker for materials containing starch and this has a significant influence on foaming mechanism such as coalescence. A higher cooling rate reduces the coalescence rate and as a consequence improves the cellular structure.³⁹

Vibrational spectroscopy (FTIR)

The FTIR technique was applied to investigate possible chemical interactions between EVA and

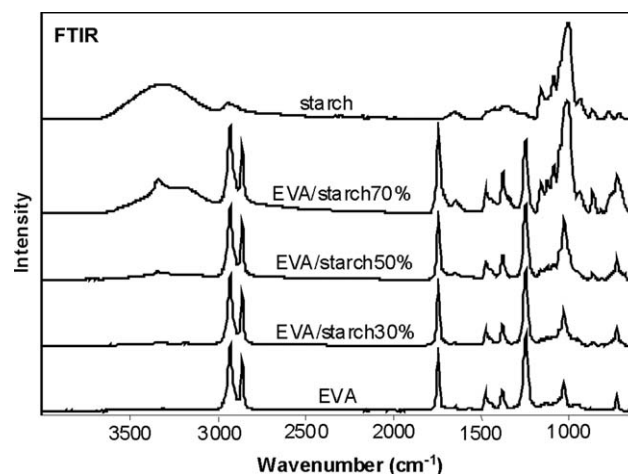


Figure 8 FTIR bands for starch powder, EVA pellet and EVA/starch blends.

TABLE III
Assignments of the Main FTIR Bands of EVA and Starch

EVA		Starch	
Band (cm ⁻¹)	Assignments	Band (cm ⁻¹)	Assignments
1016	C—O stret.	900-1250	C—O stret.
1235	C—O stret.	1243	O—H bending
1369	C—H bending	1325-1445	C—H bending
1462	C—H bending	1462	C—H bending
		1650	O—H bending (adsorbed water)
1734	C=O stret.		
2850	C—H stret. Sym.		
2915	C—H stret. antisym.	2920	C—H stret.
		3300	O—H stret.

starch. Figure 8 shows the FTIR spectra obtained in the ATR mode for starch powder, EVA pellets, and EVA/starch blends. Because the FTIR spectra of the EVA/starch blends are practically a superposition of the FTIR spectra of the neat materials, it can be undoubtedly concluded that both EVA and starch do not present a significant chemical interaction when forming the blends. The latter would lead to the raise of a new band and/or frequency shifting and relative intensity variation for the bands related to chemical groups involved in the chemical interaction. The FTIR results are a consequence of the physical mixture between EVA and starch as observed by SEM images and indicated by thermal analysis data as well. The assignments of the main FTIR bands for both EVA⁴⁰ and starch^{41,42} are given in Table III.

CONCLUSIONS

Blends containing ethylene-vinyl acetate copolymer (EVA) and native corn starch at 30, 50, and 70% in weight were fabricated. Starch and EVA were found in separated phases according to SEM images; however forming well compacted blends as pointed by density data. The DSC showed that the crystallinity of the blends is very low (~ 6%), i.e., the blends are pretty much amorphous. The density, hardness and thermal conductivity are very dependent on the starch content, being higher for higher amounts of starch in the blend. The melt flow index (MFI), however, varies in an opposite way. The FTIR revealed the absence of chemical interactions between EVA and starch leading to blends formed by a physical mixture in full agreement with the SEM images. The structure and physical properties determined for EVA/starch blends containing a chemical blowing agent strongly

indicate that these materials are suitable to be used as precursors for foaming.

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