



## SYNTHESIS AND CHARACTERIZATION OF BIODEGRADABLE GRAFTED COPOLYMERS

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### KEYWORDS

Ethyl vinyl acetate, polylactic acid, transesterification, biodegradable

### ABSTRACT

This work aimed to prepare biodegradable copolymers based on ethylene vinyl acetate and polylactic acid using transesterification reactions. The materials were prepared in the melt and then characterized by elemental analysis, infrared spectroscopy, X-ray, scanning electron microscopy, gel permeation chromatography and rheology. Selective extractions for all samples were made, and the results indicate that a maximum of 25% of EVA-g-PLA copolymer was synthesized by this method. Biodegradation tests were carried out using the standard ISO 14851 (1999), which specifies a method for determining the biochemical oxygen demand in a closed respirometer. The results demonstrate that the procedure used allowed the synthesis of biodegradable copolymers with mechanical properties similar to conventional polymers.

### INTRODUCTION

The rapid growth of plastic production is considered as a serious source of environment pollution. Approximately 100 million tons of plastics are produced each year and within a short period of time almost half of them are disposed to the environment (Stevens 2002). Despite synthetic polymers are more effective than the natural ones, due to the best properties (as mechanical properties, resistance, etc.) they do not decompose naturally when disposed, which causes a serious environmental problem (Saha et al. 2003). Due to this problem, in the recent years, there has been increasing interest in the development of low-cost and environmentally friendly materials through polymer modification (Tjong et al. 1998, Choi et al. 1996). The use of biodegradable polymers, as an alternative to conventional non-biodegradable plastics, could contribute to the solution of this environmental problem.

Biodegradable polymers are polymers which completely degrade by the action of biological micro organisms. Biodegradable polymers can be divided in two types: completely biodegradable polymers and the biodegradable polymers which are not completely biodegradable (Choi et al. 1996). Biodegradable polymers are polymer blends composed by a completely biodegradable polymer and a non-biodegradable polymer. Completely biodegradable polymers have not proved to be useful for commercial applications due to their high price or limitations of thermal and mechanical properties (Choi et al. 1996). An additional drawback of polymers biodegradation is its complexity concerning to their structures and compositions. The biodegradability of polyesters depends mainly on their chemical structure and on the hydrolysable ester bonds in the main chain, which are susceptible to microbial attack. Other factors, such as, molecular weight, degree of crystallinity, stereoregularity and morphology, also affect the rate of polymer biodegradation (Kim et al. 2001; Kang et al. 1999). Biodegradable polymers can be derived from renewable (corn or wood cellulose) or petroleum sources. Aliphatic polyesters are one of the most promising biodegradable materials because they are readily susceptible to biological attack (Huang 1985). As an example, polylactic acid (PLA), which has melting temperature around 160-180 °C, has received much attention as alternative biodegradable polymer (Tsuji and Ikada 1998). PLA can be obtained from renewable agricultural sources, because lactic acid monomers are extracted from the fermentation of crop like corn starch and sugar feed stocks (Lunt 1998). Its production consumes carbon dioxide, providing significant energy savings (Drumright et al. 2000, Whiteman 2000, Snook and Thesis 1994). Thus, its production presents advantages over other synthetic materials.

Blending polymers has been used to develop new polymeric materials with specific properties, this method has also been used to prepare new materials with enhanced biodegradability. Blends of biodegradable polymers with various synthetic materials have been studied for a variety of industrial applications (Machado



et al. 2007). The results showed that even though biodegradability can increase, the final properties are not achieved. An alternative approach to produce these materials can be by synthesis of grafted copolymers combining the best properties by grafting synthetic polymers onto natural ones. This method was used which to balance the properties of homopolymers (Klempner and Frisch).

Within one polymer (copolymers) different repetitive units can be present can be either distributed statistically along the polymer chains (random copolymers), alternately, form a block (block copolymers) or a branching structure (grafted copolymers). These different structures, despite having the same overall composition, can have different properties. Moreover, copolymers have been developed to generate new materials with a enhanced performance. The source of interest for these materials is linked to the *in situ* compatibilization of polymer blends (Machado et al. 2006), where a graft copolymer is prepared during the polymer blending inside the compounding machine, to reduce surface tension, avoid droplets coalescence and consequently generate polymer blends with higher properties.

Ethylene vinyl acetate (EVA) copolymers have a broad range of industrial applications (Tambe et al. 2008), such as, packaging, adhesives, wire, cable and health care. Since these copolymers have good properties and high resistance to biodegradation it would be a challenge to develop new materials based on EVA with enhanced biodegradability. Therefore, in this work copolymers of EVA and PLA were prepared using titanium propoxide as a catalyst. The morphological, physical, mechanical, rheological and biodegradable properties of the prepared copolymers were characterized.

## EXPERIMENTAL

### Materials

Ethylene vinyl acetate 28% (28% VA) of vinyl acetate, (Escorene Ultra Lot. 61E466) supplied from Exxon was used as non-biodegradable polymer and polylactic acid (PLA) supplied by Aldrich was used as a biodegradable polyester. Titanium propoxide ( $\text{Ti(OPr)}_4$ ) from Aldrich was used as transesterification catalyst. The sample composition is shown in Table 1.

Table 1: Composition of the prepared samples

Sample	EVA (wt. %)	PLA (wt. %)	Ti(OPr) <sub>4</sub> (wt. %)
EVAPLA0	60.0	40.0	0.0
EVAPLA1	59.5	38.6	1.9
EVAPLA2	59.5	39.5	0.9
EVAPLA3	59.5	39.8	0.7
EVAPLA4	59.5	40.0	0.5

### Compounding

The pellets of both polymers were dried in a vacuum oven at 60°C for 24 hours before use. Copolymers of EVA and PLA were prepared in a Haake batch mixer (Rheocord 90; volume 50 ml), equipped with two rotors running in a counter-rotating way. The rotor speed was 50 rpm and the set temperature was 160 °C. The copolymers were prepared using the following sequence: first EVA pellets were introduced into the hot mixer, after melting, PLA and catalyst were added. Titanium propoxide was collected and carried to the mixer in a syringe under an argon atmosphere, to prevent oxidation. After 20 min the rotors were stopped and the total sample was removed.

### Copolymer identification and characterization

The EVA-g-PLA copolymers produced were isolated from the other components by selective extraction.

The morphology of the samples, after fracture in liquid nitrogen and gold plating, was analysed using a FEI Quanta 400 Scanning Electron Microscope.

Gel permeation chromatography (GPC) of the samples dissolved in  $\text{CHCl}_3$ , using a Waters 150-CV chromatographer, was performed to characterize the molar mass, (number average molecular weight ( $M_n$ ), and the weight average molecular weight ( $M_w$ )).

X-ray analysis were carried out in an automatic diffractometer, Philips Analytical X-ray PW 1710 BASED, using  $k\alpha$  radiation of a copper ampoule ( $I=1.54056 \text{ \AA}$ ), operating at a cathode current of about 30 mA and a voltage around 40KV. The diffractograms were obtained between 0° and 60° (2 $\theta$ ) with a scanning speed of 2 $\theta \text{ min}^{-1}$ . The standard calibration was made using a silicon standard. The samples, in form of film form were placed in an aluminium samples holder.

Oscillatory rheological measurements of initial polymers and produced samples were carried out in a AR - G2 rotational rheometer at 160 °C using a parallel-plate geometry. The gap and diameter of the plates were 1 mm and 2.5 cm, respectively. A frequency sweep from 0.01 to 100 Hz under constant strain was performed for each sample. The tests were performed in triplicate.

Biodegradability of the materials was evaluated using the biochemical oxygen demand method (BOD). The only available carbon source for microorganisms in the prepared middle is present in the polymeric material. The biodegradation extent was also evaluate by GPC and FTIR.

## RESULTS AND DISCUSSION

Table 2 shows the amount of copolymer extracted from each prepared sample. As expected, the amount of each polymer extracted without catalyst (EVAPLA0) is the same as the amount of each polymer used initially and



the amount of copolymer is zero. In other cases, three different fractions were obtained: fraction 1 and 2, corresponds to PLA and EVA, respectively, and fraction 3 to the copolymer (EVA-g-PLA) formed during reaction. All fractions were analysed by NMR to get information on its composition. The spectra obtained for fractions 1 and 2 confirmed that only PLA and EVA were extracted. EVAPLA1 exhibit the highest amount of copolymer around 25 wt. %, followed by EVAPLA2, EVAPLA3 and finally EVAPLA4. The amount of copolymer obtained for EVAPLA1 is higher than in other samples, which indicates that the extent of grafting reaction was higher in this case. This difference could be related with the amount of catalyst used for the synthesis of each copolymer, which was higher in this case.

Table 2: Amount of each fractions extracted

Sample	Fraction 1 (wt.%)	Fraction 2 (wt.%)	Fraction 3 (wt.%)
EVAPLA0	40.0	60.0	-
EVAPLA1	20.0	55.0	25.0
EVAPLA2	34.0	29.0	8.0
EVAPLA3	41.0	57.0	2.0
EVAPLA4	39.0	59.0	2.0

Figure 1 shows an example of the morphology of the samples. While the presence of two phases and bad adhesion is clear in Figure 1a (sample without catalyst), very small particles are detected for the samples containing the higher amount of copolymer. The difference can be explained by the presence of copolymer at the interface, which acts as a compatibilizer.

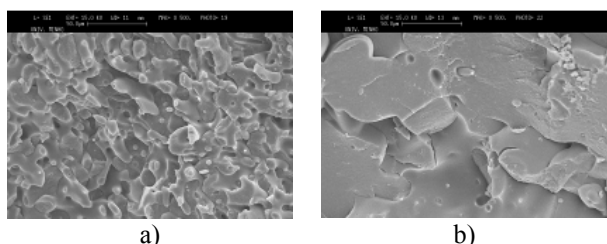


Figure 1: SEM micrographs of a) sample EVAPLA0 and b) sample EVAPLA1.

As shown in Figure 2, the reaction extent was followed by the molecular weight. GPC curves of samples differ in magnitude and elution time. It is possible to verify that the molar mass increases as the amount of catalyst increases. For EVAPLA1 and EVAPLA2, the chromatograms are different from the others, which exhibit two peaks. For EVAPLA3 and EVAPLA4 only a single peak is detected and the chromatograms are very similar to the one obtained for the physical blend. The difference between the samples can be explained

by the presence of a significant amount of copolymer formed.

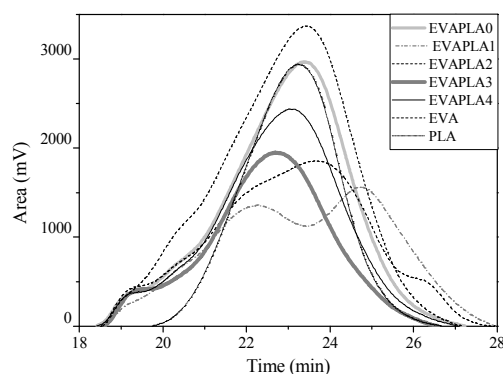


Figure 2: Chromatograms of EVA, PLA and prepared samples.

The X-ray diffraction spectra of all samples are present in Figure 3. The EVAPLA0 sample has sharp diffraction peaks at 21.35° and a few small peaks around 23.6°. EVAPLA4 shows similar peaks as EVAPLA0, suggesting similar structure. Even though new peaks were not detected for EVAPLA3, a shift to lower angles occurred. Samples EVAPLA1 and EVAPLA2 exhibit the peaks of EVAPLA0 and a new peak at 15°. This result suggests that the copolymer formed has a different structure.

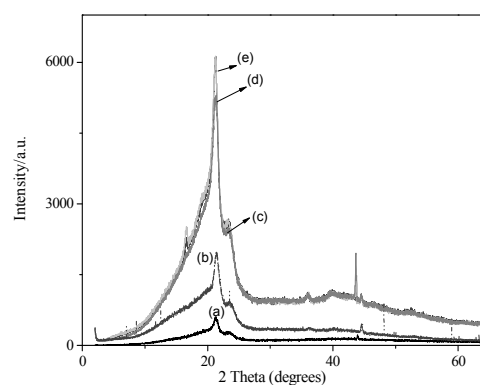


Figure 3: XRD spectra of EVAPLA0 (a) (b) EVAPLA4 (c) EVAPLA3 (d) EVAPLA1 and (e) EVAPLA2

To investigate the influence of prepared samples structure on the rheological behaviour, oscillatory rheological measurements were carried out. The complex viscosity results obtained from the initial polymers and prepared materials are depicted in Figure 4. Despite all samples shown a non-Newtonian behaviour, significant differences exist among them. The material prepared without catalyst has lower complex viscosity than those with catalyst. When  $Ti(OPr)_4$  was used, the complex viscosity at low



frequencies, shifts for high values. This is due to the presence of copolymer formed. The complex viscosity increases as the amount of copolymer increases, EVAPLA1 exhibits the higher viscosity. These results are in agreement with the extractions results.

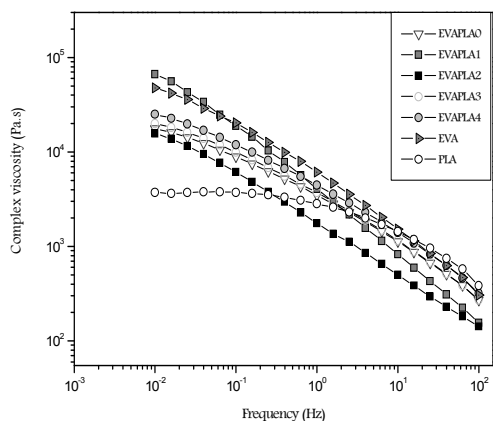


Figure 4: Complex viscosity of initial polymers and prepared samples.

This since formed copolymer results from the transesterification reaction of ester groups of EVA and PLA it is a grafted copolymer, with has a more complex structure than the initial linear polymers. Therefore an increase of viscosity is expected as the amount of copolymer increases.

The biodegradability of the synthesized materials and initial polymers was characterized by the biochemical oxygen demand (BOD) method using a closed respirometer (ISO 14851, 1999). The results obtained during 60 days of biodegradation are depicted in Figure 5. Among all samples polymers, EVA showed the lowest degree of biodegradability (8.9%) and PLA the highest (52.9%). Adding PLA to EVA (EVAPLA0) increased the biodegradability (10.7%) of EVA. Even better biodegradability results were obtained when grafted copolymers were presented, namely for EVAPLA1 (24.2%). The increase in biodegradability of samples containing the grafted copolymers can be due to the copolymer structure, which favors the formation of amorphous zones, increasing the microbial accessibility. The extent of biodegradation of initial polymers and samples was evaluated by FTIR spectroscopy. The spectra obtained before and after biodegradation tests are presented in Figure 6. Each figure contains two spectra, one before and other after biodegradation test. As expected, in the case of EVA (Figure 6a) no significant changes can be detected in the spectra, since EVA is not a biodegradable polymer.

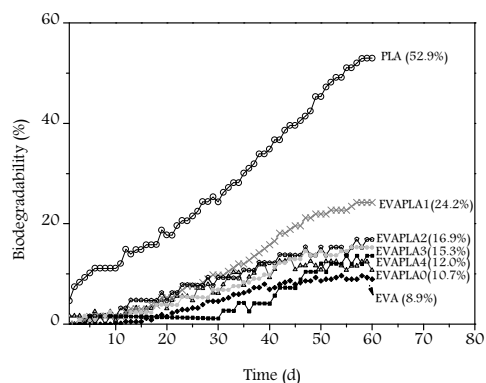


Figure 5: Biodegradability of the initial polymers and samples according to ISO 14851(1999)

The major changes occurred for PLA (Figure 6b), the transmittance data on a common scale shows that all peaks decreased in size after biodegradation. The reduction in the CH-asymmetric and CH-symmetric stretches at  $2920\text{ cm}^{-1}$  and  $2850\text{ cm}^{-1}$ , respectively, indicated a reduction in the molecular weight of the PLA. The decrease of peaks related to carbonyls ( $1800\text{ cm}^{-1}$  and  $1700\text{ cm}^{-1}$ ) and ethers ( $1100\text{ cm}^{-1}$ ) indicated chain scission. A reduction of the peak at  $1460\text{ cm}^{-1}$  was associated with decrease of  $\text{CH}_3$  side groups. In the case of EVAPLA1 (Figure 6 c)) a decrease of the intensity of all peaks can be observed, which is in agreement with the BOD results. The spectrum of all copolymers show a decreased in the intensity of all peaks (C-H, C=O, C-O), which can be explained by carbon consumption by the micro organisms.

Since the FTIR results indicate a decrease of molar mass, GPC measurements were also performed. The molecular weight results of the samples before and after biodegradation, presented in Figure 7, confirmed that changes of molar mass occurred during biodegradation. PLA and EVAPLA1 exhibit the bigger differences, in accordance with FTIR spectra. Moreover, the molecular weight distribution shifted to the right side (data not shown) confirming that scission of the main chain occurred and smaller molecules were formed.

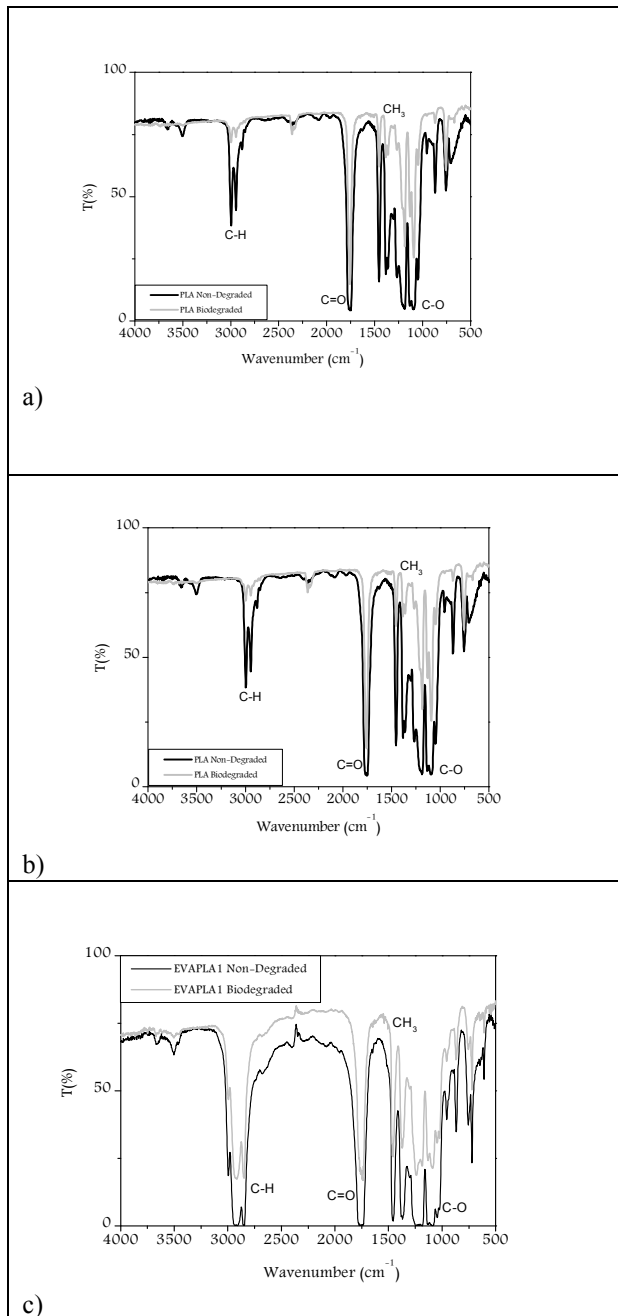


Figure 6: FTIR spectra of undegraded (black line) and biodegraded (gray line) blends: a) EVA b) PLA c) EVAPLA1.

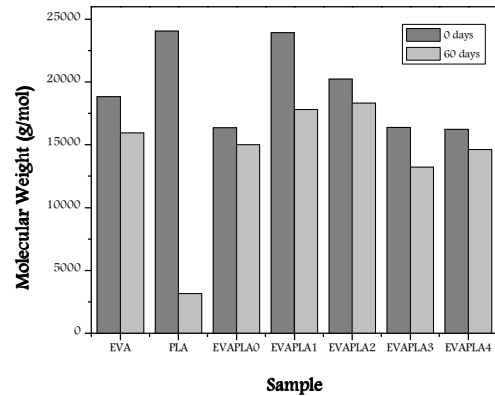


Figure 7: Molecular weight of the samples before and after biodegradation.

## CONCLUSIONS

The amount of copolymer increased as the amount of amount of catalyst increase. Biodegradability results, showed that PLA is more biodegradable than EVA based on biochemical oxygen demand (ISO 14851:1999). Differences in biodegradability behaviour were observed among the prepared samples. Moreover, EVAPLA1 was the more biodegradable one. The qualitative and quantitative results obtained by FTIR and GPC corroborate the results obtained by the standard biodegradability test. The results obtained showed that this synthesis method is a promising route to produce biobased materials that could be used in technological applications.

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