Synthesis of Biodegradable Copolymers based on Ethylene Vinyl Acetate and Polylactic Acid

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Abstract

In the present study biodegradable copolymers of ethylene vinyl acetate and polylactic acid were synthesized using transesterification reactions, the structure, morphology, mechanical properties and biodegradability of the produced materials were characterized. Ethylene vinyl acetate was modified with polylactic acid in an internal mixer using titanium propoxide as transesterification catalyst. The graft copolymers were characterized by elemental analysis, infrared spectroscopy, rheology, scanning electron microscopy and thermal analysis. Selective extractions for all copolymers 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. This procedure allowed to synthesize biodegradable copolymers with mechanical properties similar to conventional polymers.

Introduction

In recent years, concern has increased on the deterioration of our environment due to solid waste pollution [1]. One way to solve this problem is by replacing commodity synthetic polymers by biodegradable polymers. Any marketable plastic product must meet the performance requirements of its intended function, therefore natural biodegradable plastics are blended with synthetic polymers to produce plastics which meet these functional requirements.

Ethylene vinyl acetate (EVA) copolymers have a broad range of industrial applications [2], such as packaging, adhesives, wire, cable and health care. In packaging, EVA copolymers are used as heat seal layers for snacks and cheese, and bags for ice, frozen food and agricultural materials. The range of EVA applications has widened considerably reflecting an appreciation for the versatility of the material.

Aliphatic polyesters are one of the most promising biodegradable materials because they are readily susceptible to biological attack [3]. Aliphatic polyester, produced from renewable resources has received much attention in the research of alternative biodegradable polymers [4, 5]. An example is polylactic acid (PLA) which can be extracted from the fermentation of crop like corn starch and sugar feed stocks [6]. Moreover PLA production consumes carbon dioxide, providing significant energy savings and it is recyclable and compostable [7].

Blending is an important approach to develop new polymer materials and have been used to produce biodegradable polymers with enhanced properties. The compatibility of the blend components has a great influence on their performances, such as, the phase structure and physical properties in practical use. Miscibility is essentially the ability to form a homogeneous system of two or more polymers. Biodegradability of polymer blends is mainly determined not only by the biodegradability of the blend components but also by the blend composition, phase structure (miscibility and crystallinity), surface blend composition, molecular structure and the length of the polymer chain [8, 9].

A different and more efficient way to produce biodegradable materials is by the synthesis of copolymers based on a non-biodegradable and a biodegradable polymer, respectively. The present work aims to prepare biodegradable polymeric materials based on copolymers of a nonbiodegradable and a biodegradable polymer. Thus, copolymers of ethylene vinyl acetate, and polylactic acid were prepared in a batch mixer. Characterization of the copolymer formation was performed using several analytical techniques, such as, SEM and rheology.

Experimental

Materials. Ethylene vinyl acetate (EVA) with 28%(28%VA) of vinyl acetate (Escorene Ultra Lot. 61E466) supplied from Exxon was used as a non-biodegrable polymer and polylactic acid (PLA) ($M_w = 22000$ g/mol) supplied by Aldrich was used as a biodegradable polyester. Titanium propoxide ($Ti(OPr)_4$) was used as transesterification catalyst. The amount of EVA was kept constant and the relative amount of catalyst and PLA was changed in order to synthesize copolymers with different structure. The composition of each sample is shown in Table 1.

Table 1 - Sample composition

Sample	EVA	PLA	Ti $(OPr)_4$
EVAPLA0	60.0	40.0	0.0
EVAPLA1	59.5	38.6	1.9
EVAPLA2	59.5	42.0	0.7

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 the EVA pellets were introduced into the hot mixer, after melting, PLA and catalyst were added. Titanium propoxide was collected and carried to the mixer inside the syringe in an argon atmosphere, to prevent hydrolysis. After 5 min , when a constant torque was reached, the rotors were stopped and the total sample was removed.

Extractions of homopolymer

The amount of the homopolymers, mixed with the graft copolymers synthesised, was extracted by solvent extraction. First, solubility tests showed that EVA was soluble in hot toluene, but insoluble in acetone. PLA was soluble in acetone at room temperature but insoluble in hot toluene. Thus, two grams of each sample were added to 160 mL acetone and stirred at room temperature for 5 days, approximately. Then, this suspension was filtered and the clear solution was precipitated in methanol, the resulting precipitate was dried until constant weight. This product is referred as fraction 1. The insoluble fraction of the first filtration was extracted in hot toluene during 3 days. The solution obtained was evaporated and dried. The fraction obtained is referred as fraction 2. The residue of this second extraction was washed with methanol and subsequently dried. This residue composes the third fraction, which is the copolymer. Without catalyst, the residual fraction is null, as expected. For EVAPLA1 and EVAPLA2, the amount of copolymer formed during the reaction is approximately 25% and 2.0%, respectively (See Table 2).

Table 2-Percentage weight of different fractions

Sample	Fraction 1	Fraction 2	Fraction 3
EVAPLA0	40	60	-

EVAPLA1	20	55	25
EVAPLA2	41	57	2

Material characterization.

Polymer synthesis. The synthesis of the block copolymer was accomplished through a reaction using titanium propoxide as catalyst. The formation of the copolymers occurs according to the following mechanism [10]: Copolymer

FTIR. FTIR measurements of the produced materials were recorded in the range of $4000 - 500\ cm^{-1}$, using 16 scans with a resolution of $4\ cm^{-1}$ (Perkin Elmer 1720 spectrometer). Thin films of the materials were obtained by compressing-moulding and directly analyzed using a solid film support.
Rheological Properties. The rheological behaviour of blend and of graft copolymers were measured using a AR - G2 rheometer on which a 40 mm diameter parallel plate was mounted. The experiments were performed at $160°C$, frequency range was set a $0.01 \sim 100\ Hz$, the applied strain and the plate gap was set a 10 and 1 mm , respectively. The tests were performed in duplicate for each sample.
Morphology. EVAPLA blend and copolymers were fractured in liquid nitrogen and then gold plating, the morphology was analysed using a FEI Quanta 400 Scanning Electron Microscope.
Elemental Analysis. The composition of all samples was determined by elementary analysis on a LECO CHNS-932. The samples' chemical formulas, calculated with C, H and O mass fractions of C, H and O , are shown in Table 3.

Table 3 - Elemental analysis of all samples.

Sample	Carbon (%)	Hydrogen (%)	Oxygen (%)	Chemical formula
EVAPLA	66.7	9.5	23.9	C_4H_6O
EVAPLA1	69.1	10.0	20.9	C_4H_8O
EVAPLA2	67.6	9.7	22.7	C_4H_7O

Biodegradability. The Oxitop method allows determining the biochemical oxygen demand (BOD) in a closed respirometer. The bottles were hermetically closed by a manometric head which allow following the pressure evolution inside the bottle. The extent of biodegradation was quantified as the pressure drop and was converted to the oxygen consumption daily during the essay. Essays were carried out in 510 mL bottles contained the polymer, 2 mL of inoculum, 50 mL of mineral medium. The source of the test organisms is activated sludge freshly sampled from a well-operated municipal-sewage treatment. For each test, blank test with microbial inoculum and without samples were also performed for checking the micro-organisms activity. These values were subtracted from the measured values to obtain exact values of the degradation activity. BOD in the bottles for the blank values was due the endogenous oxidation activity of the micro organisms of the inoculum and took place without any addition of biodegradable carbon

source. In biodegradation tests it was essential to determine this endogenous activity and to correct BOD measured from the test assays with test substance by subtracting the blank values.

Polymers in powder form at a concentration of 1250 ppm were immersed into each medium; the polymer was the sole carbon source presented in the middle. Test bottles were incubated at 30°C in darkness and regularly stirred. Samples were tested in triplicate.

The amount of O_2 consumed in polymer's biodegradation (after correction with the blank test) was expressed as mg. $L^{-1}O_2$ per mg of carbon, presented in the monomer. To normalize the BOD it is necessary determine the elemental composition of the monomer. The mg of carbon in the polymer $C_cH_hO_o$, with a relative molecular mass M_r, was calculated according to:

$$\mathrm{mg(C)} = \frac{12.011}{M_r\ (\mathrm{monomer})}\ (n°C * 62.5) \qquad (1)$$

Results and Discussion

The results obtained from the selective extraction (Table 2) indicate that the amount of copolymer formed for EVAPLA was null, which would be expected since it was prepared without catalyst. When catalyst was used a small amount of copolymer was obtained and the amount increased significantly as the amount of catalyst increased.

In the FTIR spectra for all samples no new band has appeared. The similarity between the spectra of copolymers and blend is obvious at the first glance, which is not surprising since new groups are not formed in the grafting reaction, because the product reaction is an ester resulting from the transesterification between ester groups from PLA and EVA, catalyzed by titanium propoxide. Thus, this technique did not allow to confirme that copolymers were obtained. Figure 1 shows the rheological behaviour of the synthesized materials (complex viscosity and storage modulus). All show a non-Newtonian behaviour; at low frequencies it can be observed that the viscosity of the copolymers is higher than the viscosity of the blend (EVAPLA). The sample EVAPLA1 presents the higher viscosity, followed by EVAPLA2. The increase of viscosity at low frequencies can be explained by the presence and amount of the grafted copolymers, which is in agreement with the extraction data

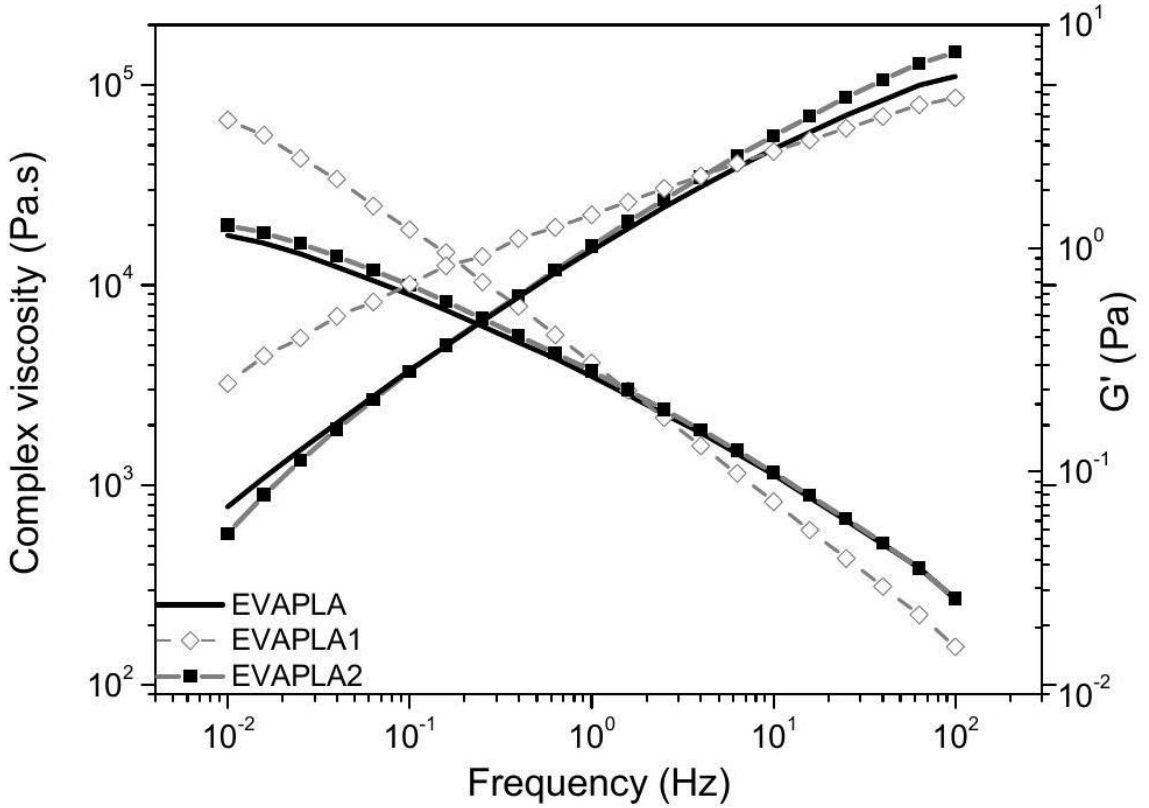
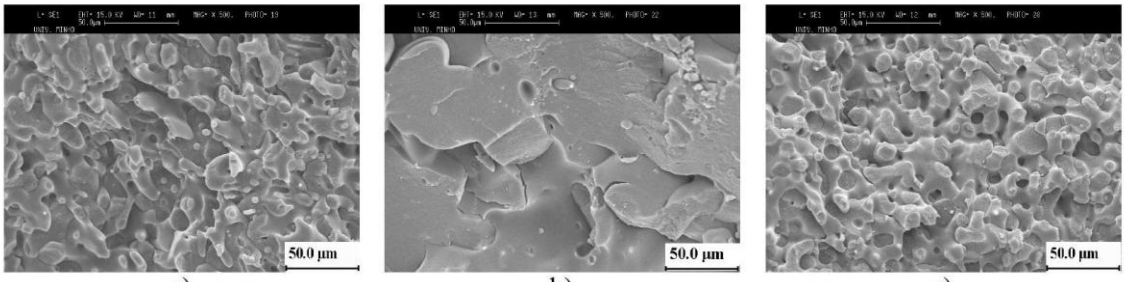


Fig. 1 - Complex viscosity and storage modulus versus frequency for all samples. When compared to the other samples, the sample with EVAPLA1 shows higher viscosity and higher storage modulus at low frequencies. This behaviour can be explained by the formation of EVA-g-PLA copolymer and its amount. According to the reaction synthesis the copolymer results from the reaction between ester groups of the two polymer chains, thus the formed copolymer can have one or several links between the two polymer chains. As a consequence the formed copolymer will behave as a branch/crosslinking structure which results in higher complex viscosity and elasticity at low frequencies.

The morphology of the EVAPLA blend (Fig. 2a) and graft copolymers (Figures 2b) and 2c) presented in Figure 2 are in agreement with extractions and rheological behaviour. As it was observed before significant differences exist among the samples. When $Ti(OPr)_4$ was added to the blend, the complex viscosity at low frequencies, shifts for high values. This effect was more pronounced when increases the amount of catalyst. This result seems to be attributed to the branch/crosslinked structure formed, as mentioned above, and consequently the particles size reduces significantly. This is due to the formation of the graft copolymer from EVA and PLA blend components, which acts as a compatibilizer decreasing the particle size.

In Fig. 2a it is possible to observe that the adhesion between PLA and EVA is not good, SEM micrograph of EVAPLA without catalyst shows a coarse morphology. A poor adhesion can be observed in the EVAPLA sample (Fig. 2a) and it is possible to detect droplets of polylactic acid in the EVA matrix. This fact can be related with the weak interactions between blend components, However, the morphology changed when catalyst was added, namely for sample EVAPLA1. An increase in $Ti(OPr)_4$, improves compatibility,

i.e., more regular and fine dispersion.



a) b) c)

Fig. 2 - SEM micrographs of the blend a) EVAPLA and copolymers b) EVAPLA1 c) EVAPLA2.

The normalized biochemical oxygen demand values of the copolymers (EVAPLA1 and EVAPLA2) and blend (EVAPLA) determined in a closed respirometer (ISO 14851:1999) are presented in Table 4. These results show that pure PLA presents the highest 0_2 consumption. The faster degradation of this one compared to the samples is due the presence of EVA, which is a synthetic polymer, so microorganisms have more difficult to degrade the samples which contains not only the biodegradable polymer but also a synthetic one. As expected, a difference in biodegradability behaviour can be observed between the copolymers and EVAPLA blend. The copolymer containing higher percentage of catalyst was more biodegradable than the other containing less, but both are less biodegradable than EVAPLA.

The biodegradability tests suggest that PLA is more biodegradable than the blend and this one more biodegradable than copolymers. One possible explanation for this result could be the number of amorphous zones, because as it well known, the biodegradation occurs preferably in the amorphous region because of the higher accessibility to the microorganisms. Under this point of view, comparing the biodegradability of EVAPLA and copolymers, and according the SEM results, it is possible observe that the particles size are higher in the case of the blend, which contributes to the formation of void spaces and consequently, enhance the capability of microorganisms to break the polymers chains and increase biodegradation. Copolymers biodegradability increases with the increase of the amount of titanium propoxide. Further experiments are necessary to explain this difference.

Table 4 - Normalized biochemical oxygen demand values (after 20 d essay) expressed as mg/L of 0_2 divided by mg of polymeric C of each sample.

Sample	Normalized BOD ($mgL^{-1}mg^{-1}$)
PLA	19
EVAPLA	5
EVAPLA1	4
EVAPLA2	2

Summary

The purpose of this work was to prepare biodegradable copolymers using a non-biodegradable (ethyl vinyl acetate) and biodegradable polymers (polylactic acid), in order to obtain biodegradable copolymers. Polymers were prepared in a haake batch mixer using titanium propoxide as catalyst. The results indicate that with an increase in the amount of titanium propoxide, the viscosity of graft copolymers gradually increase. The FTIR spectra of graft copolymers did not provide strong proof of grafting, because new groups are not formed in the grafting reaction. Morphological studies of blend and copolymers also support copolymer formation, due the compatibility differences between blend components.

The biodegradability tests performed showed that EVAPLA sample is more biodegradable than correspondent copolymers. The results mentioned above suggest that blending non-biodegradable and biodegradable polymers is an effective route to produce materials with a higher compatibility and consequently better properties, keeping its biodegradability.

References

[1] S. Lee and J. Wook Lee: Rheology Journal Vol. 17 (2005), p. 71
[2] J. W. Qian, X. Wang, G. R. Ki and C. Wu: Macromolecules Vol. 30 (1997), p. 3283
[3] S.J. Huang, in: Encyclopedia of Polymer Science and Engineering Vol. 2 (1985), p. 220
[4] H. Tsuji and Y. Ikada: Journal of Applied Polymer Science Vol. 67, issue 3 (1998), p. 405
[5] G. Perego, G. D. Cella and C. Bastioli: Journal of Applied Polymer Science Vol. 59, issue 1 (1996), p. 37
[6] J. Lunt: Polymer Degradation and Stability Vol. 1-3 (1998), p. 145
[7] R.E. Drumright, P.R. Gruber, D.E. Henton: Advanced Materials Vol. 23 (2000), p. 1841
[8] Y. Tokiwa and T. Suzuki: Journal of Applied Polymer Science Vol. 2 (2003), p. 441
[9] Y. Chen, L. Tan, L. Chen, Y. Yang and X. Wang: Brazilian Journal of Chemical Engineering Vol. 2 (2008), p. 321
[10] W. Bahloul, V. Bounor-Legaré, F. Fenouillot, P. Cassagnau: Polymer Vol. 50 (2009), p. 2527