Effect of PCL and EVA Molar Mass on the Development of Sustainable Polymers

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Abstract

Biodegradable grafted copolymers, EVA-g-PCL, have been synthesized by reactive extrusion, through transesterification reaction between ethylene-vinyl acetate copolymer (EVA) and poly(ε-caprolactone) (PCL) using titanium propoxide ($Ti(OPr)_4$) as catalyst. The effect of EVA and PCL molar mass on the amount of grafted copolymer and materials properties was investigated. The prepared blends were characterized by several analytical techniques, such as, selective extractions, rheology, TGA, DSC, SEM, mechanical properties, and the biodegradability was evaluated based on biochemical oxygen demand method.

The results showed that the amount of copolymer increases as the amount of catalyst increases. Moreover, using EVA and PCL with high and low molar mass, respectively, allowed to obtain a material exhibiting properties similar to conventional polymers and higher biodegradability.

Keywords: Biodegradability, Copolymers, Morphology, Transesterification

Introduction

The use of biodegradable polymers is an alternative to conventional nonbiodegradable ones and could contribute to the solution of the environmental problem and limited petroleum resources (1,2).

Nowadays there is a growing interest in the synthesis of fully biodegradable polymers, being the more well known, due to their thermoplastic and biodegradability properties, the aliphatic polyesters (3), such as, poly(ε-caprolactone) (PCL), polylactide (PLA), and other aliphatic polyesters (4-7). Nevertheless, biodegradable polymers have some drawbacks, such as, premature degradation, unfavorable economic evaluation, and high production costs (7). Thus, to overcome this problem, it is necessary to develop new routes to enhance the properties of biodegradable polymers and reduce its cost.

An alternative can be through the synthesis of biodegradable polymers produced by the combination of fully biodegradable polymers and inexpensive conventional synthetic ones. Even though these polymers are not completely biodegradable, they have economic advantages and better properties than fully biodegradable ones. They can be prepared by polymer blending or copolymer formation during extrusion. Blending has become an attractive technique to produce new materials with a positive

effect on the mechanical properties and a relatively low cost (814). However, for thermodynamic reasons, most polymers are phase separated and require compatibilization (15). The challenge is to generate in situ with a compatibilizer, which would contribute for a fine morphology and enhanced properties (14, 16-19). This can be synthesized, during extrusion, for example by living copolymerization, chemical modification by post polymerization and also coupling between two appropriately functionalized polymer chains (20,21).

Moura et al. (22), in a previous study, investigated the synthesis of grafted copolymers of EVA/PLA and EVA/PCL by in situ polymerization of lactide (LA) and ε-caprolactone (ε CL) in the presence of molten EVA. The results showed that samples prepared by in situ polymerization with titanium phenoxide as catalyst, exhibited better mechanical performance and enhanced biodegradability than the correspondent polymer blends. Using a different approach, Moura et al. (23) also prepared grafted copolymers by transesterification reactions between EVA and PLA. It was observed that EVA reacted with PLA, by a transesterification reaction using titanium propoxide ($Ti(OPr)_4$) as catalyst, and a significant amount of copolymer was formed. This method allowed for the production of biodegradable polymers with properties similar to conventional ones.

The present work aims to prepare biodegradable polymers of EVA and PCL by transesterification reactions, also using $Ti(OPr)_4$ as catalyst and to investigate the effect of the molar mass of the initial polymers on copolymer formation and consequently on properties and biodegradability. Therefore, EVA and PCL with different molar mass were used and the ratio between

PCL and catalyst was varied. The materials were prepared in a batch mixer under constant processing conditions and then characterized using several analytical techniques, such as, selective extractions, FTIR, rheology, DSC, TGA, SEM, and mechanical tests. Biochemical oxygen demand (BOD) was carried out to evaluate the biodegradability.

Experimental Section

Materials

Two grades of ethylene-vinyl acetate copolymer (EVA28 with 28wt% of vinyl acetate [VA]) and respectively $M_n = 18.000\ g.mol^{-1}$ and $M_n = 7.900\ g.mol^{-1}$ supplied from ARKEMA were used as a nonbiodegradable synthetic polymer and poly(ε-caprolactone) (PCL) with two different molar mass ($M_n = 10.000\ g.mol^{-1}$ and $M_n = 60.000\ g.mol^{-1}$) supplied by Aldrich was used as a biodegradable polymer. Titanium propoxide ($Ti(OPr)_4$), also from Aldrich, was used as a catalyst. Table 1 shows the composition of the prepared materials.

Synthesis of EVA-g-PCL Graft Copolymers

The pellets of both polymers were dried in a vacuum oven at 60°C for 24 h before use. Samples were prepared in an internal mixer (Haake Rheocord 90; volume 50 cm^3), equipped with two rotors running in a counter-rotating way. The rotor speed was 50 rpm and the set temperature was 160°C. After 20 min of mixing, the rotors were stopped and the sample was removed. The materials were prepared using the following sequence: first EVA pellets were introduced into the hot mixer; after melting, PCL and the catalyst were added simultaneously. The catalyst was collected and carried to the internal mixer in a syringe under argon atmosphere, to prevent hydrolysis.

Materials Characterization

The synthesized EVA-g-PCL copolymers and blends were characterized by several analytical techniques described in the following section.

Table 1. Samples composition.

Sample	EVA1 [a] (wt.%)	EVA2 [b] (wt.%)	PCL1 [c] (wt.%)	PCL2 [d] (wt.%)	$Ti(OPr)_4$ (wt.%)
A1	60.0	-	40.0	-	0.0
A2	59.5	-	39.6	-	0.9
A3	59.5	-	38.6	-	1.9
B1	-	60.0	40.0	-	0.0
B2	-	59.5	39.6	-	0.9
B3	-	59.5	38.6	-	1.9
C1	-	60.0	-	40.0	0.0
C2	-	59.5	-	39.6	0.9
C3	-	59.5	-	38.6	1.9

Copolymers Extraction

The EVA-g-PCL copolymers were isolated from the homopolymers according to the method previously developed by Moura et al. (22), based on polymers solubility tests summarized in Table 2.

Structural Characterization

Rheological Properties. Oscillatory rheological measurements of original and produced polymers were carried out in an AR - G2 rotational rheometer at 160°C using a parallel-plate geometry. The gap and diameter of the plates were 1 mm and 4.0 cm , respectively. A frequency sweep from 0.01 to 100 Hz under constant strain was performed for each sample. Samples were previously prepared by compression moulding at 160°C.
TGA and DSC. All samples were analyzed using a TA Q500 Instruments thermobalance operating under a nitrogen flow atmosphere (50 mL/min). Samples were heated from 35°C to 600°C at a heating rate of 10°C/min.

The melting temperature of all samples was measured using a differential scanning calorimeter (Pyris Series - Diamond DSC). Samples were first heated from 35°C to 120°C at a heating rate of 10°C/min, cooled down to room temperature at the same rate, under nitrogen, in order to eliminate the thermal history of the material. Then, samples were heated again until 120°C was achieved.

SEM. The morphology of the samples before and after biodegradation was analyzed with a FEI Quanta 400 Scanning Electron Microscope (SEM). Samples were previously fractured in liquid nitrogen and coated with a gold thin film.
Mechanical Properties. Mechanical experiments were performed in a ZWICK apparatus using a test speed of 5 mm/min, at room temperature and relative humidity of 50%. The tests were performed on 2.5 cm × 0.8 cm rectangular samples in a longitudinal direction. At least six specimens of each sample were tested. Prior to mechanical measurements, films were prepared by compression molding using the samples that were collected from the mixer.

Biodegradability Assessment. Biodegradation tests were carried out in aqueous environment under aerobic conditions according to the standard ISO 14851:1999, which specifies a method for determining the biochemical oxygen demand (BOD) in a closed respirometer. The complete procedure is described in Moura et al. (22).

FTIR. FTIR spectra of all samples before and after biodegradation were recorded using a 4100 Jasco spectrometer in the range of $4000 - 500\ cm^{-1}$, using 16 scans and a resolution of $4\ cm^{-1}$. Thin films of the initial materials and the residues after biodegradation, were prepared by compression molding and analyzed directly using a solid film support.

Table 2. Polymers solubility.

	EVA	PCL	EVA-g-PCL
Acetone	Insoluble	Soluble	-
Toluene (Hot)	Soluble	Insoluble	-
Acetone/Toluene (Hot)	-	-	Insoluble

Elemental Analysis. The composition of all samples was determined by elementary analysis on a LECO CHNS-932. The amount of carbon, hydrogen, and oxygen was determined.

Results and Discussion

Copolymer Identification

Transesterification reactions between EVA and PCL catalyzed by $Ti(OPr)_4$ led to EVA-g-PCL formation as it is shown in Fig. 1. Therefore, the solubility of EVA and PCL was explored (see Table 2) in order to dissolve them selectively and to isolate the copolymer formed. After selective extractions, three different fractions were obtained: fraction 1 and 2, corresponding to PCL and EVA, respectively, and a third fraction corresponding to the copolymer structure (EVA-g-PCL). The first and second fractions were analyzed by ^{1} H-NMR to obtain information on its composition (data not shown) and the spectra obtained confirmed that only PCL and EVA were extracted. Unfortunately, ^{1}H-NMR analysis of EVA-g-PCL copolymer was not realized as it was not possible to reach a good solubilization in a series of organic solvents. The fraction amount of EVA-g-PCL extracted from each sample was quantified and the values are depicted in Fig. 2. As expected, for physical blends (A1, B1, and C1) the amount of copolymer formed was nil, which means that no reaction took place without catalyst. Conversely, for all other samples, copolymer was formed and its amount increases mainly with the amount of catalyst.

Furthermore, the copolymer amount obtained using EVA with different molar mass (A3 and B3) is similar, being slightly higher for the lower molar mass EVA2 (see Fig. 2, B3). This can be due to the similar and relatively low molar mass of both EVA2 and PCL1 (7.900 and 10.000 g g mol^{-1}, respectively) that are more prone to be grafted/cross-linked (24).

In a similar way, when PCL molar mass changes, the difference between the copolymer amounts obtained using higher PCL molar mass was also low. The results show that samples prepared with identical polymer molar mass have a slightly higher copolymer formation (12% versus 11%), which could be due to similar viscosity (25).

As oscillatory rheological measurements at low frequency are sensitive to molecular structure, the rheological behavior of initial polymers and prepared samples was investigated. The complex viscosity of the neat polymers and prepared materials as a function of frequency, at 160°C is shown in Fig. 3. Whereas, PCL1, PCL2, and EVA2 exhibited a Newtonian behavior, EVA1 has a non-Newtonian behavior, in the investigated frequency range (0.01 ~ 100 Hz), which can be related with their

——CH2—CH2—CH—CH2—

Fig. 1. Reaction mechanism of EVA-g-PCL copolymer formation by transesterification reaction.

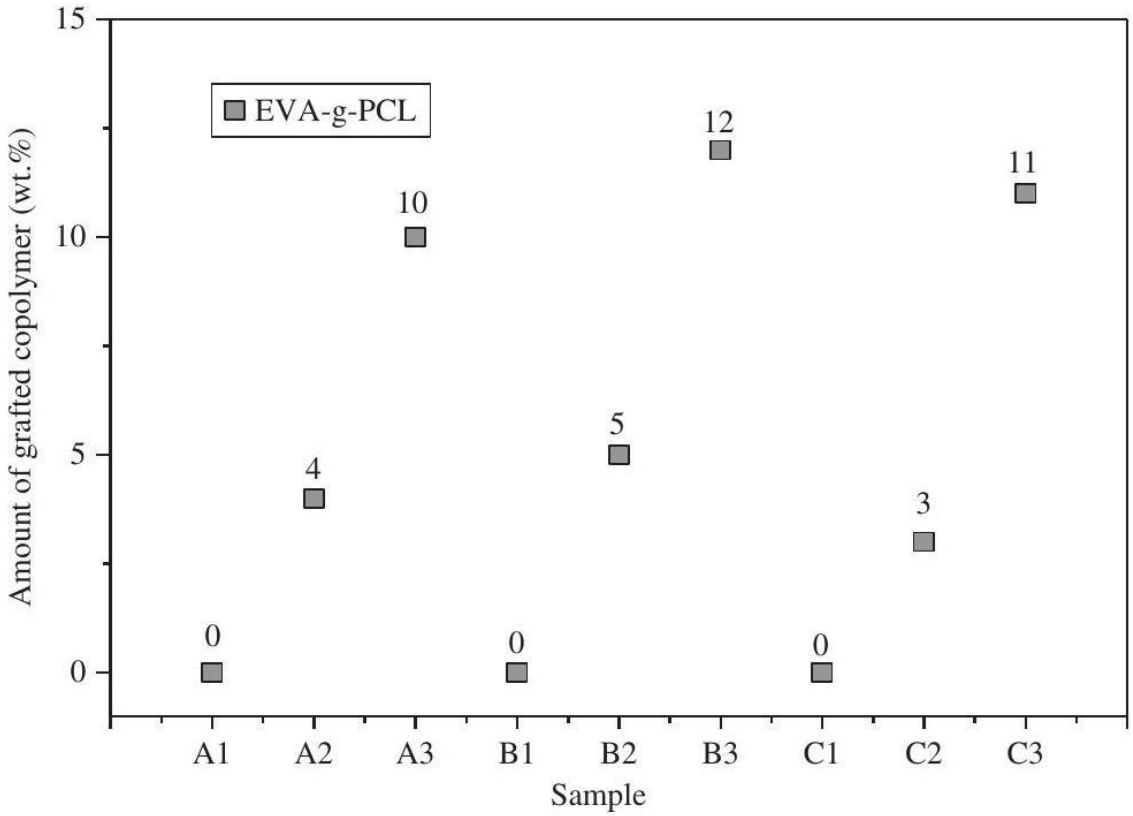


Fig. 2. Fractions amounts (wt.%) of copolymers extracted.

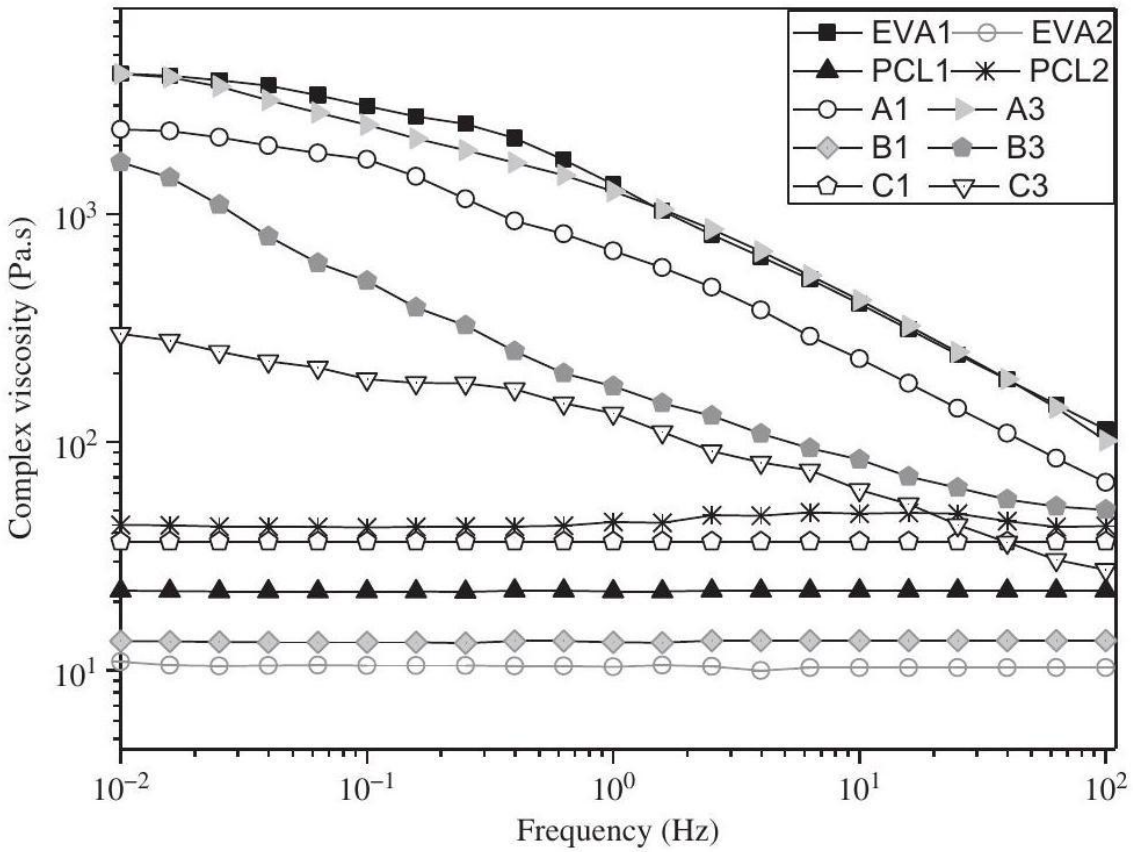


Fig. 3. Rheological behavior of the individual components and prepared materials.

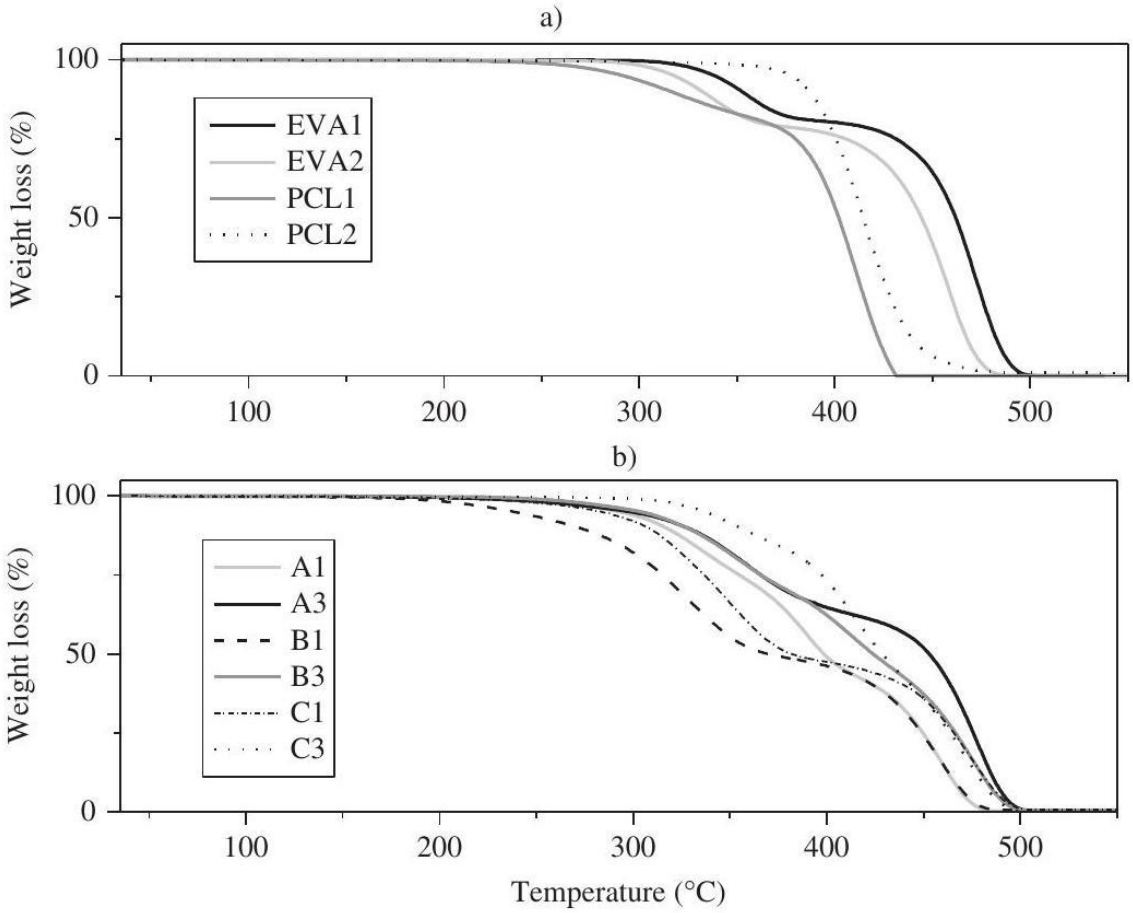


Fig. 4. Thermograms of (a) neat polymers and (b) prepared samples.

molar mass. Regarding the prepared materials, A1 shows a nonNewtonian behavior and its complex viscosity (η) is between the neat polymers. Sample A3 has higher complex viscosity than the corresponding blend A1 (1.8E3 and 2.8E3 Pa.s for A1 and A3, respectively), this difference can be associated to the amount of copolymer formed (10%).

Samples B, prepared with low molar mass polymers (both EVA and PCL), exhibited a different behavior. While B1 has a very low complex viscosity (1.3E1 Pa.s) and a Newtonian behavior, B3 shows higher viscosity (4.3E2 Pa. s) and a shear thinning behavior, mainly at low frequencies. The differences observed are due to the significant amount of copolymer (12%)

formed in sample B3 and its molecular structure. Samples C1 and C3 show similar behavior has B1 and B3, C1 has lower viscosity (3.7E1 Pa.s) and an intermediate behavior between neat polymers, that is, shear thinning was also not noticed. Conversely, the sample containing higher copolymer amount (C3) has higher viscosity (3.0E2 Pa.s) and shear thinning behavior namely at low frequencies.

Fig. 4a depicts the thermal behavior (weight loss) of the different EVA, PCL, and Fig. 4b of the prepared samples. EVA1 exhibits a first mass lost (18.8%) at around 304°C, which can be attributed to the decomposition of the acetate groups due to the release of acetic acid (26). At approximately 382°C, a

second weight lost (81.2%) can be noticed, corresponding to the degradation of the

olefinic part of the copolymer (C-C and C-H bonds). Similar decomposition mechanism can be observed for EVA2, except a shift of the initial decomposition temperature toward lower temperature, which can be attributed to its lower molar mass. Actually, EVA2 exhibits a first mass lost (20.5%) at around 299°C and a second weight lost (79.4%) at approximately 375°C.

Both PCLs present a similar behavior with only one-step decomposition profile. The higher thermal stability of PCL2 is due to its higher molar mass. Comparing PCLs to both EVAs, the former exhibits lower thermal stability. They are completely decomposed (0% residue) at 432°C and 473°C, respectively, for PCL1 and PCL2 (Fig. 4a). This indicates different degradation mechanisms due to structural difference between the two polymers, EVA and PCL.

Figure 4 b shows that the samples containing copolymers (A3, B3, and C3) exhibit higher thermal stability than the corresponding physical blend, but the relative position is different. Sample C3 presents the higher initial thermal stability, first onset temperature around 320°C, followed by samples B3 and A3 (261°C and 257°C, respectively). This behavior can be explained both by the copolymer amount formed and the thermal stability of the initial polymer. Sample B1 presents the lowest thermal stability due to the lower thermal stability of the initial polymers and to the absence of any copolymer.

Morphology and Physical Properties

Figure 5 depicts the morphology of the various samples analyzed by SEM after fracture in liquid nitrogen. The morphology of the physical blends (Fig. 5a-c) consists in PCL particles dispersed in an EVA matrix. Even though the micrographs of Fig. 5b and 5c have lower magnification (500 ×) than the one presented in Fig. 5a (200 ×), it is clear that the size of the PCL dispersed phase decreases from A1 to B1 and even more for C1. This difference can be associated with the polymers viscosity. As the EVA molar mass decreases between samples A1 and B1, the compatibility increases. As expected, the size

Table 3. Melting temperature (T_m, °C) of neat polymers and prepared samples.

Sample	T_m (°C)
EVA1	78.4
EVA2	72.9
PCL1	55.3
PCL2	59.4
A1	57.8
A2	54.7
A3	50.6
B1	55.3
B2	57.2

B3	53.4
C1	63.7
C2	55.9
C3	55.0

of the PCL dispersed phase becomes smaller as the amount of copolymer increases, being almost undetectable for A3, B3, and C3 (magnification of 200 ×). The decrease in particle size is associated to the copolymer formed, which has a compatibilization effect, reducing the interfacial tension between blend components and, therefore, the size of the dispersed phase. Additionally, the compatibility of EVA/PCL samples due to the presence of copolymer, the effect of EVA molar mass is also noticeable. Comparing SEM micrographs of A3 and B3, it can be perceived that the compatibility increases with decreasing EVA molar mass.

Table 3 and Fig. 6 display the melting temperature (Tm) and melting temperature as function of amount of grafted copolymer, respectively, obtained from DSC measurements for neat polymers and prepared samples. From Table 3, sample A1 has a value between the initial polymers. Owing to the immiscibility, confirmed by SEM between EVA1 and PCL1, it would be expected that both polymers kept their thermal properties. Nevertheless, DSC curves show only on peak, which can be

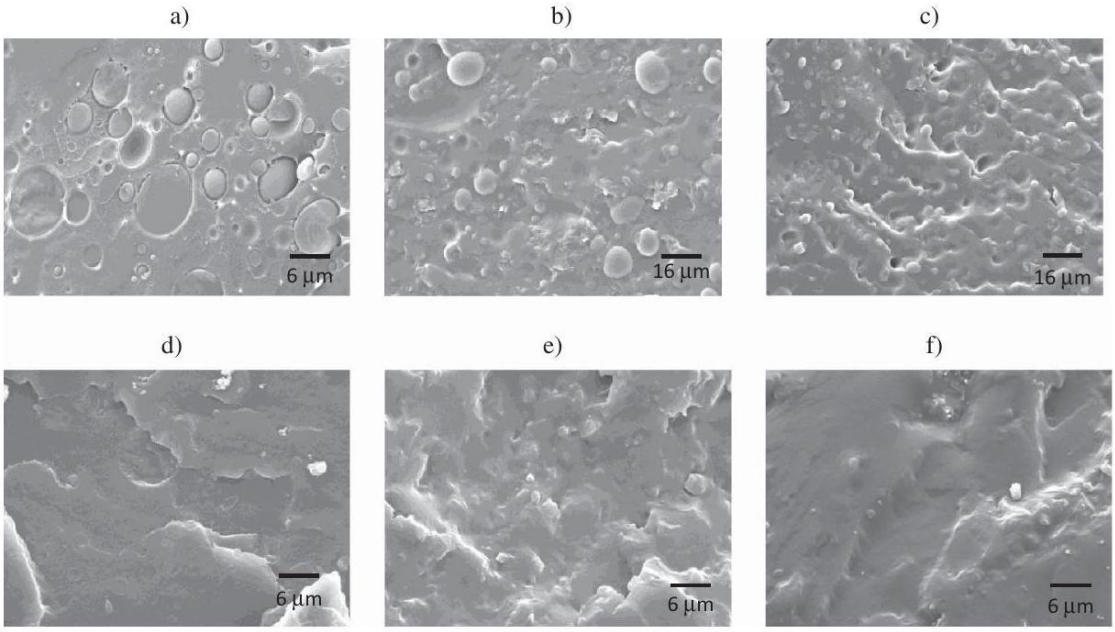


Fig. 5. SEM micrographs of samples (a) A1; (b) B1; (c) C1; (d) A3; (e) B3; and (f) C3.

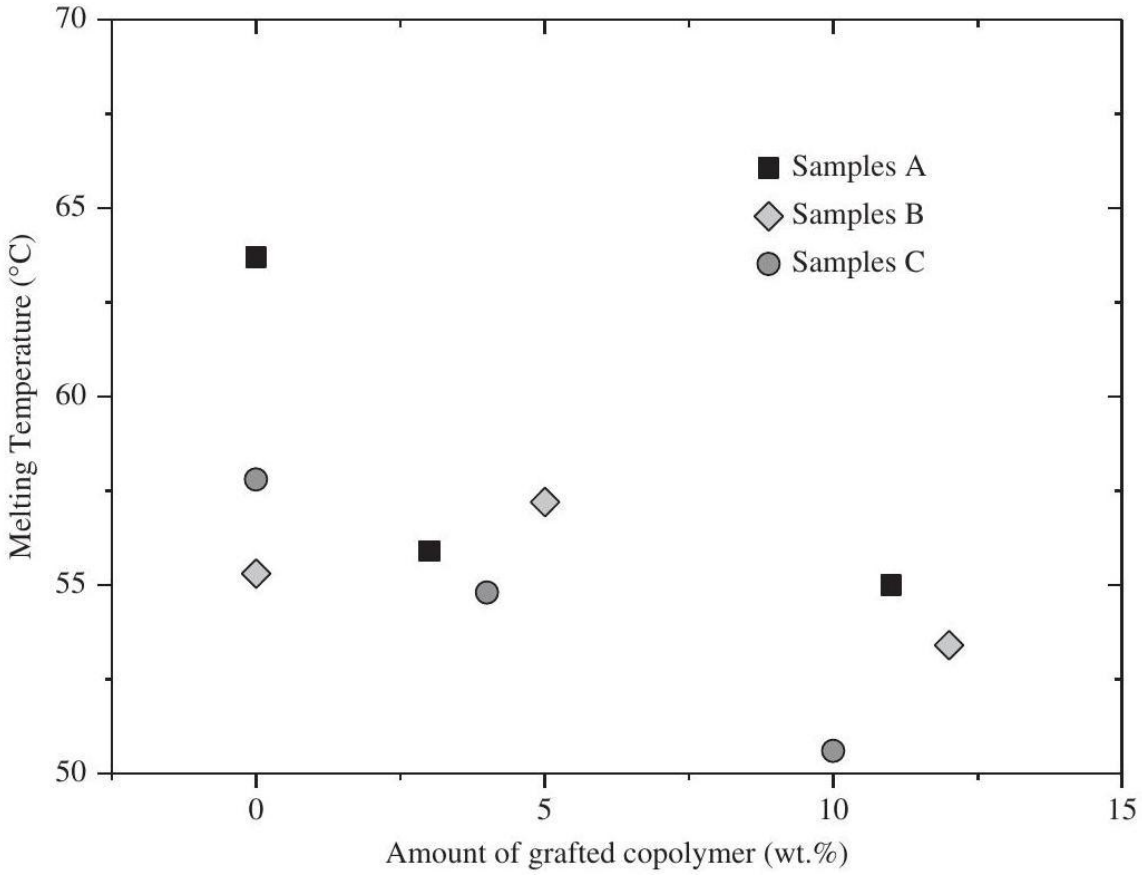


Fig. 6. Melting temperature as function of amount of grafted copolymer.

due to similar melting temperature of neat polymers. Figure 6 shows that the melting temperature of the samples (A2 and A3) decreases as the amount of copolymer increases. This can be associated with increase in compatibility as the copolymer amount increases, which is supported by the SEM analysis. Moreover, the covalent bonds between PCL/EVA segments, leads to a lower regularity of the molecular structure.

Changing EVA1 by EVA2, the melting temperature of B1 is similar to neat PCL1. Even though the melting temperature decreases as the copolymer amount increases (53.4°C for B 3), the difference is not as high as it was observed for samples A (Fig. 6).

Changing PCL1 by PCL2, the melting temperature obtained for C 1 , physical blend, is higher (63.7°C). Sample C 3 presents considerable changes (55.0°C), which can be explained by the SEM results (Fig. 5f), in this case it is hard to identify two phases.

All the results evidence that the presence of copolymer promotes a decrease of the melting temperature. Similar results were obtained by Jiang et al. (27), whom synthesized graft copolymer of PCL and EVOH. They attributed the decrease of the melting temperature to the more complex architecture of the copolymer and the relatively low molar mass of PCL side chains.

The results of tensile strength (σ) as a function elongation at break (ε) of both EVA and prepared samples are depicted in Fig. 7. The results for PCL1 and PCL2 are not shown, because PCL1, under the conditions used to test the samples, was very brittle. As it can be noted, blending PCL1 and EVA1 (Fig. 7a) results in a material that has lower tensile

strength and lower elongation at break than EVA1. As expected, the worst properties were observed for sample A1. For samples A2 and A3, both tensile strength (2.5 and 2.9 MPa for A 2 and A 3 , respectively) and elongation at break (171 and 409%) increase as the amount of copolymer increases. The elongation at break of sample A3 is similar to EVA1 (380%). This improvement can be
explained by the presence of copolymer at the interface, which decreases the interfacial tension and improves the compatibility effect as observed by SEM results, the size of PCL dispersed phase decreasing significantly from A1 to A3.

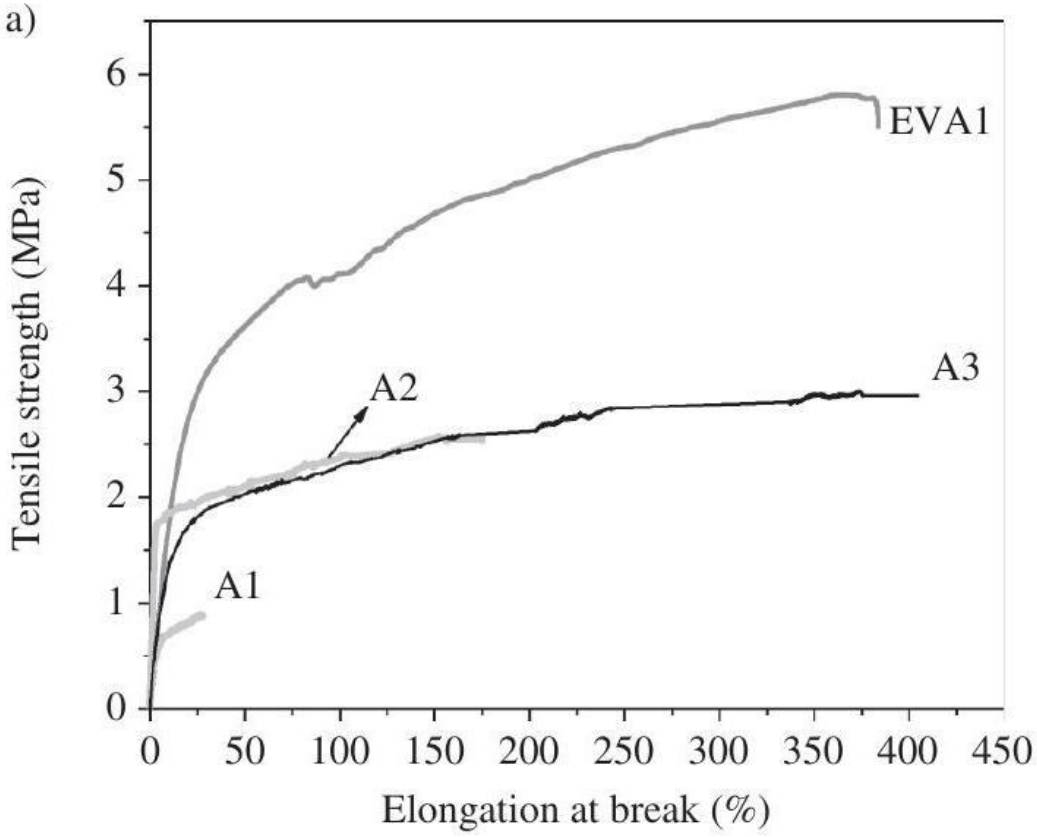
Blending EVA2 with either PCL1 or PCL2, results in materials with enhanced tensile strength, as it can be seen in Fig. 7b and 7c. As it was observed previously, both tensile strength and elongation at break increases with the amount of copolymer (samples B2, B3, C2, and C3). EVA2 has a tensile strength of 1.2 MPa and samples B2 and B3 values of 1.3 MPa and 1.4 MPa , respectively. Thus, sample B3 is more rigid and has the higher elongation at break (61%).

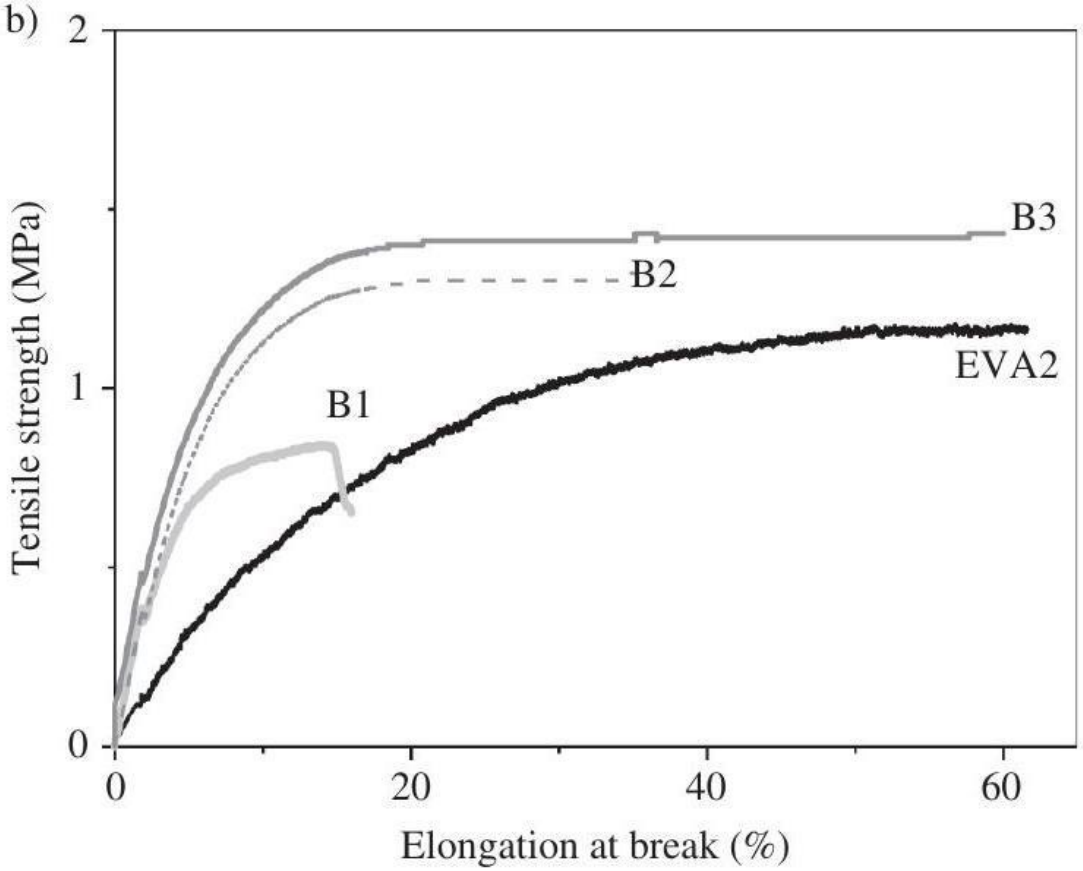
Although, changing PCL1 by PCL2, the tensile strength of sample C3 is higher than for EVA2, which can be explained by both PCL2 (21.3 MPa) tensile strength and the amount of copolymer obtained (11%). Also, its elongation at break (58%) becomes similar to EVA2, which is a good result, as PCL2 has a very low elongation break (9.2%).

The differences in tensile properties of all prepared samples by transesterification reactions can be related with the molar mass of the initial polymers used in their preparation and the amount and chemical structure of the copolymer formed. Likewise, enhancement of tensile properties for samples prepared with polymers that have similar molar mass would be expected, as it is well-known that the presence of compatibilizer has a positive effect in tensile properties (28).

Biodegradation

The biodegradability based on the biochemical oxygen demand (BOD) method is expressed as the amount of 0_2 consumed during biodegradation divided by their theoretical oxygen demand (ThOD), using the elemental analysis data (see Table 4) and the respective results are presented in Fig. 8. Among the neat polymers, both EVA1 and EVA2, show the lowest biodegradability and PCL1 the highest. For EVA1 and EVA2,


a)
Tensile strength (MPa)
Elongation at break (%)
EVA1
A3
A2
A1
0
1
2
3
4
5
6
0
50
100
150
200
250
300
350
400
450


b)
Tensile strength (MPa)
Elongation at break (%)
B3
B2
EVA2
B1
0
1
2
0
20
40
60


c)
5

Fig. 7. Tensile properties, at room temperature, of EVAs and prepared samples.
even though they have different molar mass values, it is clear that the effect of this parameter on EVAs biodegradation was insignificant, because the results obtained from BOD were very similar (12.8% and 13.7%, respectively), which is associated with the fact that EVA is a conventional nonbiodegradable polymer.

Degradation of aliphatic polyesters is usually related with their chemical and physical properties, such as, the surface area, hydrophilic and hydrophobic properties, molar mass, glass transition temperature and melting temperature, degree

Table 4. Elemental analysis of all samples.

Sample	Carbon (%)	Hydrogen (%)	Oxygen (%)	Chemical formula
A1	72.8	11.1	16.1	$C_6H_{10}O$
A2	73.5	11.7	14.9	$C_7H_{12}O$
A3	73.7	11.2	15.1	$C_7H_{12}O$
B1	71.5	11.2	17.3	$C_6H_{10}O$
B2	71.4	11.1	17.5	$C_5H_{10}O$
B3	71.3	11.1	17.6	$C_5H_{10}O$
C1	71.5	11.1	17.4	$C_5H_{10}O$
C2	71.3	11.2	17.5	$C_5H_{10}O$
C3	71.2	11.1	17.8	$C_5H_{10}O$

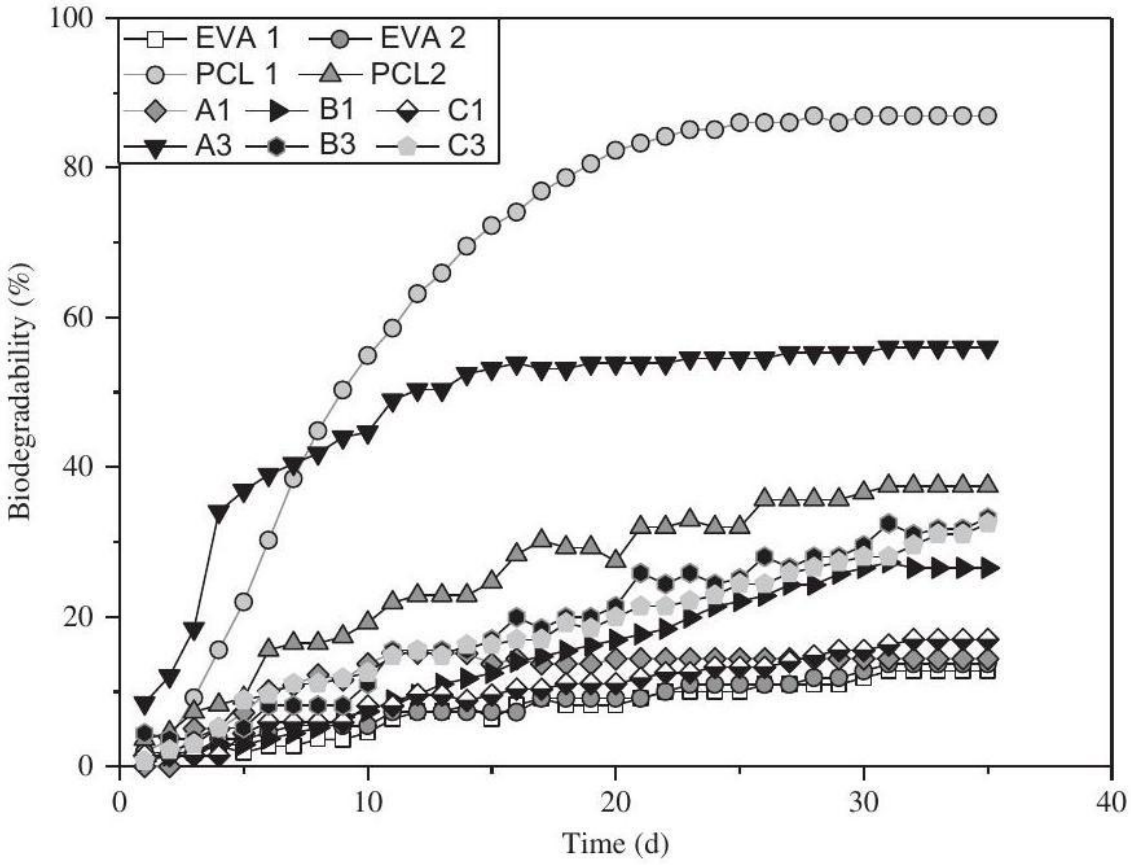


Fig. 8. Percentage of biodegradation of the copolymers and blend according to ISO 14851 (1999) (color figure available online).

of crystallinity, and chemical structure (29). Therefore, while PCL1 showed a biodegradation value around 87%, the value for PCL2 was much smaller (37%). Even though, both are aliphatic polyesters and biodegradable, PCL2 has much higher molar mass, which influences the biodegradability, as stated before. Moreover, PCL1 has a degree of crystallinity around 37.1% and PCL2 a value of 42.2% (Table 3). The degree of crystallinity plays an important role on biodegradability, as enzymes mainly attack the amorphous domains of a polymer. The molecules in the amorphous region are loosely packed, and thus more susceptible to degradation (29). Another parameter that could contribute for these biodegradation values, is the smaller melting temperature of PCL1 (55.3°C) compared to PCL2 (59.4°C).

Thus, biodegradability prediction based on physicochemical analyses of the polymers is very complex, because it depends on several parameters, as previously stated. It is difficult to compare biodegradability results obtained with different methods, using polymers with distinct molar mass. For instance, the biodegradability of PCL under composting conditions (58°C) is 4.3% and 21.6% for PCL with molar mass of 80.000 $g.mol^{-1}$ and 50.000 $g.mol^{-1}$, respectively, was considerably lower than the one obtained in the present study (30). Nevertheless, the literature values cannot be directly compared with the values obtained in the present study, once the molar mass, biodegradability methods, experimental conditions, and length of the assays were different.

However, using a method similar to the one that was used in the present study, a biodegradability of 80% was achieved for a PCL with a molar mass of 43.000 $g.mol^{-1}$ (31). Comparing this result with the one obtained with PCL1 (87.0%), allowed for the attribution of the difference to the lower molar mass (10.000 $g.mol^{-1}$) of the PCL1, which enhanced microbial attack. For PCL2, the obtained value is lower than the one achieved by Starnecker et al. (31). This result is also related with higher molar mass of PCL2 (60.000 g mol^{-1}).

Blending EVA1 or EVA2 with PCL increases the blend biodegradability, as the biodegradability of A1 (14.4%), B1 (26.4%), and C1 (16.7%) increased when compared to neat EVAs. Furthermore, the biodegradability was higher for samples containing copolymers, namely for sample A3 (55.9%), B3 (33.2%), and C3 (32.4%). The increase in biodegradability of these samples when compared to samples A1, B1, and C1, can probably be due to both the decrease of melting temperature (see Fig. 6) (32, 33), copolymer presence (Fig. 2) and blend morphology (Fig. 5).

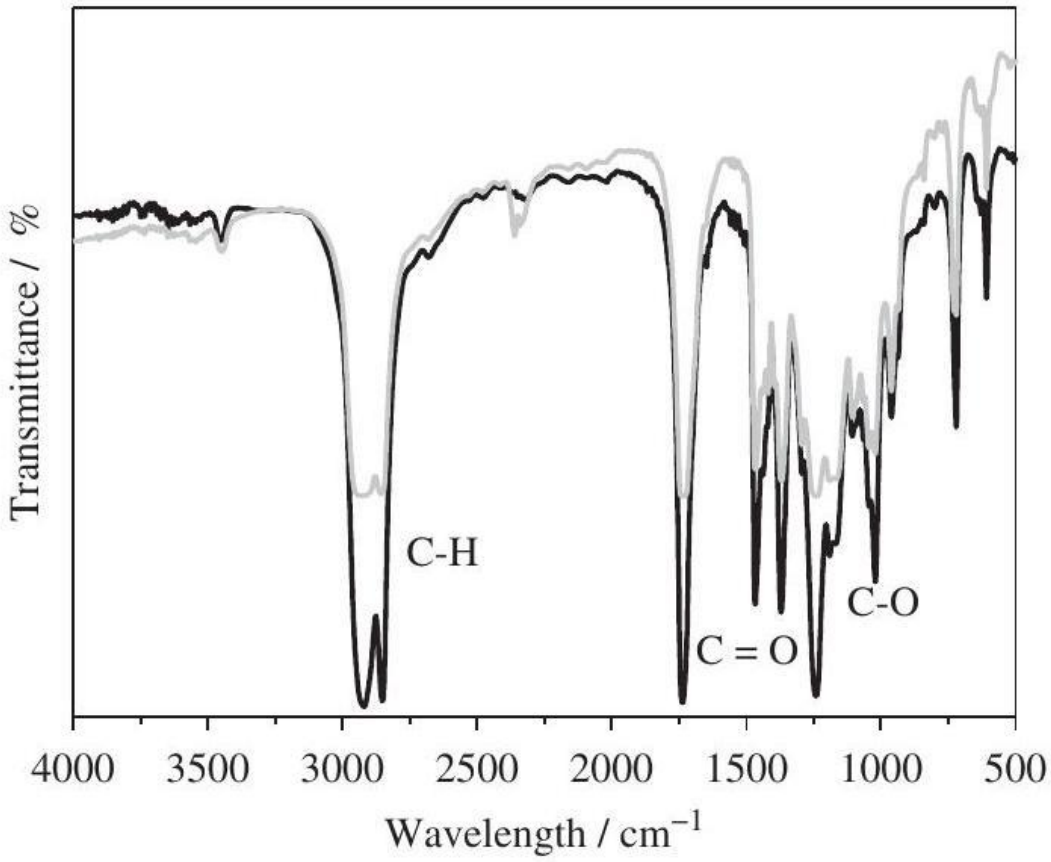
Literature studies reported that grafting reactions favor the formation of branched/cross-linked structures, promoting the decrease of the crystallinity and thus the increases of the amorphous zones proportion (34). Furthermore, for each individual serie (A, B, and C), it seems that the microbial accessibility to EVA groups increased when a higher amount of PCL was grafted to EVA (Fig. 8).

To evaluate the extent of biodegradation of all samples, FTIR spectra of initial and biodegraded samples were recorded. Two spectra, corresponding to initial and biodegraded material were performed. As expected, in the case of EVA, no significant changes occurred, because EVA is a synthetic nonbiodegradable polymer. The major changes occurred for PCL1 (data not shown).

FTIR spectra of A3 (Fig. 9a) shows that major changes occurred during biodegradation. The differences are probably related to PCL1 consumption in the sample, during the metabolism of microorganisms, resulting in a reduction of molar mass, as EVA practically does not degrade, as previously described. Even though similar results were obtained for B3 (Fig. 9 b), the decrease in the intensity of all peaks is less pronounced, which is in agreement with the BOD results. These results can be explained based on the small metabolism of oxygen consumption by microorganisms, as suggested by the BOD test, resulting in lower consumption of carbon in the polymer chains by the microorganisms, i.e., that can be associated to a small reduction in the intensity of the peaks corresponding to the groups C-H, $C = 0$, C-O. Sample C3 (Fig. 9c) shows a reduction in the intensity of all peaks, which is in agreement with the biodegradation obtained from BOD test.

The remaining powder of all samples after 35 days in the sludge, under biodegradation, were collected and submitted to a scanning electron microscopy analysis. The results shown in Fig. 10 indicated that microorganisms presented in the activated sludge degraded PCL and they could also be responsible for the hydrolytic degradation of EVA amorphous region, which is related with the hydrophilic nature of this polymer. Hydrolysis

a)


Transmittance / %
C-H
C = O
C-O
4000
3500
3000
2500
2000
1500
1000
500
Wavelength / cm^{-1}

b)

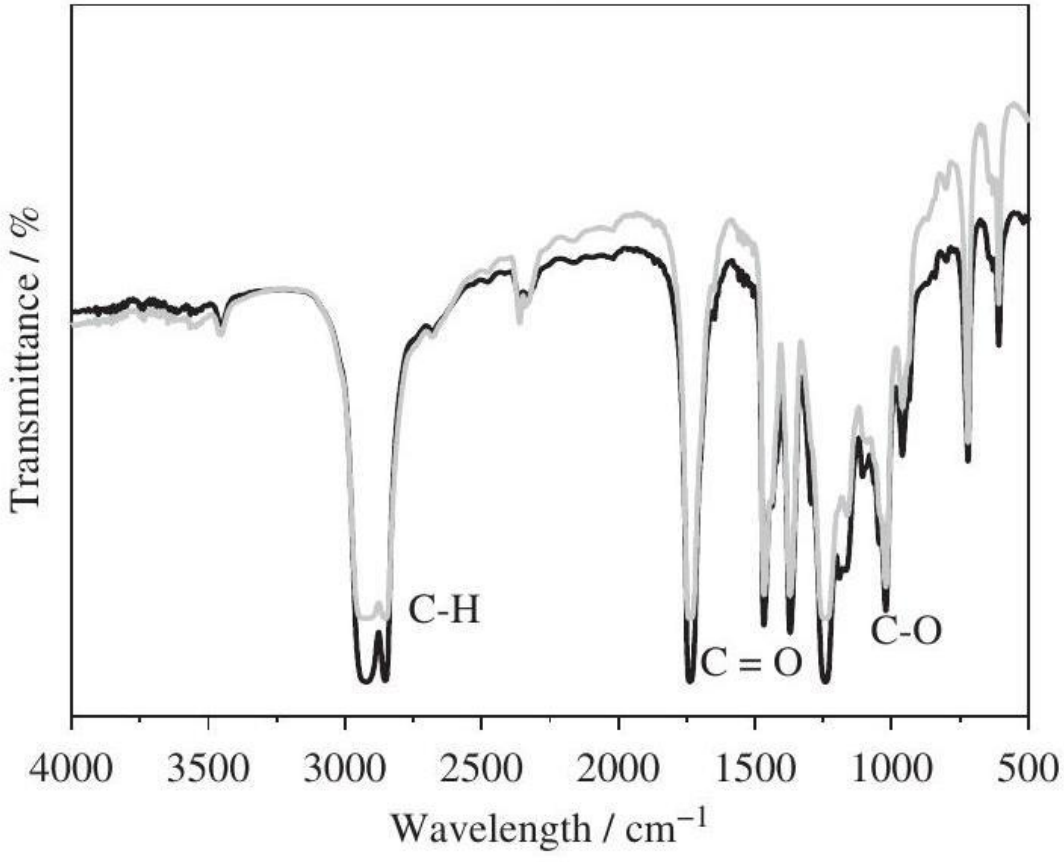

Transmittance / %
C-H
C = O
C-O
4000
3500
3000
2500
2000
1500
1000
500
Wavelength / cm^{-1}

Fig. 9. FTIR spectra of undegraded (black line) and biodegraded (gray line) blends: (a) A3, (b) B3, and (c) C3.
occurs by penetrating water in the EVA backbone, attacking the chemical bonds in the amorphous phase and converting them into shorter water soluble fragments, promoting a reduction in molar mass.

Although it seems that the most part of PCL has been consumed, the structure of polymeric matrix was not significantly changed. As it can be observed, degradation occurs randomly at the polymer surface making it rough and forming holes.

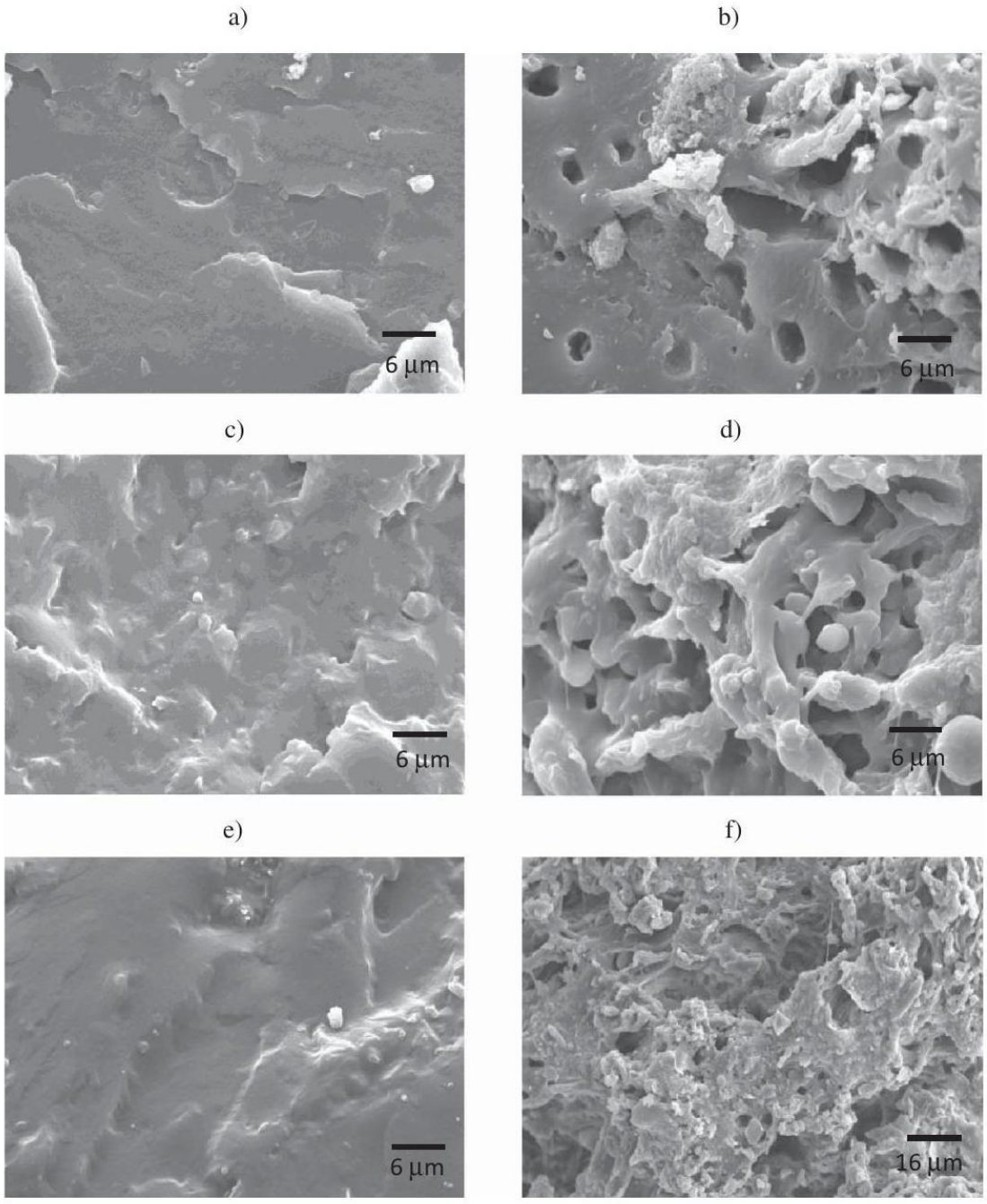


Fig. 10. SEM surface of samples before and after 35 days of biodegradation: before (a) A3, (c) B3, and (e) C3, and after (b) A3, (d) B3, and (f) C3.

Conclusions

This article investigated the effect of molar mass on the preparation of biodegradable materials trough transesterification reactions. Therefore, blends of EVA ($M_n = 18.000\ g.mol^{-1}$ and $M_n = 7.900\ g.mol^{-1}$) and PCL ($M_n = 10.000\ g.mol^{-1}$ and $M_n = 60.000\ g.mol^{-1}$) with different amount of catalyst were prepared by melt mixing and characterized by several techniques.

The amount of copolymer, around 10wt%, determined by selective extractions, was similar for all samples prepared with the highest amount of catalyst and seems to be slightly dependent of the molar mass of the selected polymers. SEM, rheology, thermal analysis, mechanical properties, and biodegradability tests were sensitive to molar mass of the initial polymers and copolymer formation and respective amount. From all the results it can be concluded that sample A3 seems to be the one that has better mechanical properties and higher biodegradability. Therefore, using EVA and PCL with high and low molar mass, respectively, allowed the preparation of a material with higher physical properties and biodegradability.

Thus, the research presented in this article showed that it possible to prepare polymers, using conventional nonbiodegradable
and biodegradable polymers with appropriate molar mass, which have properties similar to conventional polymers and enhanced biodegradability. Moreover, this can be a promising route to produce new polymers that could be used in technological applications.

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[a] EVA1 ($M_n = 18.000\ g.mol^{-1}$).
[b] EVA2 ($M_n = 7.900\ g.mol^{-1}$).
[c] PCL1 ($M_n = 10.000\ g.mol^{-1}$).
[d] PCL2 ($M_n = 60.000\ g.mol^{-1}$).