Universidade do Minho
Escola de Engenharia

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Development of Biodegradable Materials by Reactive Extrusion

Junho de 2011

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Development of Biodegradable Materials by Reactive Extrusion

Tese de Doutoramento
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Professora Doutora Ana Vera Machado

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To my parents

"O nosso mérito está nos troféus que conseguimos ao longo da nossa vida e que só nós sabemos disso"

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Moura, I. Machado, A.V. Nogueira, R. Bounor-Legare, V. 2011. Bio-based Grafted Polyesters Prepared by *In Situ* Ring-Opening Polymerization. *Reactive & Functional Polymers* 71: 694–703, (Chapter 4).

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ABSTRACT

Plastic materials produced from petrochemicals are used in a wide range of applications, such as, packaging, automotive, healthcare application, industry and communication or electronic industries. Most of these plastics are extremely durable, requiring more than 100 years for their degradation. Therefore, they may accumulate in the environment and became a significant source of environmental pollution. A possible solution to solve this problem, could be to replace commodity synthetic non-biodegradable polymers by biodegradable ones.

Reactive extrusion (REX) has been used as an attractive method to prepare new polymeric materials. It allows to prepare new materials, in the melt, by blending, polymerization, grafting, branching and functionalization. Polymerization or chemical modifications reactions in the melt were identified as an efficient and economic way for low cost production, which enhances the commercial viability and cost-competitiveness of these materials. Thus, the main goal of this thesis is to investigate new routes to prepare biodegradable polymers by reactive extrusion.

Blends of biodegradable polymers (starch-based thermoplastics (TPS), poly(ε-caprolactone (PCL) and polylactide (PLA)) and non-biodegradable synthetic polymers, such as, polyolefins were investigated. High density polyethylene/polyethylene-grafted-maleic anhydride (HDPE/PE-g-MA) blends and biodegradable polymers (PCL, PLA and TPS) with different compositions were prepared. The blends were characterized using several techniques and different standard methods were used to evaluate the aerobic biodegradation. The results showed that even though biodegradability can increase, due to lower compatibility between the polymers, the specified final mechanical properties were not achieved.

A different approach used to prepare biodegradable/bio-based polymers was based on the synthesis of copolymers of non-biodegradable and biodegradable polymers. One procedure was based on the synthesis of grafted copolymers, by *in situ* polymerization of lactide (LA) and ε-caprolactone (ε-CL) in the presence of molten EVA, using titanium phenoxide ($Ti(OPh)_4$) as catalyst. The method used allowed copolymer formation, which even in small amount, promote an enhancement of thermal and mechanical properties of EVA and an increase of its biodegradability. Therefore, *in situ* polymerization is a promising route to produce biodegradable/bio-based materials with mechanical properties similar to conventional polymers.

The other route used to prepare biodegradable/bio-based copolymers was through transesterification reactions between EVA and PLA or PCL, catalysed by titanium propoxide ($Ti(OPr)_4$) leading the formation of EVA-g-PLA or EVA-g-PCL copolymers, respectively. The effect of the grafted copolymer amount on physical properties, mechanical properties and biodegradability was investigated. The results obtained show that both, *in situ* polymerization of monomers and/or transesterification reactions, are promising routes to produce biodegradable/bio-based materials with mechanical properties similar to conventional polymers and higher biodegradability, which can be used in technological applications.

RESUMO

Os materiais plásticos produzidos a partir de produtos petroquímicos são utilizados numa vasta gama de aplicações, tais como, embalagens, automóveis, aplicação de cuidados de saúde, indústria, comunicação e indústrias eletrónicas. A maioria destes plásticos são extremamente duráveis, requerendo mais de 100 anos para a sua decomposição. Deste modo, acumulam-se no meio ambiente e tornam-se uma fonte significativa de poluição ambiental. Uma possível solução para a resolução deste problema, poderá ser a substituição de polímeros sintéticos convencionais não biodegradáveis por polímeros biodegradáveis.

A extrusão reactiva devido ao facto de ser um método atractivo, tem sido utilizada para preparar novos materiais poliméricos, uma vez que permite obter materiais no estado fundido, por mistura, polimerização, enxerto, ramificação e funcionalização. As reacções de polimerização química ou modificação no estado fundido, são uma forma eficiente e económica para a produção de materiais de baixo custo, o que aumenta a viabilidade comercial e competitividade dos mesmos. Assim, o principal objectivo desta tese é investigar novos métodos para preparar polímeros biodegradáveis por extrusão reactiva.

Misturas de polietileno de alta densidade/polietileno enxertado com anidrido maleico (HDPE/PE-g-MA) e polímeros biodegradáveis (PCL, PLA e TPS), com composições diferentes foram preparadas, sendo posteriormente caracterizadas utilizando várias técnicas e diferentes métodos padrão de modo a avaliar a sua biodegradabilidade aeróbia. Os resultados obtidos evidenciaram que ainda que a biodegradabilidade aumente, devido à incompatibilidade entre os polímeros, as propriedades mecânicas especificadas não foram conseguidas.

Uma outra abordagem utilizada para preparar polímeros biodegradáveis/bio-baseados, consistiu na síntese de copolímeros de polímeros sintéticos não-biodegradáveis e polímeros biodegradáveis. Um dos procedimentos baseou-se na síntese de copolímeros enxertados de etileno vinil acetato (EVA), recorrendo à polimerização *in situ* do ácido lático (LA) e ε-caprolactona (ε-CL), na presença de EVA fundido, usando fenóxido de titânio ($Ti(OPh)_4$) como catalisador. Este método permite a formação de copolímero, o qual mesmo em escassa quantidade, promove uma melhoria das propriedades térmicas e mecânicas do EVA e um aumento da sua biodegradabilidade. Por conseguinte, a polimerização *in situ* é um método promissor para a produção de materiais biodegradáveis/bio-baseados com propriedades

mecânicas semelhantes aos polímeros não-biodegradáveis. Outro método utilizado para a preparação de copolímeros biodegradaveis resumiu-se a reacções de transesterificação, entre o EVA e PLA ou PCL catalisada por propóxido de titânio ($Ti(OPr)_4$), levando a formação de copolímeros de EVA-g-PLA ou EVA-g-PCL, respectivamente. O efeito da quantidade de copolímero enxertado nas propriedades mecânicas, propriedades físicas e biodegradabilidade foi investigado. Os resultados obtidos indicam que ambos os métodos, polimerização *in situ* e transesterificação, são processos promissores para a produção de materiais biodegradáveis/bio-baseados com propriedades mecânicas semelhantes às dos polímeros convencionais e maior biodegradabilidade, podendo desta forma, serem utilizados em aplicações tecnológicas.

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ABREVIATIONS

ATU - Allylthiourea
BOD - Biological oxygen demand
cBT - Cyclic butylene terephthalate
CH_4 - Methane
CO_2 - Carbon dioxide
d - Days
DBTO - Dibutyltin oxide
DSC - Differential scanning calorimetry
EAA - Ethylene-acrylic acid
ε-CL - ε-caprolactone
EO - Ethylene oxide
EVA - Ethylene vinyl acetate
FTIR - Fourier transform infrared
HDPE - High density polyethylene
H_2O - Water
LA - Lactide
LDPE - Low density polyethylene
MA - Maleic anhydride
Mater-Bi® - Thermoplastic starch with PLA or PCL
MFI - Melt flow index
min - Minutes
NMR - Nuclear magnetic resonance
-OH - Hydroxyl
O_2 - Oxygen
PA - Polyamide
PBT - Polybutylene terephthalate
PC - Polycarbonate
PCL - Poly(ε-caprolactone)
PE - Polyethylene
PEG - Polyethylene glycol
PE-g-MA - Polyethylene-grafted-maleic anhydride
PET - Polyethylene terephthalate
PGA - Polyglycolide
PHA - Polyhydroxylalcanoate
PHB - Polyhydroxybutyrate
P(3HB) - Poly(3-hydroxybutyrate)

PLA - Polylactide
PLGA - Poly(lactic-co-glycolide)
PO - Propylene oxide
PP - Polypropylene
PPG - Polypropylene glycol
PS - Polystyrene
PTMEG - Poly(tetramethyl-ether) glycol
PU - Polyurethane
PVA - Polyvinyl alcohol
PVC - Polyvinyl chloride
REX - Reactive extrusion
ROP - Ring-opening polymerization
rpm - Rotation per minute
SEC - Size exclusion chromatography
SEM - Scanning electron microscopy
Tg - Glass transition temperature
TGA - Thermalgravimetric analysis
THF - Tetrahydrofuran
ThOD - Theoretical oxygen demand
$Ti(OPh)_4$ - Titanium phenoxide
$Ti(OPr)_4$ - Titanium propoxide
Tm - Melting temperature
TPS - Thermoplastic starch
UV - Ultraviolet
VA - Vinyl acetate
Wt - Weight fraction
Xc - Degree of crystallinity
XRD - X-ray diffractometry

SYMBOLS

A - Ampere
mA - milliampere
cm - centimetres
ε - Elongation at break
E - Young modulus
ΔGm - Free mixing energy
ΔH_f - Melt entalphy per gram
ΔH_f° - Theoretically melt enthalpy per gram
gm - Gram
g/L - Grams per liter

G'- Storage modulus
η - Complex viscosity
Hz - Hertz
Ip - Polydispersivity
kg/h - Kilogram per hour
kV - Kilovolt
mg/L - Milligrams per liter
mL - Millilitre
mL/L - Millilitre per liter
mL/min - Millilitre per minute
mm - Millimetres
mm/min - Millimetres per minute
mN/m - Milinewton per meter
$\overline{M}n$ - Number average molar mass
MPa - Megapascal
$\overline{M}r$ - Relative molecular mass
$\overline{M}w$ - Mass average molar mass
μm - Micrometers
Pa - Pascal
Pa.s - Pascal second
ppm - Parts per million
σ - Tensile strength
T - Temperature
t - Time
v/v - Volume concentration
w/v - Mass volume concentration
% - Percentage

1 | THESIS OVERVIEW AND GENERAL INTRODUCTION

This chapter starts with a general introduction of the thesis, the motivation of the present work and the thesis outline. Next, an overview of the properties of biodegradable/bio-based polymers is made.

This state of the art focus on how reactive extrusion (REX) can be applied to develop biodegradable/bio-based polymeric materials, more particularly based on aliphatic polyesters, since this method has been successfully used as a route for polymerization, chemical modification and blending polymers. Next, polymer blends of a synthetic non-biodegradable and biodegradable polymers and also copolymers preparation will be reported.

1.1 BACKGROUND

Polyolefins are the synthetic polymers with the highest commercial success, accounting for more than 47% of Western Europe's total consumption, 24.1 million tonnes per year. They present a combination of physical properties, which are ideally suited to a wide variety of applications such as food and drinks packaging [1]. However, synthetic materials such as polyolefins are difficult to biodegraded by microorganisms and have a long life-time [2-4]. In its natural form polyethylene (PE) is not biodegradable, due to the higher hydrophobic character and also high molar mass ($\overline{Mn}$), but a comprehensive study of polyolefins biodegradation has shown that some microorganisms could use polyolefins with low $\overline{Mn}$ [5]. Thus, to convert conventional PE into biodegradable PE, it is necessary to modify their characteristics, such as, $\overline{Mn}$ and degree of crystallinity (X_c), which contribute for high resistance degradation [6]. Bonhomme et al. [7] and Wang et al. [8] performed biodegradation studies of PE and the results indicated that chemical degradation occurred by two different pathways: hydro and oxo-biodegradation. Other researchers also observed that the oxidation products of polyolefins are biodegradable [9-16]. The explanation is that these products have low $\overline{Mn}$ values and incorporate oxygen (O_2), containing groups, such as, acid, alcohol and ketone. This is the basis of the term oxo-biodegradable polyolefins.

Another synthetic polymer widely used in the packaging industry is ethylene vinyl acetate (EVA), which is a copolymer of ethylene and vinyl acetate. The weight percent (wt.%) of vinyl acetate usually varies between 10% to 40% and the remainder is ethylene. It behaves like an elastomeric material in softness and flexibility and can be processed like other thermoplastic. EVA copolymers have a broad range of industrial applications, such as packaging, adhesives, wire, cable and health care. Also, due to the mechanical properties, these copolymers are used perhaps, in a broadest spectrum of applications of any synthetic polymeric material [17, 18]. Therefore, it would be interesting to have products made from this polymer with biodegradable potential.

Nevertheless, synthetic non-biodegradable polymers have an undesirable influence on the environment and a well known resistance to degradation [19], which became a problem with waste disposal. Once such material became part of the natural ecosystem, the negative effect of it long-lasting contributes for environmental contamination [20]. The growing environmental awareness and the new environmental regulations are forcing the industries to seek for more

ecologically friendly materials for their products, namely in applications where they are used for a short period of time before becoming waste [21].

Thus, due to the lower sensitivity to biodegradation, there is a tendency to replace coventional polymers by polymers that could undergo easily the biodegradable process. The use of these materials, namely in applications with short life-cycle, such as, packaging, would be an ecologically alternative to reduce the solid plastic waste [22]. Some examples of polymers that are biodegradable are polylactide (PLA), poly(ε-caprolactone) (PCL), polyamides (PA) and polyvinyl alcohol (PVA) and also some oligomeric structures. The use of these materials is an alternative to conventional synthetic non-biodegradable plastics, which could contribute to the solution of the environmental problem [23]. The target market is mainly packaging materials, hygiene products, agricultural tools and consumer goods. Nevertheless, still exist a competition between commodity synthetic non-biodegradable plastics and biodegradable ones, due the low cost of the former [24].

Aliphatic polyesters or aliphatic-aromatic co-polyesters are the most well known petroleum source-derived biodegradable polymers [25]. In recent years, there is a growing interest on the synthesis and development of fully biodegradable polymers. The most important synthetic aliphatic polyesters are PLA and PCL, which are usually prepared by ring-opening polymerization (ROP) of the respective cyclic monomers, lactide (LA) and ε-caprolactone (ε-CL). This method provides sufficient polymerization control, resulting in polymers with required $\overline{Mn}$ and with the desired end-groups.

The achievement of improved materials properties, low production costs and ability to biodegrade, using different approaches by reactive extrusion (REX) could be an alternative to replace conventional synthetic non-biodegradable polymers by biodegradable/bio-based ones. The use of these materials, namely in applications with short life-cycle, such as, packaging would be an ecologically alternative for reducing the solid plastic waste [22].

1.2 MOTIVATION

Plastic materials produced from petrochemicals are used in a wide range of applications and most of them are extremely durable, requiring many years to degrade and, consequently, became a significant source of environmental pollution. Even though, after use, plastics can be disposed in different environments, they have some adverse risks. A possible solution to solve this problem could be to replace commodity synthetic non-biodegradable polymers by biodegradable ones.

The commercial relevance of biodegradable polymers and its growth in the market justifies the large number of studies that have been published describing the production of biodegradable materials with desired properties. However, it is necessary to take into account that any marketable plastic product must meet the performance requirements of its intended function and, most of the biodegradable polymers do not meet these functional requirements, i.e., they do not have the performance specifications required for a given application. Therefore, the development of biodegradable polymers with good performance, which after use would be susceptible to microbial and environmental degradation, using adequate solid waste management disposal practices, without any adverse environmental impact, became a challenge.

For this purpose, REX has been used as an attractive method to prepare new materials based on biodegradable polymers. It allows to prepare new materials, in the melt, in an efficient and economic way for low cost production, which enhances the commercial viability and cost-competitiveness of these materials.

Thus, the main goal of this thesis is to investigate new routes to prepare biodegradables polymers by reactive extrusion. The knowledge build up can be used for the biodegradable/bio-based materials production and enhancement the respective properties.

1.3 THESIS OUTLINE

This thesis is organized in seven Chapters:

CHAPTER 1 presents the context and motivation of the present work, as well as its main objectives. A general overview of synthetic non-biodegradable and biodegradable polymers that emphasizes their development and its effect on final properties is reported, being the difference between biodegradable and bio-based also established, as well as the factors that influence polymers biodegradation. Besides that, a short review of synthetic non-biodegradable polymers, modification and processing conditions of biodegradable polymers are also given.

CHAPTER 2 reports the influence of blending biodegradable polymers, PLA, PCL and starch-based thermoplastics (TPS), Mater-Bi®, with high density polyethylene (HDPE) and polyethylene modified with maleic anhydride (PE-g-MA). The effect on mechanical and rheological properties, morphology and potential for biodeterioration of these polymeric blends was assessed. Microbial growth test was also carried out, in order to evaluate the potential for biodeterioration of these blends, using a pure culture of *Pseudomonas fluorescens.*

CHAPTER 3 describes the assessment of the biodegradability of the blends stated in Chapter 2, using two different standard methods: biochemical oxygen demand method, based on ISO 14851:1999, and microbial growth test established according ASTM G 22-76.

CHAPTER 4 is devoted to the synthesis of EVA-g-PLA and EVA-g-PCL copolymers by *in situ* polymerization of LA and ε-CL, in the presence of molten EVA copolymer, using titanium phenoxide ($Ti(OPh)_4$) as catalyst. The amount of copolymer formed was identified through selective extractions. The materials were characterized by ^1H NMR, rheology, TGA, DSC and SEC. Furthermore, morphology prepared samples was explored by SEM. The mechanical performance was evaluated by tensile tests and the biodegradability was monitored based on biochemical oxygen demand method and FTIR as well. Thus, physical properties and biodegradability were discussed based on the influence of copolymer amount formed for each sample.

CHAPTER 5 describes the study of the synthesis of EVA-g-PLA grafted copolymers, carried out by REX, through transesterification reaction between EVA and PLA, using titanium propoxide ($Ti(OPr)_4$) and titanium phenoxide ($Ti(OPh)_4$) as catalysts. The extent of the grafting reaction was estimated by selective extractions and the morphology was analyzed by SEM. Then, morphology of samples with copolymer formation was compared with the respective physical blend. The effect of copolymer formation and its amount on rheological, thermal and mechanical properties and also biodegradability was also addressed.

CHAPTER 6 deals with the effect of EVA and PCL molar mass on the synthesis of EVA-g-PCL grafted copolymers, prepared applying the same method described in Chapter 5, using only titanium propoxide ($Ti(OPr)_4$) as catalyst. The results acquired from this chapter deal with the expected response, taking into account the ones obtained in the previous chapter.

CHAPTER 7 presents the general conclusions regarding the work carried out in this thesis and suggestions for future work.

1.4 Bio-based and Biodegradable Polymers

The words bio-based and biodegradable, both incorporate the prefix "bio", but they cannot be used indistinctly. Both, bio-based and biodegradable polymers can form the basis of an environmentally preferable and sustainable alternative to conventional synthetic non-biodegradable polymers, based exclusively on petroleum feedstock's [26].

The American Society for Testing and Material (ASTM) defines a bio-based material as "*an organic material, in which carbon is derived from a renewable resource, via biological processes. These materials include all plant and animal mass derived from carbon dioxide (CO_2) recently fixed via photosynthesis, per definition of a renewable resource"* [26, 27].

Therefore, a bio-based material should be organic and containing carbon from biological sources, which is synthesized by many types of living mater (bacteria, animals and plants), being portion of the ecosystem [28]. However, the use of a bio-based material must take into account what happens to the product after the use and its impact in the environment. Since the most important factor of sustainability and environmental responsibility, is related to the disposal of the products after use [28]. Thus, the United Stated Department of Agriculture (USDA), in the ASTM D 6866, defined a percentage of natural carbon that is required to carry the term bio-based [29]. This standard was developed to attest the biological content of bioplastics, i.e., to determine exactly the amount of the material that comes from renewable resources.

For example, HDPE can be totally bio-based, i.e., containing only renewable carbon, but it still non-biodegradable. Thus, a polymer that contains only renewable raw materials could be or not biodegradable, it depends also on the molecular structure and on the chemical or biological methods used for polymerization. Accordingly, for single use and short-life disposable materials applications, bio-based materials should be engineered to be biodegradable [26]. A product that is entitled bio-based does not means that is based entirely on renewable resources. Rather, many of these products combine both, petroleum with natural based materials, in order to provide satisfactory properties, and simultaneously, reducing the overall of synthetic polymers contained in the products.

Biodegradable polymeric materials can be disposed in safe and ecologically ways through waste management's composting, soil application, and biological wastewater treatment. According to ASTM D 6400-99 [30], the common definition of biodegradable is *"a degradable plastic in which the degradation results from the action of naturally occurring microorganisms such as bacteria,*

fungi and algae". Essentially, a polymer is called biodegradable, when under the right conditions, the microorganisms present in the environment can chemically breakdown the polymer chain and use it as a food source. The process of biodegradation essentially converts carbon into energy, taking place in many environments including soils, compost sites, waste management, water treatment facilities, and marine environments. However, not all materials are biodegradable under the same conditions. While some are susceptible to microbes found in a wastewater treatment plant others need microbes found in the soils [31, 32].

Thus, the biodegradation process occurs in two different steps: first, the long polymer chains are shortened or cut at the carbon-carbon bonds [31]. This process can be started by different factors including heat, microbial enzymes, moisture or other environmental conditions. This first step is not synonym of biodegradation and is usually called degradation [31]. In the second step, called biodegradation, the short carbon chains are used as a food source and are converted into water (H_2O), biomass, carbon dioxide (CO_2) and methane (CH_4) (depending upon process takes place under aerobic or anaerobic conditions). Figure 1.1 illustrates the biodegradation process under aerobic conditions.

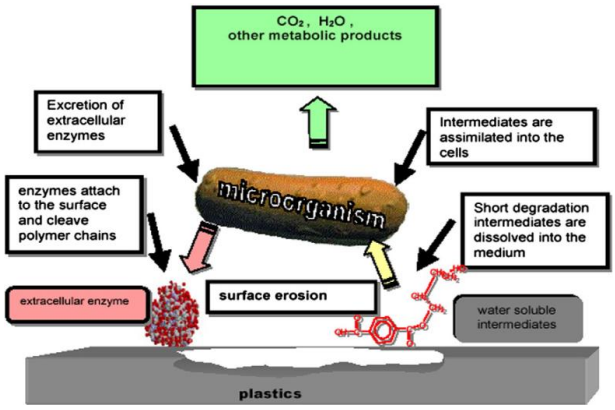


Figure 1.1 General mechanism of plastic biodegradation under aerobic conditions [33].

Moreover, there is also a difference between biodegradable and compostable polymers. Even both break down the polymeric chain into smaller fragments, due to the action of microorganisms, and transform the latter into CO_2, H_2O, minerals and biomass and/or CH_4 must occur, a compostable polymer should disintegrate and biodegrade quickly and cannot leave visible, distinguishable or toxic residues. To be called compostable, a product should meet D 6400 standard [30], which is the regulatory framework for the United States and sets a less stringent threshold of 60% biodegradation within 180 days, again within commercial composting conditions.

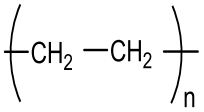
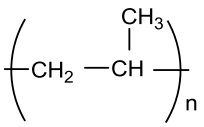
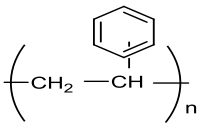
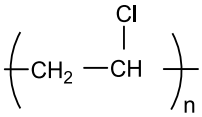
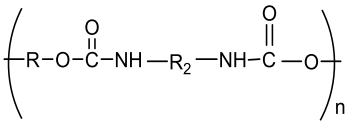
Unfortunately, most products are designed with limited concern related to its ultimate disposability. These are designed to be biodegradable, i.e., they fragment into smaller fragments and may even degrade to residues that are invisible to the naked eye, but they are not completely biodegradable within a short period of time. These plastic residues will migrate into the H_2O and in the ecosystem causing damage to the environment [34].

Biodeterioration and biodegradation of polymer substrate can rarely reach 100%, because only a small portion of the polymer will be incorporated into microbial biomass and other natural process [35, 36].

1.5 Synthetic Plastics

The demand of synthetic polymeric materials has been fairly increasing during the last decades and presently, they are one of the most attractive categories of materials [21]. This success is mainly related to their properties namely, low cost, aesthetic qualities, and resistance to physical ageing and biological attack [37]. It is estimated that global synthetic plastic production is approximately 140 million tons per year [38, 39]. The most widely used plastics are polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), polyurethane (PU), poly(ethylene terephthalate) (PET), polybutylene terephthalate (PBT) and nylons (Table 1.1).

Table 1.1 Structures of conventional plastics [38, 39].

Polymer	Chemical structure	Market share by volume produced
PE		29%
PP		12%
PS		9%
PVC		17%
PU		5%
Others		28%
Total		100%

In fact, polyolefins are the synthetic polymers with the highest commercial success. They present a combination of physical properties, such as, flexibility, strength, lightness, stability, impermeability, and easiness of sterilization, that are ideally suited to a wide variety of applications, as mentioned before [1]. However, synthetic polymers have an undesirable influence on the environment and a higher resistance to degradation [19], which became a problem with waste disposal (Figure 1.2).

Thus, the growing environmental awareness and the new environmental regulations are forcing the industries to seek for more ecologically friendly materials for their products, namely in applications where they are used for a short period of time before becoming waste [21].

Figure 1.2 The negative effect of synthetic non-biodegradable plastics waste disposal.

Under natural conditions, the degradation of synthetic plastics is a very slow process that involves environmental factors, followed by the action of wild microorganisms [40-42]. The degradation depends on physical and chemical properties, being the main mechanism hydrolysis or oxidation [43]. Hydrolysis occurs by penetrating water in the polymer backbone, attacking the chemical bonds in the amorphous phase and converting them into shorter water soluble fragments, promoting a reduction in $\overline{Mn}$ (Figure 1.3). Then, metabolization of the fragments and bulk erosion also occur, leading to the loss in the physical properties, making it more accessible for further microbial assimilation [44-46]. Conversely, some synthetic polymers, generally vinyl polymers, are not susceptible to hydrolysis. Therefore, the prevailing degradation mechanism occurs by oxidation, due the presence of an oxidizable functional group [2].

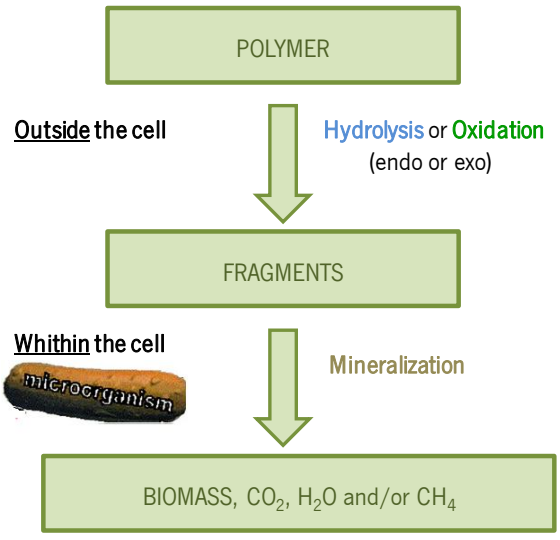


Figure 1.3 Schematic representation of polymer degradation versus biodegradation [47].

Due to the lower sensitivity to biodegradation, there is a tendency to replace such polymers by others that could undergo easily the biodegradable process. The use of these materials, namely

in applications with short life-cycle, such as, packaging would be an ecologically alternative for reducing the solid plastic waste [22].

Some examples of synthetic polymers that are biodegradable are PLA, PCL, PA and PVA and also some oligomeric structures, like ethylene, styrene, isoprene, butadiene, acrylonitrile and acrylate [48].

1.5.1 Polyethylene (PE)

Polyolefins are difficult to biodegraded by microorganisms and have a long life-time [2, 3, 4]. In its natural form PE is not biodegradable, due to the higher hydrophobic character and also high $\overline{M}n$, but a comprehensive study of polyolefins biodegradation has shown that some microorganisms could use polyolefins with low $\overline{M}n$ [5]. Thus, to convert conventional PE into biodegradable PE, it is necessary to modify their characteristics, such as, $\overline{M}n$ and X_c, which contribute for high resistance degradation [42].

Bonhomme et al. [7] and Wang et al. [8] performed biodegradation studies of PE. The results indicated that chemical degradation occurred by two different pathways: hydro and oxo-biodegradation [7]. Other researchers also observed that the oxidation products of polyolefins are biodegradable [9-16]. The explanation is that these products have low $\overline{M}n$ values and incorporate O_2, containing groups, such as, acid, alcohol and ketone. This is the basis of the term oxo-biodegradable polyolefins. Oxo-biodegradation involves two stages: first oxidative degradation occurs followed by the biodegradation of the oxidized products. When a molecule undergoes oxidative degradation, the size is reduced and at a given size the microbial degradation starts. It has been demonstrated, that the biodegradation of polar molecular fragments from PE occurs quite quickly [49].

Another alternative to accelerate the attack of microorganisms to polyolefins is by blending biodegradable polymers, like starch, PCL and PLA, to guarantee at least a partially biodegradation. This effect will be discussed later in this thesis.

1.5.2 Ethylene Vinyl Acetate (EVA)

Another synthetic polymer widely used in the packaging industry is EVA, which is a copolymer of ethylene and vinyl acetate. The wt.% of vinyl acetate usually varies between 10% to 40% and the remainder is ethylene. It behaves like an elastomeric material in softness and flexibility and can

be processed like other thermoplastic. The material has good transparency and gloss, barrier properties, low-temperature toughness, stress-crack resistance, hot-melt adhesive waterproof properties, and resistance to ultraviolet (UV) radiation. EVA copolymers have a broad range of industrial applications, such as packaging, adhesives, wire, cable and health care. Also, due to the mechanical properties, these copolymers are used perhaps, in a broadest spectrum of applications of any synthetic polymeric material [17, 18]. Therefore, it would be interesting have products made from this polymer with biodegradable potential.

1.6 Biodegradable Polymers

Limited resources of petroleum-based polymers and increased environmental awareness, has attracted a higher interest towards biodegradable and bio-based polymers (Figure 1.4) for industrial applications [50].

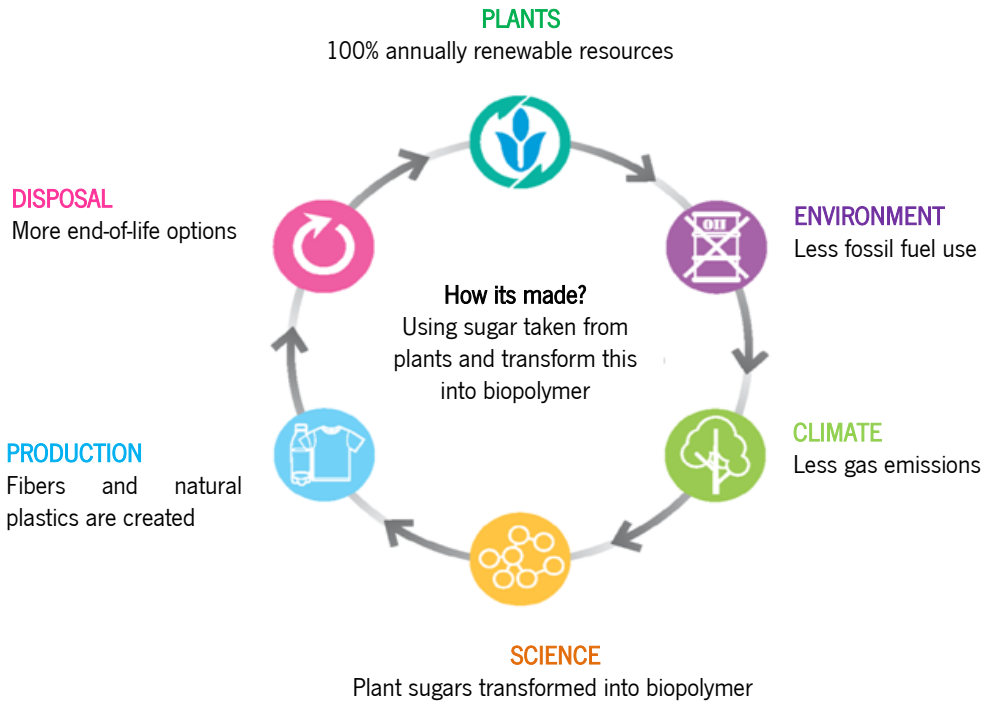
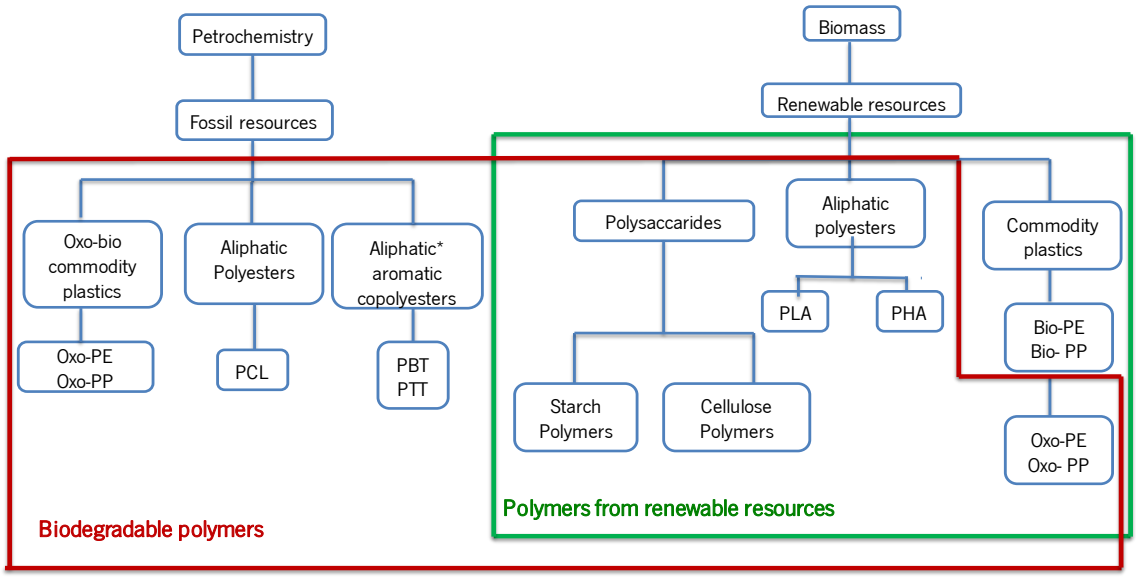


Figure 1.4 Lifecycle of biopolymers.

The use of these materials is an alternative to conventional synthetic non-biodegradable plastics, which could contribute to the solution of the environmental problem [23]. Thus, the consumption of biodegradable polymers has increased in the last decades, being the target market mainly,

packaging materials, hygiene products, agricultural tools and consumer goods. Nevertheless, still exist a competition between commodity non-biodegradable plastics and biodegradable ones, due the low cost of the former [24].

Biodegradable polymers can be derived from renewable or petroleum resources (Figures 1.5 and 1.6). The former are produced in nature during the growth cycles of all organisms [32] and their synthesis generally involves enzyme-catalyzed, chain growth polymerization reactions of activated monomers, which are typically formed within cells by complex processes and the latter are petroleum based. Thus, industry, beyond synthetic non-biodegradable petroleum based plastics and the renewable source-based biodegradable polymers, is also thinking in terms of aliphatic/aromatic ratio by using chemical processes to achieve petroleum-based biodegradable plastics [51].



*Partially from chemistry

Figure 1.5 Resources of biodegradable polymers [47].

(a)

(b)

Figure 1.6 Resources of (a) non-renewable synthetic biodegradable and (b) natural biodegradable plastics.

According to Narayan [27] biodegradable polymers can be divided as follow:

1. Biopolymers or natural biodegradable polymers formed in nature during the growth cycles of all organisms. The synthesis implys enzyme-catalyzed, chain growth polymerization reactions of activate monomers, which are formed within cells by some metabolic processes (for example, starch and cellulose).
2. Polymers with hydrolysable backbones – these polymers are susceptible to biodegradation, which includes aliphatic polyesters, PA and PU.
3. Polymers with carbon backbones – the biodegradation of this kind of materials involves first an oxidation process. An example is PVA, which is not susceptible to hydrolysis. Biodegradable vinyl polymers contain functional groups that are easily oxidizable and a catalyst are added to promote their oxidation or photo-oxidation, or both [52].

1.6.1 Aliphatic Polyesters

Aliphatic polyesters or aliphatic-aromatic co-polyesters are the most known petroleum source-derived biodegradable polymers [25]. In recent years, there is a growing interest on the synthesis and development of fully biodegradable polymers, such as, PCL, polyhydroxybutyrate (PHB) and its copolymer with hydroxyvaleric acid, PLA and aliphatic polyesters from different lactide derivatives [53-55].

Aliphatic polyesters made from dimethylesters and diols are expected to be of the most economically competitive biodegradable polymers [56, 57]. Moreover, it was found that polyesters derived from diacids of medium size monomers (C_6-C_{12}) are more readily degraded by microorganisms than those derived from longer monomers [58]. A synthetic polymer can only be biodegradable by enzyme catalysts, if the polymer chains are able to fit into the enzymes active

site. This is the reason why flexible aliphatic polyesters are degradable and the rigid aromatic polyesters are not [52, 59, 60]. Another major feature of these polymers is their compatibility with the natural environment and their ability to undergo hydrolytic and biological degradation [61]. Their biodegradability depends mainly on their chemical structure and especially of the hydrolysable ester bonds in the main chain, which are susceptible to microbial attack. Other factors, such as, $\overline{Mn}$, X_c, stereoregularity and morphology, also affect the rate of biodegradation [56, 62, 63].

Nevertheless, the most important synthetic aliphatic polyesters are PLA and PCL, which are usually prepared by ROP of the respective cyclic monomers, LA and ε-CL. This method provides sufficient polymerization control, resulting in polymers with required $\overline{Mn}$ and with the desired end-groups.

1.6.1.1 Poly(ε-caprolactone) (PCL)

PCL is prepared from ROP of ε-CL, as illustrated in the Figures 1.7 and 1.8:

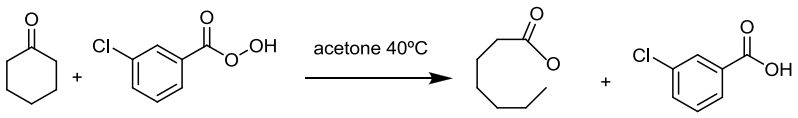


Figure 1.7 Synthesis of ε-CL monomer.

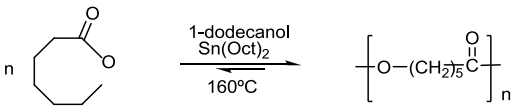


Figure 1.8 Synthesis of PCL.

PCL is appreciated by its biodegradable properties, it can be biodegraded aerobically by a large number of microorganisms in various microbiological environments [64]. Moreover due to its flexibility it has been found to be miscible with many other polymers [52, 64]. However, the high cost and low performance of PCL for some applications has prevented its widespread industrial use [65].

1.6.1.2 Polylactide (PLA)

PLA can derive from renewable and petroleum-based resources [66]. The production of PLA presents advantages over other synthetic materials: i) PLA can be obtained from renewable agricultural sources (for example, corn), ii) its production consumes CO_2, providing significant energy savings and iii) PLA is recyclable and compostable [67-69].

Early economic studies have shown that PLA is an economically feasible material that can be used as a packaging material [70]. PLA properties are determined both by the polymer architecture (stereochemical make up of the backbone) and the $\overline{Mn}$, being the latter controlled by the addition of hydroxylic compounds. The control of the polymer stereochemical architecture allows precise control over the crystallization rate and the crystallinity degree, mechanical properties and processing temperature [71]. Also, PLA is a polyester with one of the highest melting temperatures, around 160-180 °C and it can exists as two stereoisomers, designated as D and L, or as a racemic mixture, designated as DL. While the D and L forms are optically active, the DL form is inactive. Poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) are semi-crystalline while poly(DL-lactide) (PDLLA) is amorphous [72].

Bacterial fermentation is used to produce LA from corn or cane sugar. However, LA cannot be polymerized as a useful product, because during polymerization reaction, molecules of H_2O are generated, and its presence degrades the forming polymer chain. Thus, PLA of high $\overline{Mn}$ is produced from ROP of LA using a catalyst (Figure 1.9), by solvent-free continuous process and distillation method [22].This mechanism does not generate additional H_2O, and thus, a wide range of $\overline{Mn}$ is accessible.

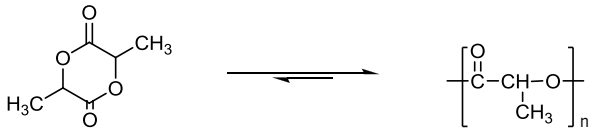


Figure 1.9 Synthesis of PLA.

PLA is currently used in industrial packaging and biomedical applications [73]. Nevertheless, it has been demonstrated that is not suitable for hard tissue regeneration, due to its weak mechanical properties [74-78].

1.6.1.3 Starch

Starch, is a carbohydrate consisting of a large number of glucose units joined together by glycosidic bonds containing, generally, 20% to 25% amylase and 75% to 80% amylopectin. It occurs widely in plants, like rice, corn, cassava and potatoes. In all of these plants, starch is produced in form of granules, varying in size and in composition according the plant used (Figure 1.10). Starch granules are hydrophilic, and the water content of starch varies with relative humidity changes. While the branched amylopectin component contains crystalline areas, the linear amylase is mostly amorphous. Starch granules can be gelatinized in water at lower temperatures in alkaline solution and can be used as a thickening, stiffening and gluing agent, giving wheat paste [79].

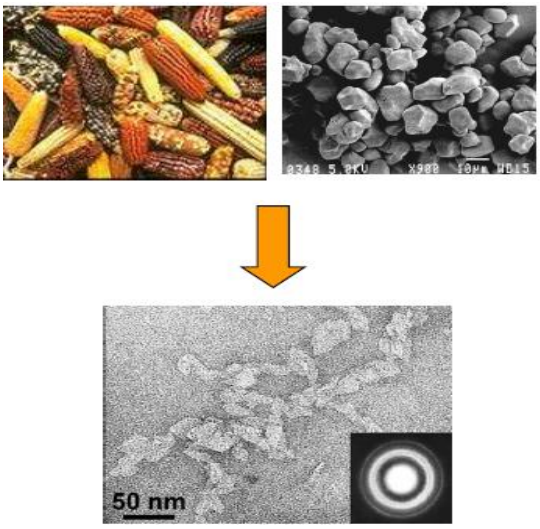


Figure 1.10 Structure of nanocrystals obtained from starch [80].

There are several degradable plastics made from starch [27, 52, 81] For instance, a fully biodegradable starch-based polymer is prepared from corn or potato starch, along with smaller amounts of food-grade additives. The resin is suitable for manufacturing injection-moulded pieces, films and starch-based loose-fill packaging material [82]. These pieces degrade in an active biological environment.

Starch has a wide variety of applications, including adhesives and industrial emulsions, construction, glass fiber, medical gloves, personal care, packaging and agricultural.

The interest in this biopolymer has been recently renewed due to its abundance, low-cost, availability, biodegradability, possibility of blending with conventional polymers and it can be

processed using conventional polymer processing equipment, such as, extrusion and injection moulding [83].

1.7 Modes of Biodegradation

1.7.1 Enzymes Mechanism

Two categories of enzymes are involved in biological degradation of polymers: extracellular and intracellular depolymerases [84, 85]. Such kind of enzyme has different action mechanism; some enzymes change the substrate through a free radical mechanism, while others follow alternative chemical routes (typical examples, are biological oxidation and hydrolysis). During degradation, exoenzymes from microorganisms, break down complex polymers, yielding smaller molecules of short chains, like oligomers, dimmers and monomers. These are small enough to pass the semi-permeable outer bacterial membranes to be utilized as carbon and energy source. However, the biodegradative pathways associated with polymers are determined by environmental conditions. When O_2 is available, aerobic microorganisms are mostly responsible for destruction of complex materials, with the formation of biomass, CO_2 and H_2O. Contrarily, under anaerobic conditions, microorganisms are responsible for polymer deterioration, being the primary products microbial biomass, CO_2, H_2O and CH_4 [86].

Polymer degradation involves changes in physical properties, due to chain scission along the polymer backbone [87, 88]. Since the degradation mode depends on the initiation process, it can be classified as thermal, mechanical, photochemical, biological or chemical [88]. Additionally, the environmental conditions such as moisture, temperature and type of microorganisms influence polymer degradation. Moreover, it also depends on the structural properties of the polymer, as chain orientation, stereochemical configuration, X_c, $\overline{Mn}$, $\overline{Mn}$ distribution and degree of crosslinking are among the important ones [89-91].

1.7.2 Biological Oxidation

Many enzymes can react directly with O_2, which has a special role in the metabolism of aerobic organisms. The enzyme can be hydroxylases (eq. (1)), which is responsible for the hydroxylation, i.e., a chemical process that introduces hydroxyl (-OH) groups into the organic compound, or can be oxygenases ((eq. (2)), in this case O_2 transfers from molecular to the substrate. The substrate has another type of biological oxidation when the O_2 molecule, is not incorporated into the

substrate but rather its function of an hydrogen acceptor. Enzymes of this type are called oxidases and one type produces H_2O ((eq. (3)) and the other peroxides ((eq. (4)).

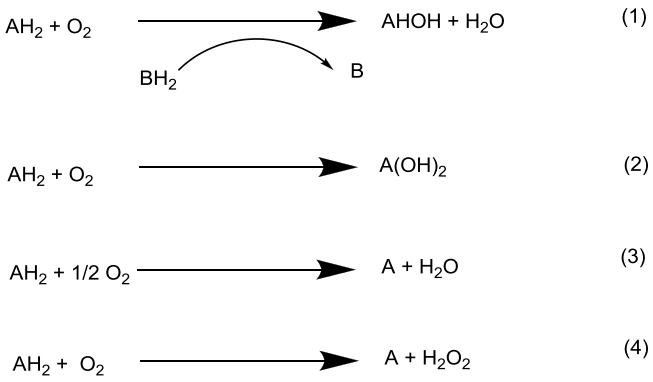


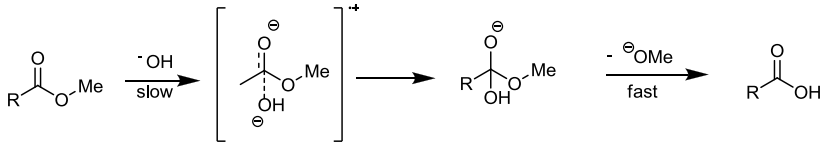
Figure 1.11 Biological oxidation equations.

Biodegradable polymers disposed in bioactive environments degrade, not only by the enzymatic action of microorganisms such as bacteria, fungi, and algae, but also by non-enzymatic processes, such as, chemical hydrolysis that breaks down the polymer chain, as stated before.

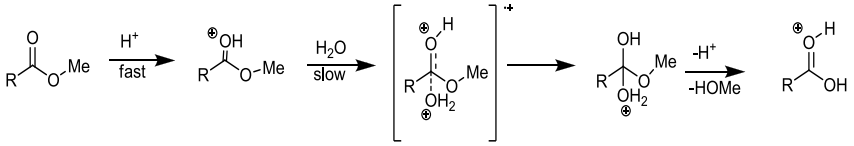
1.7.3 Biological Hydrolysis

Polymers with hydrolyzable backbones have been found to be susceptible of biodegradation. Among others are polyglycolide (PGA), PCL, poly(lactic-co-glycolic) (PLGA), polyether-polyurethane and poly(amide-enamines)s.

Hydrolysis occurs by scission of chemical bond in the main chain by reaction with H_2O [72]. The hydrolysis of esters can occur through both, acid and base catalyzed mechanisms. While in the base catalyzed mechanism (Figure 1.12 (a)) the reactant goes from a neutral species to a negatively charged intermediate, in the acid catalyzed (Figure 1.12 (b)) a positively charged reactant goes to a positively charged intermediate. Additionally, the mechanism associated with hydrolysis of ester linkage in neutral or acidic media is different from the one in alkaline media [92]. Both, in neutral or acidic media, the hydrolysis is initiated by protonation and is followed by the addition of H_2O and the cleavage of the ester linkage [92]. In alkaline media, $-OH^-$ ions are attached to the carbonyl carbons and followed by the breaking of the ester linkages.



(a)



(b)

Figure 1.12 Ester hydrolysis (a) base and (b) acid catalyzed mechanism.

Several different hydrolysis reactions can occur in biological organisms, being the general equation represented in Figure 1.13. The degradation kinetics of different raw materials changes substantially, which might be attributed to the hydrophilic or hydrophobic nature of the different polymers.

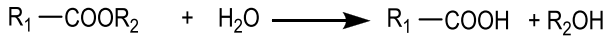


Figure 1.13 General equation of esters hydrolysis.

1.8 Biodegradation Parameters

Biodegradation is a very complex process, which is affected by different factors, including type of microorganism, polymer features and nature of pre-treatment. Furthermore, polymer $\overline{Mn}$, Tg, X_c, type of functional groups, tacticity and additives play an important role [85, 93].

1.8.1 Effect of Polymer Structure

Biodegradability is mainly determined by the molecular structure and the length of the polymer chains [94-96]. Natural polymers, as starch, are generally degraded in biological systems by hydrolysis followed by oxidation [97]. Most of the synthetic biodegradable polymers contain hydrolysable backbones. For instance, ester linkages are susceptible to biodegradation by microorganisms and hydrolytic enzymes. Since many proteolytic enzymes specifically catalyze the hydrolysis of peptide linkages adjacent to substituent's in proteins, polymers containing

substituent's, such as, benzyl, hydroxyl, carboxyl, methyl and phenyl groups, have been prepared aiming that the introduction of these substituent's might increase biodegradability [98]. Huang et al. [99] investigated the effect of stereochemistry on the biodegradation using monomeric and polymeric ester-ureas that were synthesized from D-, L-, and D,L- phenylalanines. They found out, that after enzyme-catalysed degradation, the pure L-isomer degraded faster. Shuichi Matsumura et al. [100] studied the effects of stereoregularity on biodegradation of PVA by *alcaligenes faecalis* and observed that the biodegradability of PVA was influenced by its stereoregularity, being the isoctatic moiety more biodegraded. Another parameter that influences the degree of biodegradation is the hydrophilic and hydrophobic character of polymers, since most enzyme-catalysed processes occur in aqueous medium.

1.8.2 Effect of Polymer Morphology and Degree of Crystallinity

Synthetic polymers can have short repeating units and due to this regularity the crystallinization is enhanced, making the hydrolysable groups less accessible to enzymes [101-103]. On the contrary, if the repeating units are long, the polymer has less tendency to crystallize and consequently is more susceptible to biodegradation. It is well known, that during degradation, semi-crystalline polymers suffer some changes, namely concerning the X_c.

During degradation polymers cristallinity increases rapidly, then levels off when the rate of crystallinity approaches 100%. This occurrence is due the disappearance of the amorphous phase, because biodegradation occurs preferably in the amorphous regions of the polymer, which have a higher mobility of the polymeric chains and therefore are more accessible to the microorganisms [21].

Wu [104] dedicated his study to the physical properties of maleated-PCL/starch blend and its relationship with biodegradability. The results indicated that even though PCL-g-MAH/starch shows higher compatibility, a slightly lower biodegradation rate was observed in a soil environment, compared to the non-compatibilized one. Pandey et al. [105], found out that the biodegradability of polyesters increases with compatibilization within PCL-starch compositions. Also, Ha et al. [106], observed that the rate of enzymatic degradation of poly(3-hydroxybutyrate) (P(3HB)) films decreases with an increase in crystallinity, and it was also influenced by the size of P(3HB) spherulites. It was also suggested that the PHB depolymerise; firstly hydrolyses the amorphous P(3HB) chains on the surface of the film occurred and subsequently erodes P(3HB) chains in the crystalline state [107]. Other factors, such as, shape, size, number of the

crystallites have also a significant effect on the chain mobility of the amorphous regions and thus, affect the rate of the degradation.

1.8.3 Effect of Molar Mass

A lot of studies have been performed on the effect of $\overline{Mn}$ on the biodegradation rate [50, 100, 108]. An increase of $\overline{Mn}$ results in a decrease of degradability by microorganisms. Contrarily, monomers, dimmers and oligomers of a polymer´s repeating units are much easier to degrade and mineralize [22].

Some polymers remain relatively immune to microbial attack as long as their $\overline{Mn}$ remains high. While some plastics, such as, polyolefins and PS do not support microbial growth, low $\overline{Mn}$ hydrocarbons can be degraded by microorganisms. Some natural molecules, such as, starch and cellulose, suffer conversions to low $\overline{Mn}$ components by enzyme reactions, which occur outside the cells [52]. Nevertheless, this process cannot be applied to some polymers, when their molecules are too big to enter into the cells.

Photodegradation and chemical degradation may decrease sufficiently the $\overline{Mn}$ to occur microbial attack. For instance, low density polyethylene (LDPE) with an average $\overline{Mn}$ of 150.000 g.mol^{-1} contains about 11 000 carbons [52]. Decreasing molecules of this size to biologically acceptable dimensions, requires extensive destruction of PE chains. This destruction could be partly accomplished by blending PE with biodegradable or natural polymers.

1.9 Reactive Extrusion

1.9.1 Reactive Process

This method differs from conventional ones, where synthesis was made separately and extruders were used only for processing (melting, pumping and shaping) [108]. REX has been receiving much attention as an industrial technique, because it has several advantages, such as, continuous process, versatility, low cost, good heat transfer, short residence time, wide range of temperatures, high viscosity and it is solvent-free process [109, 110]. Moreover it is an attractive method for melt blending, filler dispersion and various reactions (e.g. (co)polymerization, grafting, branching and functionalization) [111-114], combining polymer processing and chemical reaction.

Nevertheless, there are also some drawbacks in using an extruder as a chemical reactor, including limited residence time, efficient heat transfer, medium polarity, high viscosity (η) leading to possible strong viscous dissipation, which can promote side reactions, like thermal degradation [114]

REX is a very complex process, since it has to deal with several parameters, such as, processing, chemical reaction and heat transfer. Due to the mixing capability, higher heat and mass transfer, twin-screw extruders are generally used for REX [115]. Twin screw extruders can operate in counter rotating and co-rotating way, being the latter preferred in the REX process. The main interest on use the co-rotating system is namely, because of the high speed and throughputs, better temperature control, adjustable residence time distribution and continuous stable flow through the die [109, 116].

According to Xanthos [117] many types of reactions can be performed in an extruder, including bulk polymerization, grafting reactions, interchain copolymer formation, coupling/crosslinking reactions, controlled degradation and functionalization.

1.9.2 Reactive Blending of Immiscible Polymer Blends

Blending of polymers has become an attractive method to prepare new polymeric materials with enhanced properties and relative low cost [118-123]. One major question to be addressed in any polymers blend system is whether the constituents are miscible or immiscible. The main challenge of compatibilization is to generate good adhesion between the phases and fine morphology [124-129].

However, there are two different types of polymer blends, miscible and immiscible blends. The former are characterized by the presence of only one phase and the existence of only one glass transition temperature (Tg). Contrarily, immiscible blends are phase separated, exhibiting the Tg and/or melting temperatures (Tm) of each blend component. Miscibility is also governed by the concentration dependency of the free energy of mixing (ΔGm).

It is well known that the blend features strongly depend on the properties of the individual components, but morphology is a key factor for producing polymer blends with enhanced properties [122].

Immiscible blends can have important industrial application if they are compatibilized [130]. The main challenge of compatibilization is to generate good adhesion between the phases and fine morphology [123, 130-134].

Essentially three methods have been used to compatibilize immiscible polymer blends, which are the following [114, 135-140]:

1. *ex situ compatibilization* – consists in the addition of a pre-synthesized block or a graft copolymer, which has blocks or grafts identical to the ones existing in the polymers of the blend;
2. *in situ compatibilization* – block of grated copolymers are synthesized at the interface during blending and in this cases both polymers should have reactive groups;
3. Crosslinking or "dynamic vulcanization" – one of the phases crosslinks, which stabilizes the morphology and avoids coalescence.

Ex situ compatibilization allows to control the molecular arquitecture of the copolymer added [114]. This copolymer, called compatibilizer, should locate at the interface, reduce the interfacial tension, improve dispersion and stabilize the morphology [114]. A major drawback of this method is that each polymer blend requires a specific copolymer, whose preparation requires specific chemical routes and reaction conditions [114, 141]. Besides, due thermodynamic and dynamic reasons, there are always some copolymer chains, which cannot get the interface where they are most needed. Dispersion of the copolymer in matrix is not simply and its diffusion to the interface is generally a slow process.

In situ compatibilization of immiscible polymers produces desired copolymers, through interfacial reactions between reactive polymers during blending. This method is more attractive and cost-effective, because it allows to produce the copolymer at the interface, without separate preparation step [141]. When one of the polymers does not contain reactive groups, it needs to be functionalized previously. Generally, polymers grafted with maleic anhydride are extensively used as compatibilizers [142-144].

Other parameters like thermodynamic and rheological properties, composition and processing conditions (screw configuration, time, screw rotation speed, temperature, throughput, etc.) have a strong influence on the morphology development during blending [145].

1.9.3 Preparation of Blends of Non-Biodegradable and Biodegradable Polymers

As stated before, polyolefins constitute the majority of thermoplastics currently used as packaging materials. Since the use of plastics continuously increases, the problem of post-consumer recycling has become an important issue for economic and environmental reasons [146]. Nevertheless, recycling would be neither practical nor economical for certain applications, such as, bags, agricultural mulch films, and food packaging, since these materials contain many organic residues and have a low lifetime. For these applications, it would be better to use plastics that could degrade into safe by-products under normal composting conditions [146]. Thus, blending biodegradable polymers, such as starch, PCL and PLA with non-biodegradable polymers, such as PE, has received considerable attention [19, 25, 147, 148]. The reasoning behind this approach is that if the biodegradable component is presented in sufficient amount and if it is removed by microorganisms in the waste disposal environment, the plastic containing the remaining inert components should disintegrate and disappear [52].

Starch can be used like an additive in two different ways in biodegradable plastics: it can be compounded into plastics in the form of biodegradable filler [82], which is added to various resins systems to make films that were impermeable to water but permeable to water vapour [149] and it can be plasticized with water (5%-20%) and compatibilized with other polymers to become part of the polymeric matrix. Since TPS is a very hydrophilic product, research has been performed to modify the starch structure by acetilation to reduce the hydrophilic character of the chains [150-152]. Avérous et al. [151] described changes in mechanical properties of TPS and its relationship with crystallinity, plasticizer content and water during ageing. They found that the moisture sensitivity and the critical ageing have lead to the necessity to associate TPS with another biopolymer. Association between polymers can be, as a form of blends or multilayer products. Nevertheless, most of the times compatibilization is required in order to promote adhesion between the polymers and to achieved the product specification. Many biodegradable TPS blends have been developed, such as starch/PCL, starch/cellulose acetate and starch/PLA [153, 154]. Also, this kind of materials can to be mixed with synthetic polymers (such as, PE and PP), in order to create plastic products more degradable than conventional synthetic plastics.

Blends of PE and starch can be melt-processed to obtain products with PE–like properties. Starch either in its virgin form or chemically modified, has been used to increase its compatibility with the polymer matrix, in order to produce this type of blends. It was found that the effective accessibility of the starch, which is required for extensive enzymatic hydrolysis and removal, is

achieved only if the starch content exceeds 30% [52]. However, increasing the amount of starch leads to a decrease in mechanical properties, and the resulting material has poor properties when compared to conventional polyolefins. These worsening properties arise from the different polar characteristics of starch and most of the synthetic polymers, which leads to poor interfacial adhesion. Nakamura et al. [19] investigated the incorporation of different starches (native, adipate, acetylated and cassava starch) in a LDPE matrix, to study the possibility to obtain partially biodegradable materials. The results indicated that the increase of the starch into the LDPE matrix was responsible for the reduction on mechanical properties of the products when compared with conventional LDPE (Table 1.2).

Table 1.2 Tensile test for LDPE/starch compounds [19].

Sample	σ	ε	*E*
	(MPa)	(%)	(MPa)
Pure LDPE	12.9±0.2	131.9±4.8	139.3±6.8
LDPE + 5 wt.% native starch	12.7±0.2	58.0±1.5	113.1±7.0
LDPE + 10 wt.% native starch	11.9±0.1	50.1±1.5	122.6±5.1
LDPE + 20 wt.% native starch	11.3±0.1	30.9±1.6	151.7±11.2
LDPE + 5 wt.% RD125	12.5±0.2	55.6±3.7	118.9±6.1
LDPE + 10 wt.% RD125	12.1±0.1	50.3±1.5	131.9±5.6
LDPE + 20 wt.% RD125	11.1±0.1	35.0±1.8	151.2±9.7
LDPE + 5 wt.% adipate starch	12.9±0.1	52.6±1.4	118.5±6.5
LDPE + 10 wt.% adipate starch	12.2±0.1	43.5±1.0	129.3±9.7
LDPE + 20 wt.% adipate starch	11.3±0.1	33.7±1.1	150.8±3.6
LDPE + 5 wt.% cassava starch	12.7±0.1	55.6±1.9	113.3±5.3
LDPE + 10 wt.% cassava starch	12.0±0.2	49.2±1.4	119.0±7.8
LDPE + 20 wt.% cassava starch	11.4±0.2	36.9±1.3	149.9±6.2

Therefore, a lot of research work has been done in order to improve the compatibility/adhesion between starch and PE, including the modification of starch [155-157], modification of PE [52] and/or the introduction of a compatibilizer [158-161]. The compatibilizers include, among others, ethylene-acrylic acid (EAA) copolymer, PE-g-MA and EVA. EAA is one of the most effective compatibilizer used, but it must be used in high amounts to achieve satisfactory mechanical properties. Unfortunately, EAA lowers the biodegradation rate of starch, while at the same time it

accelerates the thermo-oxidative degradation of LDPE/starch blends when used in low amounts together with a pro-oxidant [158]. The results showed that using PE-g-MA as compatibilizer, a much better dispersion of starch within the PE matrix together with a significant reduction in the phase size was achieved [52, 158, 161]. Moreover, concerning the biodegradability results, it was observed that the compatibilized blends showed a slightly lower biodegradation than the uncompatibilized ones [158, 159].

Blending PE with other biopolymers, such as PLA and PCL, has also been studied [147, 148]. Matzinos et al. [148] observed that the effect of PCL on the mechanical properties of LDPE/TPS/PCL materials depends not only on its content, but also on the final morphology.

Mihai et al. [162] and Ljungberg et al. [163] studied the miscibility of polyolefin/PLA blends, and found out that due the differences in their chemical structures, a week interfacial adhesion and poor dispersion was achieved.

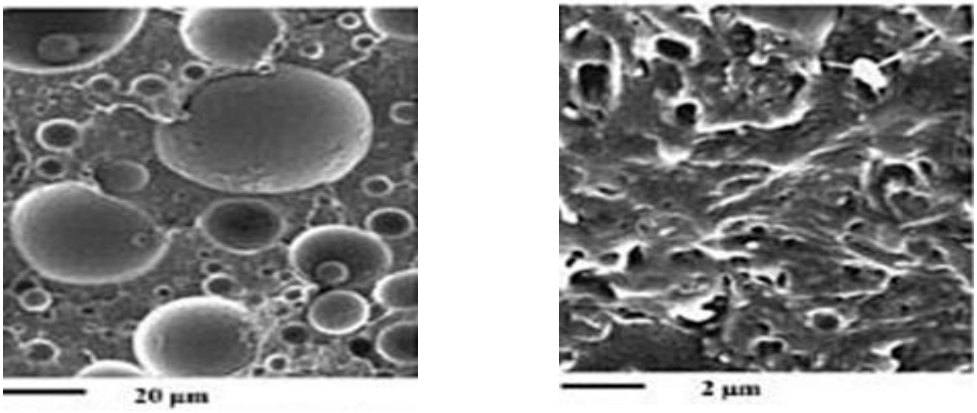


Figure 1.14 SEM micrographs of (a) 80:20 PLLA/LDPE and (b) 80:20:10 PLLA/LDPE/PE-b-PLLA blends [164, 165].

A similar system was investigated by Kramscuster et al. [164] and Shibata et al. [165], using a different approach. They used PE-b-PLLA as a compatibilizer and found out that it was possible to improve the dispersion and achieved smaller PE particles in the PLLA phase (Figure 1.14 (b)).

The above studies show a way to obtain polymers where the particle size of polymer blends is not very evident, because several parameters have to be taken into account, such as melt viscosity and elasticity, viscosity ratio, blend composition and interfacial tension. In addition, different

processing equipment, conditions and different methodologies to determine the particle size and viscosity ratio also affect the results obtained.

1.9.4 Polymer Modification

Instead of blending polymers A and B, the monomer of A can be polymerized in the presence of polymer B. The functional groups of polymer B, located along the chain or at the end, can be initiating sites, from which A chain could growth (Figure 1.15). By this way grafted or block copolymers can be formed.

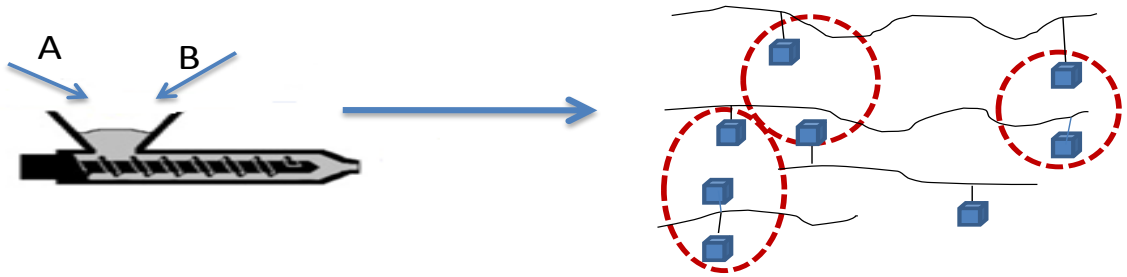


Figure 1.15 Schematic representation of *in situ* polymerization.

Generally, there are three main ways of synthesizing block or graft copolymers:

1. Living copolymerization
2. Chemical modification by post polymerization
3. Coupling between two appropriately functionalized polymer chains

Figure 1.16 illustrates schematically approaches 1 and 2, which can be associated with the "grafting from" method and the approach 3 with "grafting onto" method.

Structures of copolymers obtained through methods 1 and 2 are specifically relevant of REX, since they could not be obtained by classical copolymerization method. As referred before, the chemical reaction occurs at the interface, and thus a large quantity of copolymer is difficult to obtain. This interfacial reaction leads to compatibilization of the blends during mixing [166].

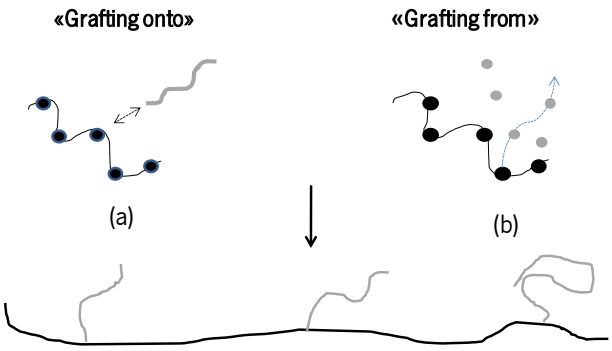


Figure 1.16 Schematic representation of "grafting onto" and "grafting from" methods [114].

1.9.4.1 Living Polymerization

Living polymerization is also called controlled polymerization. This method was developed by Michael Szwarc [167] in 1956 in the anionic polymerization of styrene with an alkali metal/naphthalene system in tetrahydrofuran (THF). This method is used for synthesizing block copolymers ROP of various cyclic biodegradable monomers such as, lactams, lactones, 1,4-dioxane-2-one, lactides and also carbonates, in a twin screw extruder, has been widely studied, due to the reaction kinetics being compatible with the process conditions (high monomer conversion in a very short range of time at high temperature and good control of the structure through the judicious choice of the polymerization catalyst). The major interest in these copolymers is also based on their potential to participate in the development of biodegradable polymeric materials.

Raquez et al. [168] published a review on specific homo and copolymerization carried out by REX, where it was showed, for the copolymerization of ε-CL with 1,4-dioxan-2-one, that in approximately 2 minutes, 100% of conversion was obtained at 130 °C using $Al(O_{sec}Bu)_3$ as catalyst. It was observed an increasing in the copolymerization yield with an increase of the molar fraction of ε-CL. The ROP of ε-CL by $Al(O_{sec}Bu)_3$ active species is well controlled and proceeds via so-called coordination-insertion mechanism, which yields polyester chains end-capped by an active aluminium alkoxide bond [169]. As a result of the trifunctionality of $Al(O_{sec}Bu)_3$, it allows the initiation and propagation of three growing polyester chains per one aluminum atom. A 3-arm star shaped PCL with a number average $\overline{Mn}$ of each arm around 200 000 $g.mol^{-1}$ have been successfully produced in the extruder within a mean residence time of less than 5 min (monomer conversions in excess of 95%) [170]. Similarly, a new process has been developed for the continuous production of PLA using REX, using tin octoate ($Sn(Oct_2)$) added with one equivalent of triphenylphosphine (as co-catalyst), which not only enhances the kinetics of LA by ROP but

also eliminates any side degradation reactions, such as, transesterification reactions [171]. Actually, it has been shown that the addition of one equimolar amount of a Lewis base like triphenylphosphine on 2-ethylhexanoic tin(II) salt ($Sn(Oct)_2$), significantly enhances the LA polymerization rate in bulk. This kinetic effect has been accounted for the coordination of the Lewis base onto the tin atom, making easier the insertion of the monomer into the metal alkoxide bond of the catalyst/propagation active species [172]. This tin alkoxide bond is formed *in situ* by reaction of alcohol and the tin(II) dicarboxylate. As reported in polymerization of ε-CL catalyzed by aluminum trialkoxides, the LA ROP proceeds via the same "coordination– insertion" mechanism involving the selective oxygen-acyl cleavage of the cyclic ester monomer. The addition of one equivalent of $P(C_6H_5)_3$ onto $Sn(Oct)_2$ allows to reach an acceptable balance between propagation and polymerization rates, so that the polymerization is fast enough to be performed through a continuous one-stage process in an extruder [173]. Using this process is also possible to produce PLA, with controlled $\overline{M}n$, by the addition of an alcohol.

Raquez et al. [174] investigated the PLA production, based on molecular parameters, using batch bulk polymerization and a single-stage continuous REX. Even though, the conversion was similar (98.5% and 99%, respectively), the time necessary to reach this conversion was very different (40 min vs 7 min). Moreover, the $\overline{M}n$ obtained was different, which was related with the diffusion and the reactivity of the monomer. Kim and White [175] described how feed rate and feed order of comonomers influenced the formation of lactam-lactone copolymers, their structure and $\overline{M}n$.

The polymerization of ε-CL and LLA, using calcium ammoniate catalyst, treated with ethylene oxide (EO) and propylene oxide (PO), was studied by Piao et al. [176]. Both exhibit high activity and they found that the living ROP behaved a quasi-living characteristic.

1.9.4.2 Chemical Modification by Post Polymerization

Another way to prepare block or graft copolymers through the "grafting from" method, consists in polymerizing a monomer in an extruder in the presence of functionalized pre-polymer or polymer (end or pendant functional groups initiating the monomer polymerization). Post polymerization modification to incorporated monomer units focus on two types of reactions. One is the removal of the protecting groups, where monomers with the desired functionality are incompatible with one or more components of the selected polymerization process. The functional monomers are polymerized with a protected functional group, which is deprotected to provide the desired functionality after the reaction is complete. The other approach is to copolymerize monomers

with one functional group, then convert that functional group into the desired functional group after the first polymerization is complete [177].
The post polymerization modification of monomer units' method has some advantages, namely that allows incorporation of functionality that is incompatible with the polymerization process, allows also the characterization of the initial copolymer prior to further functionalization and facilitates "grafting from" reactions [177].

The preparation of pre-polymers or macromonomers with functional end groups, so called telechelic polymers, is another approach to structurally unconventional architecture [178]. The functional end-groups are introduced either by functional catalyzation or end-capping of living polymers, or by a combination of the two. Therefore, monomers that were not able to copolymerize can be incorporated in a copolymer. Telechelic prepolymers can be linked together using chain extenders such as diisocyanates [179]. In this process, it is essential that the structure and end-groups of the pre-polymers can be quantitatively and qualitatively controlled [180]. REX has been used as a simple way of producing segmented copolymers [181]. Lee et. al. [182] investigated the *in situ* polymerization of caprolactam using isocyanate-terminated telechelic poly(tetramethyl ether glycol) (PTMEG). The analysis of polyetheramide triblock copolymer indicated that the conversion of caprolactam was around 95%.

A method to produce biodegradable aliphatic polyesters by REX was developed by Jacobson et al. [173]. They dedicated their studies to the effect of triphenylphosphine on the efficiency of $Sn(Oct)_2$ as a catalyst for the ROP of L,L-lactide to produce PLA. Co-rotating closely intermeshing twin-screw extruders have often been used for polymerization reactions, but in any case, the reaction time was sufficiently smaller than the residence time in the extruder. In this case, a sophisticated screw design has been used to ensure further enhancement of the polymerization reaction by using mixing elements. Under these conditions it was possible to realize a single stage process to polymerize L,L-lactide and to produce a PLA that can be used right away from the process for any known polymer processing technology.
Stevels et al. [181] reported the polymerization of L-lactide catalyzed by both, a hydroxyl-terminated PCL and a polyethylene glycol (PEG). More recently, a new process has been developed for the production of PLA using REX, based on a new catalytic system that not only enhances the ROP kinetics of L-lactide but also suppresses side and degradation reactions. This

process can be used to produce PLA continuously in larger quantities and at lower costs than before [173].

The ROP of lactones in the extruder under anhydrous conditions has also been reported and can be catalyzed by Lewis acids (ε-CL), [170, 175, 183, 184], LA [173, 185] or base (ε-CL with sodium hydride) [186]. Lewis acid catalyzed (aluminum tri-*sec*-butoxide) grafting of ε-CL on starch has been carried out under anhydrous conditions in the extruder to form high $\overline{Mn}$ grafts [184, 187, 188]. A similar process has been used to graft ε-CL on poly(ethylene-*co*-vinyl alcohol) by REX under anhydrous conditions [189, 190].

Becquart et al. [191] studied the functionalization of poly(vinyl alcohol-co-vinyl acetate)-g-CL copolymers resulting from the *in situ* polymerization of the lactone ring. They found that the -OH groups were essential to initiate the polymerization.

Jae et al.[192] dedicated their work, to the synthesis of triblock copolymers composed of PPG (polypropylene glycol) and PCL. The degree of ε-CL conversion and the $\overline{Mn}$ of PCL, increased linearly with the polymerization time or with the feed ratio of ε-CL. The study of the ROP of the ε-CL catalyzed by titanium phenoxide ($Ti(OPh)_4$) (Figure 1.17) evidenced that, on average, one phenoxide ligand initiates the ROP [193]. An increase of the polymer $\overline{Mn}$ was observed after complete monomer conversion, with a decrease of phenoxyl ester end groups concentration. Actually, this phenomenon is due to transesterification reactions favoured with end groups in case of polymerization with $Ti(OPh)_4$. In fact, the C-O bonds of phenoxyl ester terminal is more prone to nucleophilic substitution than the C-O bond in repetitive unit due to the influence of phenyl group on electronic delocalization. This leads to more selective transfer reactions and consequently to more efficiency for grafting reactions.

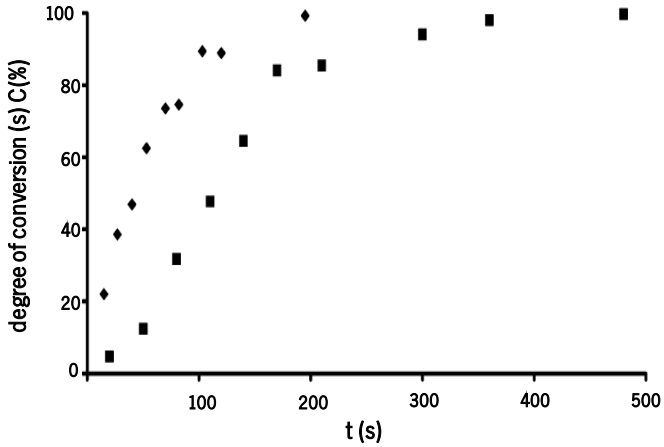


Figure 1.17 Time conversion curves for the bulk polymerization of ε-CL between the rheometer plates at T=100 °C (M_0/I_0=300) catalyzed with titanium n-propoxide (♦) or titanium phenoxide (■) [193].

1.9.4.3 Coupling Between Two Appropriately Functionalized Polymer Chains

Pesneau et al. [194] dedicated their studies to the synthesis of PBT-EVA grafted copolymers *in situ* during the processing operation by transesterification reactions between PBT and EVA, catalysed by dibutyltin oxide (DBTO). They found out that when the melt conditions enable synthesis of the grafted copolymer PBT-EVA *in situ* important changes in morphology of PE/PBT/EVA/DBTO blends are observed.

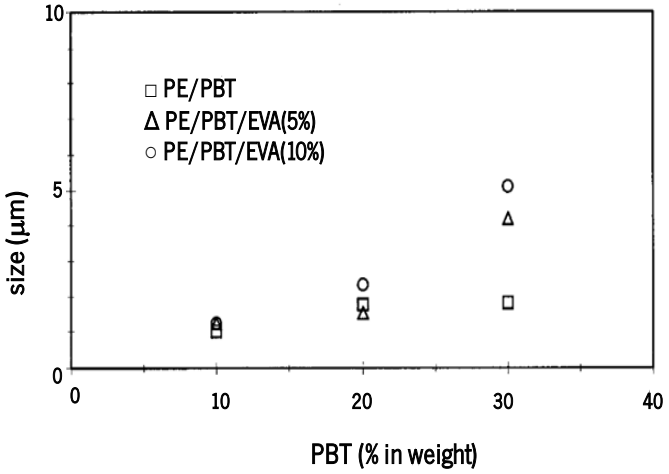


Figure 1.18 Influence of DBTO on the size of the dispersed phase [194].

Thus, the amount of grafted copolymer (PBT-g-EVA) had a significant effect on morphology, mechanical properties and rheological properties as well.

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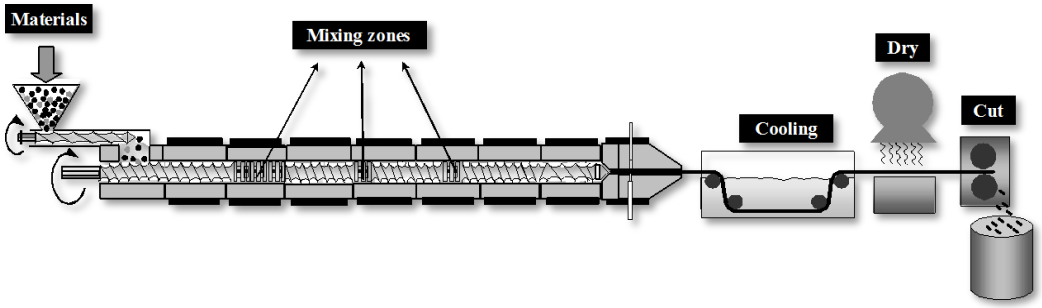
2 | Evaluation of Properties and Biodeterioration Potential of Polyethylene and Aliphatic Polyesters Blends



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2.1 INTRODUCTION

During the last decades, synthetic polymeric materials have progressively grown up to establish one of the most attractive categories of materials. This success is mainly related to their properties namely, low cost, aesthetic qualities and resistance to physical ageing and biological attacks [1]. The well known degradation difficulty of synthetic polymers, together with the growing environmental awareness and the new environmental regulations, are forcing the industries to seek for more ecologically friendly materials for their products, namely in applications where they are used for a short period of time before becoming waste. The most desirable long-term solution to this problem is the use of biodegradable plastics, which undergo degradation through the action of living organisms, the most environmentally compatible pathway for solid waste disposal [2].

Biodegradable polymers may be derived from biosources (e.g. corn or wood cellulose) or from petroleum sources [3]. The best known petroleum source-derived biodegradable polymers are aliphatic polyester and aliphatic-aromatic copolyesters. However, biodegradable polymers derived from renewable resources like polylactides (PLA) are attracting much more attention because of more eco-friendliness from their origin as contrast to the fully petroleum-based biodegradable polymers. Further, the complete biological degradability and compostability in the natural cycle and the protection of the climate through the reduction of CO_2 released are some of the other reasons why such materials have attracted the public interest [4].

Although the properties of most biodegradable polymers are comparable to many non-biodegradable plastics, the high costs and performance limitations, such as high brittleness, moisture sensitivity, low heat distortion temperature and difficult processability, have restricted the adoption of these materials to relative small niches up to now [4]. Nowadays, the challenge in replacing conventional plastics by biodegradable materials is to design materials that exhibit structural and functional stability during storage and use, being susceptible to microbial and environmental degradation using adequate solid waste management disposal practices, without any adverse environmental impact [4].

Blending biodegradable with non-biodegradable polymers is a method for reducing the overall production cost of the material, which offers simultaneously a scheme to modify both mechanical properties and biodegradation rates. The reasoning behind this approach is that, in principal, if the biodegradable component is present in sufficient amounts and if it is attacked or degraded by microorganisms in the waste disposal site, the plastic or film containing the non-biodegradable component should lose its integrity and disintegrate [5].

Among the common materials used in the packaging industry, the structure and properties of polyolefin-starch blends have been widely studied [6-14]. Blends of polyethylene with a minor amount of starch, where the former constitutes the continuous phase, can be melt processed to obtain products with polyethylene-like properties. Starch, either in its virgin form or chemically modified to increase its compatibility with the polymer matrix, has been used to form this type of blends. It was found that the effective connectivity and accessibility of the starch, which is required for extensive enzymatic hydrolysis and removal, is achieved only if the starch content exceeds 30% [5, 14]. However, increasing the amount of starch leads to a decrease in both tensile strength and elongation at break and the resulting materials have poor forming properties. These worsening properties arise from the different polar characteristics of starch from most of the synthetic polymers, which leads to poor interfacial adhesion. Therefore, a lot of research work has been done in order to improve the compatibility/adhesion between starch and polyethylene, such as the modification of starch [12, 15, 16], modification of polymeric matrix [17] and/or the introduction of compatibiliser [6, 10, 18-21] into the blends of starch and PE. The compatibilizers include the ethylene-acrylic acid (EAA) copolymer, polyethylene grafted with maleic anhydride (PE-g-MA), ethylene-vinyl alcohol (EVA) copolymer, etc. EAA is one the most effective compatibiliser used so far, but it must be used in high amounts to achieve satisfactory mechanical properties. Unfortunately, EAA lowers the biodegradation rate of starch, while at the same time it accelerates the thermo-oxidative degradation of LDPE/starch blends when used in low amounts together with a pro-oxidant [6]. The results showed that using PE-g-MA as a compatibilizer, a much better dispersion of starch within the polyethylene matrix together with a significant reduction in the phase size is achieved [5, 6, 21]. Concerning the biodegradability, it was observed that the compatibilized blends showed only a slightly lower biodegradation rate compared to their uncompatibilized materials [6, 18, 19]. Thus, even though the addition of a campatibilizer is a way to prepare biodegradable/bio-based plastic materials, some drawbacks, such as decrease of biodegration rate and toxicity take place [6, 19]. In order to overcome these disadvantages and produce materials that could be safely applied in food packaging, other compatibilizers such as citric acid have been used [22].

Blending PE with other biopolymers, such as polylactide (PLA) and poly(ε-caprolactone) (PCL), has been also studied [20, 23], in order to increase the mechanical properties of the final materials or the biodegradability. Matzinos et al. [20] found that the effect of PCL on the mechanical properties of LDPE/TPS/PCL materials depends not only on its content but on the final obtained morphology as well. However, a systematic study on biodegradability of these materials is missing.

A biodegradation test of a polymeric material is based on the incubation of the sample in the presence of microorganisms or enzymes, under defined experimental conditions. The degree of polymer biodegradation can be measured according to the mass of carbon dioxide and/or methane evolved, degradation products (e.g., monomers) released, and polymer carbon converted into biomass [24-26]. Standard test methods have been proposed by several international organizations to assess biodegradability of polymeric materials (ASTM, ISO OECD; Pagga 1997).

Thus, this work aims to prepare and evaluate the properties (mechanical and rheological) and the potential for biodeterioration of high density polyethylene (HDPE) blended with biodegradable polymers, such as PLA, PCL and Mater-Bi® (thermoplastic starch with PLA or PCL) in a co-rotating twin-screw extruder.

2.2 EXPERIMENTAL

2.2.1 Materials

High density polyethylene, HDPE 2008SN60 (MFI = 0.7 g.10 min^{-1} at 190 °C/2.16 kg), supplied by Total, polyethylene modified with maleic anhydride, PE-g-MA Lotader 3210 (MFI = 5 g.10 min^{-1} at 190 °C/2.16 kg, 3.1% weight (wt.%) Maleic Anhydride content supplied by Arkema, poly(ε-caprolactone), PCL CAPA FB100 (MFI = 0.4 g.10 min^{-1} at 190 °C/2.16 kg) kindly supplied by Solvay, and polylactide, PLA Polymer 2002D NatureWorks® (MFI = 7 g.10 min^{-1} at 210 °C/2.16 kg) from Novamont were used throughout this work. The starch-based thermoplastics (TPS), Mater-Bi®, were supplied by Novamont, Novara, Italy. Thermoplastics Mater-Bi® are blends of corn starch/poly(ε-caprolactone) (SPCL 70, 30/70 wt.%), corn starch/polylactide (SPLA 70, 30/70 wt.%) and corn starch/polylactide (SPLA 50, 50/50 wt.%). The compositions of the samples used in this work are shown in Table 2.1.

2.2.2 Compounding

All blends were tumble mixed and processed in a Leistritz LSM 30.34 laboratory modular co-rotating twin screw extruder using a barrel temperature set at 190 °C, a screw speed of 100 rpm and a throughput of 3 kg/h.

Table 2.1 Samples composition.

Sample	HDPE	PE-g-MA	PLA	PCL	Mater-Bi®
	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)
1	100	0	0	0	0
2	30	10	60	0	0
3	30	10	0	60	0
4	30	10	0	0	60[1]
5	30	10	0	0	60[2]
6	30	10	0	0	60[3]

[1] - SPLA 50 (50 wt.% TPS + 50 wt.% PLA)

[2] - SPLA 70 (30 wt.% TPS + 70 wt.% PLA)

[3] - SPCL 70 (30 wt.% TPS + 70 wt.% PCL)

The extruded material was cooled, dried and cut in small pellets. The extruder screws were design in order to contain a series of transport elements and three mixing zones improving an efficient mixing (Figure 2.1).

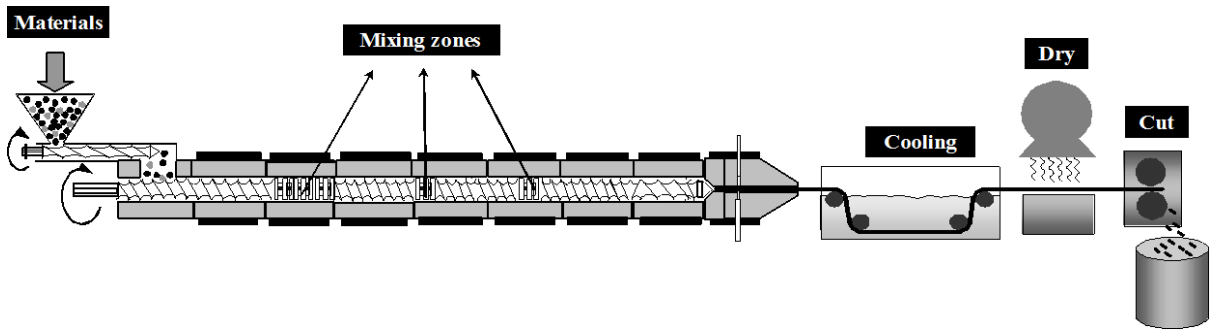

Figure 2.1 Laboratory Modular Leistritz LSM 30.34.

2.2.3 Materials Characterization

2.2.3.1 Mechanical Properties

The uniaxial tensile properties were evaluated in an Instron 4505 Tensile Machine at room temperature using a crosshead speed of 50 mm/min, relative humidity of 50% and temperature 23 °C. The tests were performed using dumbbell specimens previously injection moulded. An extensometer was used to collect low-strain data to measure the Young's modulus. At least 10 specimens of each sample were

tested. Prior to mechanical measurements, the samples were dried at 50 °C during 24 hours in a vacuum oven.

2.2.3.2 Scanning Electron Microscopy

After fracture of the samples in liquid nitrogen and gold plating, the morphology of the blends was studied using a FEI Quanta 400 Scanning Electron Microscope.

2.2.3.3 Melt Flow Index

The Melt Flow Index (MFI) of HDPE and all blends produced in the above conditions was measured in a Ceast plastometer according to the ASTM standard D 1238, at 190 °C/2.16 kg.

2.2.3.4 Rheological Measurements

The samples were characterized in steady shear flow in an Advanced Capillary Rheometer Rosand/Bohlin Instruments RH10. The shear experiments were performed at 190 °C in a range of shear rates from 100 s^{-1} to nearly 2000 s^{-1}, which easily covered the typical extrusion shear rates The tests were performed two times for each condition, being found an experimental error less than 10%.

2.2.3.5 Contact Angle

A DataPhysics equipment was used to measure the contact angle of liquids with known surface tension on HDPE and polymer blends films, using a dynamic angle. The evolution of the droplet shape was recorded. A CCD video camera and image analysis software were used to determine the contact angle evolution. The polar liquids used in this study were water (surface tension of 73.05 mN/m), ethylene glycol (surface tension of 48.40 mN/m) and methylene iodide (surface tension of 50.76 mN/m) [27]. The dynamic contact angle of each liquid was measured directly on the polymer film, 3 readings were averaged. The Owens method was used to determine the surface free energy of the polymer films from the contact angles of the three different liquids.

2.2.3.6 Microbial Growth Test

The potential for biodeterioration of the blends was assessed by the microbial growth test. The growth of a pure culture of *Pseudomonas fluorescens* was evaluated as a function of time with HDPE and all the polymer blends (Table 2.1) as sole carbon and energy sources. *Pseudomonas fluorescens*, an obligate heterotrophic bacterium indigenous in soil, was chosen as the test specimen because it has

been extensively used in biodegradation studies of aromatic compounds [28] and polymers [29-31]. The experimental procedure was adapted from ASTM G 22-76 (the essays were carried out in liquid phase instead of solid phase). The hypothesis underlying the method is that the growth of *Pseudomonas fluorescens* in a carbon-free media with polymer as the sole carbon source is due to polymer carbon converted into biomass. Each sample, shaped as a disc with 25 mm diameter and thickness of 0.25 mm, was decontaminated with ethanol 70% (v/v) and placed into sterilised conical shaped 100 mL Erlenmeyer flasks containing 40 mL of R2A carbon free medium at pH 7.0. Each flask contained one disk divided into two halves. The disk's density was lower than the water density. The flasks were closed with stoppers connected to air filters and spiked with the pure culture directly from an agar plate and incubated under static conditions at room temperature (22 °C) during 10 weeks.

Bacterial density on the surface of the polymer, forming a biofilm, was monitored by carrying out a series of total cell counts over a period of 10 weeks. Cells were enumerated by epifluorescence microscopy after DAPI staining (5 min, 2 mg/L final concentration) at 1000× magnification. Fifteen fields were counted per filter for a total of 400 microorganisms. Previously to cell enumeration, the biofilm was detached from the polymer surface in a ultrasound bath (15 min, 60 Hz) and homogenized (20 min) using a tissuemizer with SBS-dispensing tool. Each measurement was carried out in duplicate and a t-test was used where specific means were being compared. Acceptance or rejection of the null hypothesis was based on a α-level of 0.05 in all cases [32].

2.3 Results and Discussion

2.3.1 Blends Properties

Elongation at break, Young modulus and tensile strength results for all tested samples are depicted in Figures 2.2 to 2.4, respectively. As expected, the mechanical properties depend on the blend composition. The addition of PLA (sample 2) or PLA and Mater-Bi® (samples 4 and 5) to HDPE increased the stiffness, yielding a material with a higher modulus (1129, 825 and 804 MPa, respectively compared to 550 MPa of HDPE) and a lower elongation at break (6, 3 and 3.1%). Conversely, the addition of PCL (sample 3) or PCL and Mater-Bi® (sample 6) led to higher flexible materials, i. e., increased the elongation at break and decreased the Young modulus.

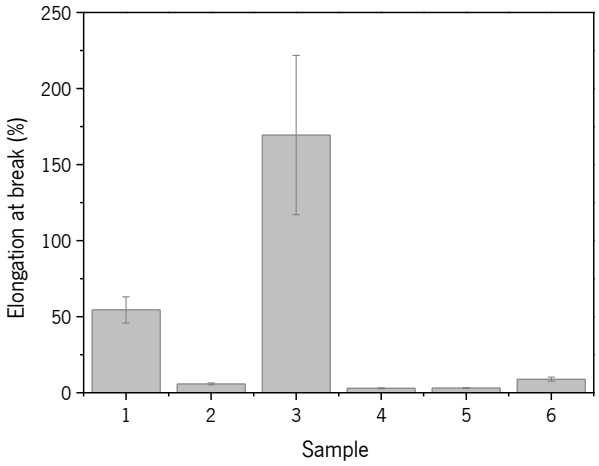

Figure 2.2 Elongation at break for HDPE and all blends.

Elongation at break increased from 55 to 180% while Young modulus decreased from 550 to 137 MPa. This effect was however moderate if TPS is also added, as it occurred in sample 6.

Concerning the tensile strength results, the higher tensile strength was obtained for the materials containing PLA. A significant improvement of 42% was observed by the addition of PLA itself (sample 2), whereas for the other samples a lower value than the one obtained for HDPE was achieved. Samples containing PCL, i.e., samples 3 and 6, exhibited a decrease of 37% and 23%, respectively. Regarding the effect of the Mater-Bi®, the results showed that for the same starch level (samples 5 and 6) the final mechanical properties were controlled by the amount of PLA and PCL. The addition of starch-based thermoplastic had a minor effect on mechanical properties.

This behaviour can be explained by the mechanical properties of the individual components (HDPE, PLA, PCL and TPS) and by the morphology of the blends. As it is known, HDPE has good mechanical properties, both elongation at break and modulus. Conversely, PLA and TPS are materials with high stiffness, high modulus and low elongation at break while PCL has low modulus and high elongation at break. The differences in mechanical properties of these polymers can be related with the chemical structure. When compared to PLA, PCL contains a major aliphatic chain having more mobility and flexibility, which explains the high elongation at break.

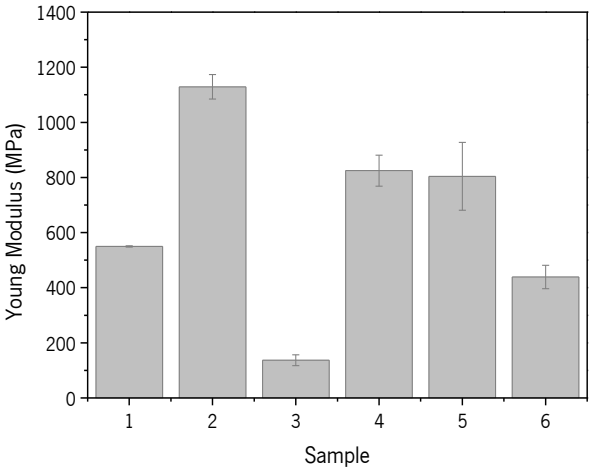

Figure 2.3 Young modulus for HDPE and all blends.

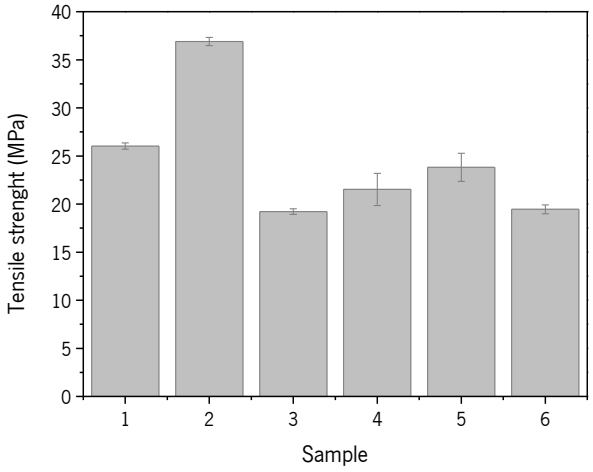

Figure 2.4 Tensile strenght for HDPE and all blends.

Since the mechanical properties depend on the morphology of the polymer blend it is crucial to study it. Usually, the minor component of the blend forms the dispersed phase, whereas the major component forms the continuous. The morphology of the blends is controlled by the processing conditions, composition, as well as the nature of the polymers (interfacial tension and viscosity ratio). Figure 2.5 depict the morphology of all studied samples, it can be observed that the adhesion between PLA and HDPE is not good (Figure 2.5 (a), sample 2), homogeneous elongated droplets of HDPE can be detected in the PLA matrix. Even with the addition of PE-g-MA, which acts as a compatibilizer by increasing the interfacial adhesion due to the chemical interaction between the hydroxyl groups of PLA and anhydride groups of PE-g-MA, the adhesion is not good enough to improve the elongation at break. In fact, the elongation at break of sample 2 is similar to the value observed for PLA.

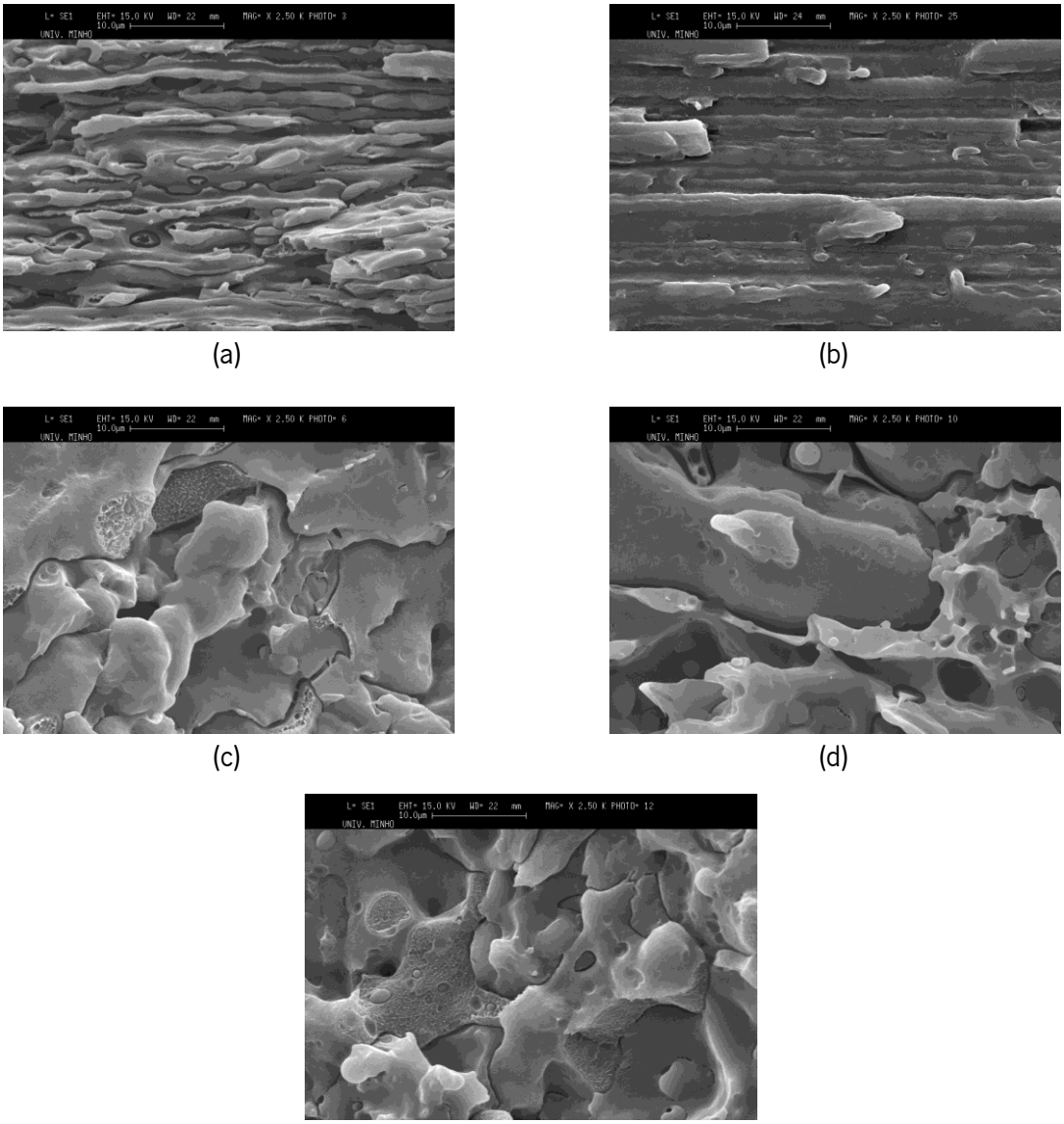

Figure 2.5 SEM micrographs of blends with (a) PLA, (b) PCL, (c) SPLA 50, (d) SPLA 70 and (e) SPCL 70.

In Figure 2.5 (b) (sample 3) it is not easy to distinguish both polymers, indicating a good adhesion between PCL and HDPE. The differences observed in morphology when either PLA or PCL are added, can be due to their chemical structures. As it is known, the ratio between ester links/aliphatic chain is higher for PLA than for PCL affecting the polarity [33]. Thus, the polarity of PLA is higher than that of PCL and consequently the compatibility of PCL with HDPE is better.

The morphology of all HDPE/Mater-Bi® blends (Figures 2.5 (c) to (e), samples 4, 5 and 6) is similar, the individual components of the blends can be detected, which can be associated with the interfacial tension among the components. As in the case of the PLA, the addition of PE-g-MA was not efficient enough to promote a good adhesion between the blend components.

MFI and shear steady viscosity at 190 °C in the shear rate range between 100 s^{-1} and 2000 s^{-1} for PE and all produced blends are presented in Table 2.2 and Figure 2.6, respectively, in order to evaluate its processability. As it can be seen, the final MFI of the samples ranged between the MFI of each individual component, keeping in a general way the value of the polymer present in higher amount (in the case of PLA and PCL). Concerning the effect of the Mater-Bi® addition, the results showed that increasing the starch-based thermoplastic quantity led to a material with a higher MFI value.

Table 2.2 MFI at 190 °C and surface energy of all samples.

Sample	1	2	3	4	5	6
MFI (g/10 min)	0.79±0.00	7.61±0.16	3.16±0.04	0.50±0.01	1.81±0.01	1.47±0.01
Surface energy (nM/m)	31.9	40.2	34.9	40.0	41.3	36.5

Shear viscosity measurements showed that HDPE and sample 4 exhibited the highest values, as anticipated from the above MFI results. The effect of the addition of a biodegradable polymer to HDPE is also in accordance with the MFI results, being the lower viscosity observed for blends with PLA and PCL (samples 2 and 3) and slightly higher for Mater-Bi®. Furthermore, it can be observed that the blend with higher starch-based thermoplastic content (sample 4) showed a higher viscosity. This behaviour, i. e., an increasing in the viscosity for a rising level of TPS, was also observed in previous works [34, 35]. For processing purposes, the above mentioned results show that blending HDPE with biopolymers leads to materials which can be extruded more easily. However, in order to overcome some potential processing difficulties, care must be taken concerning to the set extrusion temperature profile.

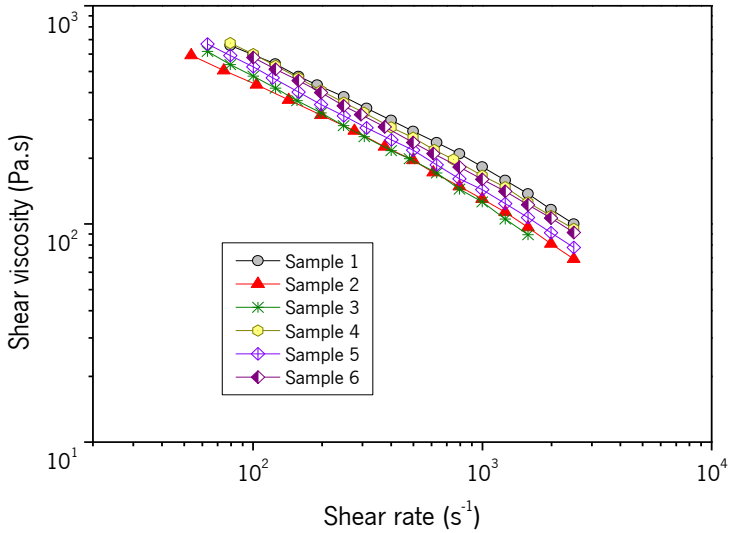

Figure 2.6 Shear viscosity for HDPE and all blends at 190 °C.

Surface tension can be defined as the amount of work necessary to form a new part of surface (against air or vapour) [36]. Since the aim of this work is to evaluate the biodetioration potential through bacterial growth attached to the polymer surface, measurements of surface tension can be very useful to correlate with the microorganisms' adhesion onto polymer surface. It is known, that the lowest the surface energy the worst adhesion is achieved between the microorganisms and the polymer surface [37]. The data presented in Table 2.2 shows the results obtained for all the samples, which exhibit surface energy values in the range 31.9-41.3 mN/m.

All samples have higher surface energy than HDPE (sample 1). The latter has a highly hydrophobic macromolecular chain explaining the low surface energy value obtained [37]. It was observed that the addition of PLA increased the surface tension of 26% while PCL contributed only to an increase of 9.4%. On the other hand, for the samples with Mater-Bi®, the ones with PLA (samples 4 and 5) have similar results to sample 2. The same behaviour was observed for samples 3 and 6. These values indicated that the addition of starch-based thermoplastic had an insignificant effect on the surface tension.

2.3.2 Biodeterioration Potential of Blends

Blends were incubated in the presence of *Pseudomonas fluorescens*, under defined experimental conditions, and an increase of cell counts along time was observed in the biofilm formed on the surfaces of samples 2 to 6, as depicted in Figure 2.7. HDPE (sample 1) shows the lowest cell count while HDPE/SPLA 50 (sample 4) exhibits the highest. This result might be related with both surface

energy, being lower for HDPE thus unfavourable to cell adhesion [37], and resistance to microbial attack, which is lower for HDPE/SPLA 50 due to the presence of starch and PLA [33].

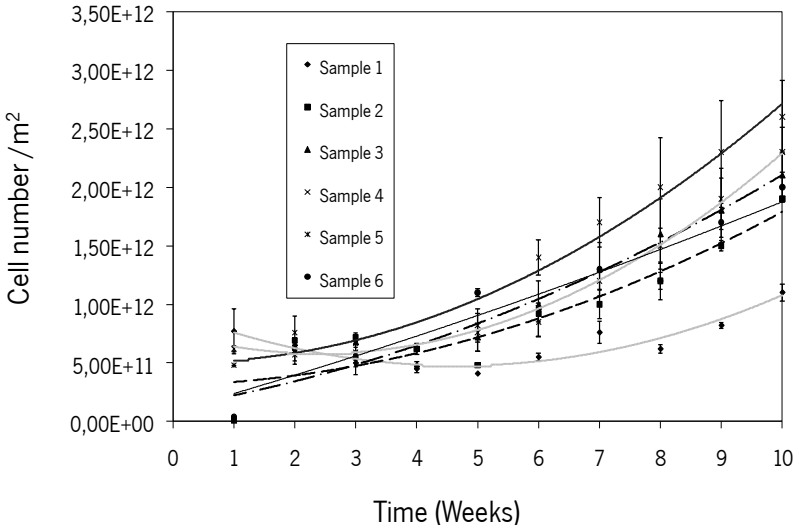

Figure 2.7 Growth curves of *Pseudomonas fluorescens* in the biofilm formed on the surface of polymeric materials as determined by bacterial counts.

The ratio between bacterial counts in the biofilm obtained after ten and two weeks of experiment lifetime for samples 1, 2 and 3 (Table 2.3), presents the highest value in the case of HDPE/PCL blend (sample 3), suggesting that PCL is less resistant to bacterial attack than PLA. Massardier-Nageotte et al. [25] reported that PCL and a TPS/PCL blend seemed to be rather biodegradable in opposition to PLA, in a biodegradability study carried out under aerobic conditions and in liquid phase.

The effect of increasing amounts of starch-based thermoplastic (0%, 18% and 30%) on the biodeterioration's potential of PLA blends are presented in Table 2.3. The present study indicates that the ratio between bacterial counts obtained after ten and two weeks of experiment lifetime is not significantly different in the cases of the blends containing 0% and 18% of starch but increases significantly in the case of 30% (t-test). The results suggest that the amount of starch might have been to low or simply not available at the polymer's surface for bacterial growth in the case of the blend containing 18% starch. At 30%, starch decreased the resistance of the blend to bacterial attack and promoted microbial growth. This result might be attributed to crystallinity and hydrophobicity of starch [12]. Usually, the biodegradation occurs preferably in the amorphous regions because of the higher mobility of the chains and their higher accessibility to the microorganisms. Starch, being less crystalline compared to PLA, is more prone to microbial attack. Additionally, its hydrophilic nature characterized by a higher number of hydroxyl groups in structure compared to the one present in PLA promotes swelling

in the culture medium enhancing biodeterioration. The effect of 18% starch-based thermoplastic on the biodeterioration's potential of a PCL blend (sample 6) was not significant (Table 2.3), as in the case of PLA and the same explanation for the observed result might be feasible. However, more detailed knowledge on the kinetics of the biological reactions and its products needs to be gained and further work is required.

Table 2.3. Ratio between the biofilm bacteria number on polymeric surface quantified in the 10th week and in the 2nd week of experiment lifetime (values listed in the table are the average ± 95% confidence interval).

Sample number	Cell number ratio (10^{th} week/2^{nd} week)
1	1.75±0.14
2	2.71±0.31
3	3.49±0.80
4	4.59±1.21
5	2.98±0.83
6	3.29±0.27

2.4 CONCLUSIONS

The purpose of this work was to prepare and evaluate the properties of blends of non-biodegradable polymers (HDPE) and biodegradable polymers, such as polylactide, poly(ε-caprolactone) and Mater-Bi® (including PLA/TPS or PCL/TPS). Samples were prepared in a co-rotating twin-screw extruder in order to improve mixing.

The uniaxial tensile tests showed that the addition of PLA leads to materials with a higher modulus and a lower elongation at break than HDPE. Conversely, the addition of PCL increases the elongation at break and weakens, as expected, the Young modulus. The addition of Mater-Bi® has a minor effect on mechanical properties. The rheological results showed that the shear viscosity of all samples is lower than that measured for HDPE, indicating that the blends are easily processed.

In considering the biodeterioration potential of the blends, it was found that HDPE/PCL has a lower resistance to bacterial attack than HDPE/PLA verified by a higher cell number on its surface after 10 weeks of incubation. The addition of 30% starch to the HDPE/PLA blend enhanced its biodeterioration potential, the same was not observed in the case of the HDPE/PCL blend containing only 18% starch.

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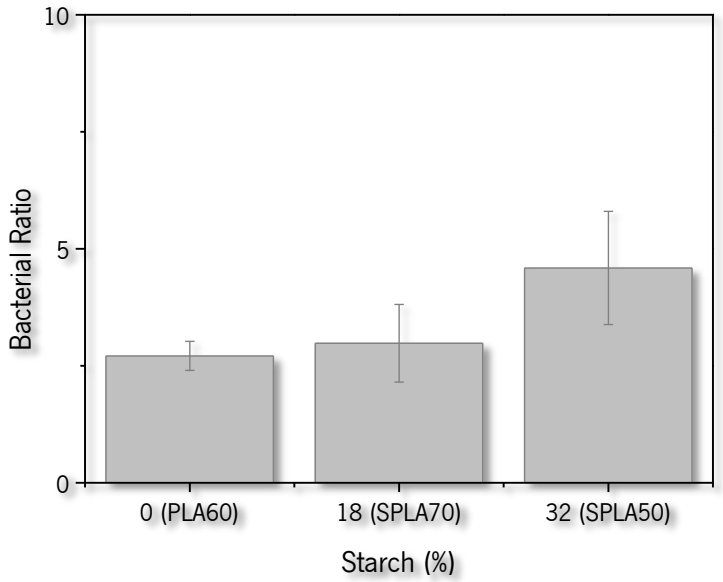
3 | Biodegradability Assessment of Aliphatic Polyesters-Based Blends Using Standard Methods



Moura, I. Machado, A.V. Duarte, F. M. Nogueira, R. 2011. Journal of Applied Polymer Science 19: 3338-3346.

3.1 INTRODUCTION

The demand of synthetic polymeric materials has been fairly increasing during the last decades and presently they are one of the most attractive categories of materials. This success is mainly related to their properties namely, low cost, aesthetic qualities, and resistance to physical ageing and biological attack [1]. Polyolefins are the synthetic polymeric materials with the highest commercial success, accounting for more than 47% of Western Europe's total consumption, 24.1 million tonnes per year. Polyolefins present a combination of physical properties (e.g. flexibility, strength, lightness, stability, impermeability, and easiness of sterilization) that are ideally suited to a wide variety of applications, such as, agricultural film, food and drinks packaging [2]. However, these polymers have poor oxygen barrier properties and a well known resistance to degradation [3, 4].The growing environmental awareness and the new environmental regulations are forcing the industries to seek for more ecologically friendly materials for their products, namely in applications where they are used for a short period of time before becoming waste.

Biodegradable polymers are derived from renewable (corn or wood cellulose) or petroleum sources. The best known petroleum source-derived biodegradable polymers are aliphatic polyesters or aliphatic-aromatic copolyesters [5]. As an example, poly-(ε-caprolactone) (PCL), generally prepared from the ring-opening polimerization of ε-caprolactone is a flexible aliphatic semi-crystalline polyester and it has been found to be miscible with many other polymers [6, 7]. Also, PCL is appreciated by its biodegradable properties, since it can be biodegraded aerobically by a large number of microorganisms in various microbiological environments [7]. However, the high cost and low performance of PCL has prevented its widespread industrial use [8].

Presently, biodegradable polymers derived from renewable sources like polylactides (PLA) compete with petroleum-based biodegradable polymers [9]. The production of PLA presents advantages over other synthetic materials: i) PLA can be obtained from renewable agricultural sources (e.g. corn) ii) its production consumes carbon dioxide, providing significant energy savings, and iii) PLA is recyclable and compostable [10-12]. Early economic studies have shown that PLA is an economically feasible material to be used as a packaging material [13]. Medical studies have shown that the level of acid lactic (LA) that migrates to food from packaging containers is much lower than the amount of LA used in common food [14]. The properties of PLA are determined both by the polymer architecture (stereochemical make up of the backbone) and the molar mass, being the latter controlled by the addition of hydroxylic

compounds. The ability to control the polymer's stereochemical architecture allows precise control over the speed of crystallization and the degree of crystallinity, the mechanical properties, and the processing temperature of the material [14]. PLA is a polyester with one of the highest melting temperatures, around 160-180 °C, thus is less susceptible to biodegradation. PLA biodegradation also depends on its crystallinity, molar mass, shape and morphology [15].

Blends of biodegradable and non-biodegradable polymers have low production costs and better mechanical properties than pure biodegradable polymers. As an example, polyolefin-starch blends commonly used in the packaging industry [16], have better mechanical properties compared to starch, and enhanced biodegradability in relation to pure polyolefin's.

Important information concerning polymer's final fate in the environment can be achieved in biodegradation studies performed in the aquatic environment. Environmental biodegradation concerns the complete conversion of organic chemicals to inorganic products mediated by microbial processes. Standard test methods have been proposed by several international organizations to assess biodegradability of polymeric materials (ASTM, ISO, OECD) [17]. All of these tests simulate natural conditions. Polymers biodegradation can be measured according to the carbon dioxide mass and/or methane evolved, oxygen consumption, degradation products released (e.g., monomers), and polymer carbon converted into biomass [17-19]. Literature studies report that two main steps are involved in the biodegradation of polyesters. Firstly, embrittlement of the polymer occurs due to random non-enzimatic chain scission of the ester groups in the polymer backbone leading to a reduction in polymer's molar mass [10, 14]. Secondly, low molar mass oligomers diffuse out of the bulk polymer and are used by microorganisms yielding degradation products [14]. The biodegradation rate of polymers can be affected not only by the degradability of the blend components themselves but also by several parameters, such as molar mass, phase structure (miscibility and crystallinity), surface blend composition, molecular structure, the length of the polymer chain and melting temperature [20-22]. Generally, a polymer having a lower melting temperature is more susceptible to biodegradation than one having a higher one because the polymeric chain is more flexible and can fit more easily into the active sites of enzymes [20]. Factors related to surface conditions can also affect the biodegradability, as surface area, hydrophilic and hydrophobic properties [23].

The purpose of this study was to evaluate the aerobic biodegradability of aliphatic polyesters based blends using standard methods. Many studies on PCL and PLA in solid state, have exhibited significant biodegradation within several days in water with activated sludge [18], nevertheless there has not been

done any study which compares biodegradability by two different methods. This work investigates and compares the biodegradability of high density polyethylene (HDPE) blended with biodegradable polymers, polylactic acid (PLA), poly (ε–caprolactone (PCL) and Mater-Bi (thermoplastic starch with PLA or PCL) under different testing methods of existing standards. Thus, our research focuses on the addition of biodegradable polymers to HDPE, as a blend with improved mechanical properties maintaining their biodegradability [5].

3.2 Materials and Methods

3.2.1 Materials

Materials used in the present study are commercially available. High density polyethylene (HDPE), 2008SN60, was provided by Total, polyethylene modified with 3.1 (wt.%) maleic anhydride (PE-g-MA), Lotader 3210, was supplied by Arkema, poly(ε-caprolactone) (PCL), CAPA FB100, was supplied by Solvay, and polylactide (PLA), Polymer 2002D NatureWorks®, was obtained from Novamont. Starch-based thermoplastics (TPS), Mater-Bi®, were supplied by Novamont. Mater-Bi® are commercially available as blends of corn starch/poly(ε-caprolactone) 30/70 (wt.%), SPCL 70, corn starch/polylactide 30/70 (wt.%), SPLA 70, and corn starch/polylactide 50/50 (wt.%), SPLA 50.

3.2.2 Blends Preparation

To compound the blends used in the present study (Table 3.1), materials were tumble mixed and processed in a laboratory modular co-rotating twin screw extruder (Leistritz LSM 30.34) using a barrel temperature of 190 °C, a screw speed of 100 rpm and a throughput of 3 kg/h. The extruded material was air cooled, dried and cut in small pellets.

Table 3.1 Composition of the blends expresses as weight percentages.

Blend	HDPE	PE-g-MA	PLA	PCL	Mater-Bi®
	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)
PLA 60	30	10	60	0	0
PCL 60	30	10	0	60	0
SPLA 50	30	10	0	0	60 (50 TPS + 50 PLA)
SPLA 70	30	10	0	0	60 (30 TPS + 70 PLA)
SPCL 70	30	10	0	0	60 (30 TPS + 70 PCL)

3.2.3 Biodegradation Tests

The aerobic biodegradation of the blends prepared in the present work was investigated using two distinct methods: microbial growth in polymeric films and biochemical oxygen demand.

3.2.3.1 Microbial Growth Test

The growth of a pure culture of *Pseudomonas fluorescens* was evaluated as a function of time with HDPE and the polymeric blends previously described (Table 3.1) as sole carbon and energy sources. The experimental procedure was adapted from ASTM G 22-76 (the essays were carried out in liquid phase instead of solid phase) [24]. Each sample, shaped as a disc with 25 mm diameter and thickness of 0.25 mm, was decontaminated with ethanol 70 % (v/v) and placed into sterilised conical shaped 100 mL Erlenmeyer flasks containing 40 mL of R2A carbon free medium at pH 7.0. Each flask contained one disk divided into two halves and the disk's density was lower than the water density. The flasks were closed with stoppers connected to air filters and spiked with the pure culture directly from an agar plate and incubated under static conditions at room temperature (22 °C). Bacterial density on the surface of the polymer, forming a biofilm, was monitored by total cell counts over a period of 10 weeks. Cells were enumerated by epifluorescence microscopy after DAPI staining (5 min, 2 mg/L final concentration) at 1000 magnification. The detailed methodology is described in Machado et al. (2007).

3.2.3.2 Biochemical Oxygen Demand Test

Biodegradation tests were carried out in aqueous environment under aerobic conditions according to the standard ISO 14851:1999 (Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium) [25] which specify a method for determining the biochemical oxygen demand (BOD) in a closed respirometer. Polymers were reduced to powder to create a suspension of the polymer in the test system. The Oxitop system used in the determination of BOD contains an individual number of reactors consisting of glass bottles with a carbon dioxide trap (sodium hydroxide) in the headspace. The bottles are supplied with a magnetic stirrer and sealed with a cap containing an electronic pressure indicator. BOD determinations were carried out in 510 mL bottles containing 62.5 mg of the test blend, 2 mL of inoculum and 50 mL of mineral medium. The mineral medium contained 40 mL/L of solution A (28.25 g/L KH_2PO_4, 146.08 g/L K_2HPO_4), 30 mL/L of solution B (3.36 g/L $CaCl_2.2H_2O$, 28.64 g/L NH_4Cl), and 30 mL/L of solution C (3.06 g/L $MgSO_4.7H_2O$, 0.7 g/L $FeSO_4.7H_2O$, 0.4 g/L $ZnSO_4$). The source of inoculum was activated sludge freshly sampled from a municipal sewage treatment plant. The BOD of the inoculum was determined in blank tests performed

only with mineral medium and inoculum. These values were subtracted from the BOD values of the blends to obtain exact values of the degradation activity. Test bottles were incubated at 30 °C in the dark with stirring for more than 28 days. The experiments were carried out with and without nitrification inhibitor, allylthiourea (ATU), at a concentration of 10 mg/L, in triplicate. The amount of O_2 consumed in polymer's biodegradation (after correction with the blank test) was expressed as a percentage of the theoretical oxygen demand (ThOD). The ThOD expressed as mass of O_2 per mass of polymer was determined by calculating the amount of O_2 necessary for aerobic mineralization of the polymer, i.e. complete oxidation of C to CO_2 [26]. The ThOD of the polymer $n(C_cH_hO_o)$, with a relative molecular mass $\overline{Mr}$ (per monomer), was calculated according to:

$$\mathrm{ThOD} = \left(\frac{31.9988}{M_r} \right) \cdot (c + 0.25h - 0.5 \cdot o) \qquad \text{Equation (1)}$$

3.2.4 Characterization Methods

The composition of all samples was determined by elementary analysis on a LECO CHNS-932.

The samples' chemical formulas are the following: PLA 60 - C_3H_8O; PCL 60 - $C_5H_{10}O$; SPLA 50 - C_5H_9O; SPLA 70 - C_3H_4O; SPCL 70 - C_3H_7O.

The biodegradation of the polymers and blends was followed by FTIR spectroscopy (Perkin Elmer 1720 spectrometer). Measurements were recorded in a transmittance mode in the range of 4400 - 400 cm^{-1}, using 16 scans with a resolution of 4 cm^{-1}. Thin films of the initial materials and the residues after biodegradation were prepared by compression-moulding and analyzed directly using a solid film support.

3.3 Results and Discussion

3.3.1 Biodeterioration of Polymer Films by the Microbial Growth Method

Blends were incubated in the presence of *Pseudomonas fluorescens* under defined experimental conditions according to the standard ASTM G 22-76 which specifies a method for determining the microbial growth of a test microorganism. An increase of bacterial ratio along time was observed in the biofilm formed on the surfaces of all blends (Table 3.2).

Table 3.2 Ratio between the biofilm bacteria number on polymeric surface quantified in the 10th week and in the 2nd week of experiment lifetime (values listed in the table are the average ± 95% confidence interval).

HDPE	PLA 60	PCL 60	SPLA 50	SPLA 70	SPCL 70
1.75± 014	2.71±0.31	3.49±0.80	4.59±1.21	2.98±0.83	3.29±0.27

HDPE, used as a negative control, showed the lowest cell count ratio while SPLA 50 exhibited the highest. There could be two main factors that contributed to the experimental results obtained: on the one hand HDPE has a lower surface energy being a less favourable material to cell adhesion [27], on the other hand resistance to microbial attack is lower for SPLA 50 due to the presence of starch and PLA [28]. The cell count ratio of PCL 60 was higher than the one of PLA 60, as depicted in Table 3.2, suggesting that PCL is less resistant to bacterial attack than PLA. This result might be explained based on chemical structure [29]. Due to the stereochemical structure of PLA, it can promote sterique hindrance and make the hydrolysis more difficult. Another parameter that become PLA less susceptible to biodegradation than PCL, has been related with melting temperature [15]. Polymers with low melting temperature are more susceptible to biodegradation because the polymeric chains are more flexible and the enzymes active sites can fit easily into them. Since PCL has lower melting temperature than PLA, it would facilitate the microorganism attack resulting in higher biodegradation. The blends morphology could also explain this difference [5]. While PLA 60 exhibits a coarse morphology, PCL 60 has smaller particles and low interfacial tension with HDPE.

The present study indicated (Figure 3.1) that the bacterial ratio obtained after ten and two weeks of experiment lifetime was not significantly different in the cases of PLA blends containing 0% (PLA 60) and 18% (SPLA 70) of starch but increased significantly in the case of 30% (SPLA 50) (t-test). The results suggested that the amount of starch might have been too low or simply not available at the polymer's surface for bacterial growth in the case of the blend containing 18% starch (SPLA 70).

These results might be explained by the physico-chemical properties of starch, namely crystallinity and hydrophobicity [30]. Usually, biodegradation occurs preferably in the amorphous regions of the polymer that have a higher mobility of the polymeric chains and therefore are more accessible to the microorganisms. Starch, being less crystalline than PLA, was more prone to microbial attack. Additionally, the hydrophilic nature of starch, characterized by a higher number of hydroxyl groups in its structure as compared to the one present in PLA, promotes swelling and hydrolysis of the polymer matrix enhancing biodeterioration [31]. The effect of 18% starch-based thermoplastic in the biodeterioration potential of the PCL blend (SPCL 70) was also not significant (Table 3.2) and the

explanation is identical to the one of PLA blend (SPLA 70), as mentioned before.

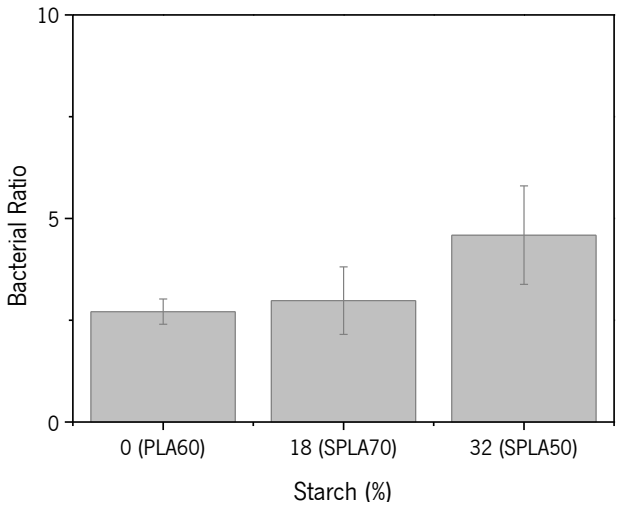


Figure 3.1 Bacterial ratio as function of % starch (0, 18 and 32%).

FTIR analysis of polymeric blends was made before and after the biodeterioration assay. There are no significant changes in both spectra. One possible explanation for this result is that bacteria mainly attacked the surface of the polymer in the amorphous phase and chain scission was not significant to be detected by FTIR.

3.3.2 Biodeterioration of Polymer Particles by the BOD Method

The biochemical oxygen demand of polymers (HDPE, PCL and PLA) and blends (PCL 60, PLA 60, SPLA 50, SPLA 70, and SPCL 70) was determined in a closed respirometer (ISO 14851: 1999) during 40 days. Biodegradability values were expressed as the amount of O_2 consumed during sample biodegradation divided by their theoretical oxygen demand (ThOD) and are presented in Figure 3.2. The experimental results suggested that PCL was more biodegradable than PLA. A similar result was obtained in the case of the blends containing either PCL or PLA, being PCL 60 more biodegradable than PLA 60. The biodegradability of PLA was increased by the addition of increasing amounts of starch, and the same was observed for PCL. The HDPE's biodegradability was negligible compared to the other polymers and blends. The biodegradability of the PLA blend increased significantly by the addition of 18% starch (t-test) which was not observed in the case of the PCL blend. Further increase on starch in the PLA blend to 30% did not increase its biodegradability significantly.

Results obtained by the BOD method are mostly in agreement with those obtained by the microbial growth method. Differences might be attributed to a reduced accessibility of microorganisms to

polymers when present in the shape of polymeric film. Ammonium ions, present in the mineral medium used in the BOD method, are a source of nitrogen for the growth of carbon oxidizing microorganisms and, given sufficient time, might also be oxidized to nitrate by autotrophic microorganisms (nitrification process). This reaction does not contribute to the metabolism of organic carbon but consumes oxygen which is quantified in the method [32].

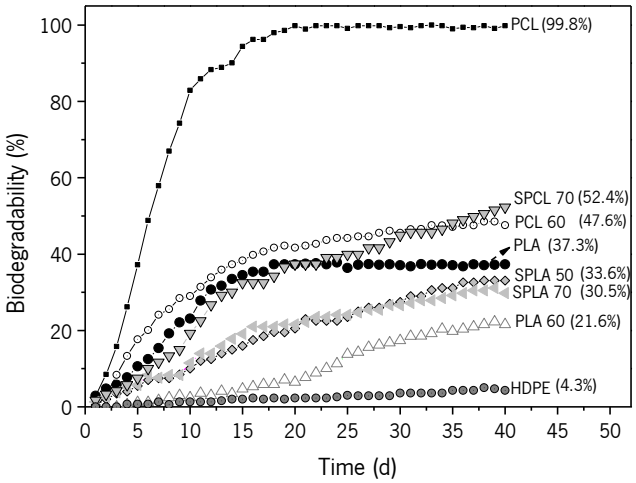


Figure 3.2 Percentage of biodegradation of the polymers and blends, without nitrification inhibitor according to ISO 14851:1999.

To assess the contribution of autotrophic ammonium oxidation to oxygen consumption, biodegradability of polymers and blends were also determined in the presence of allylthiourea (ATU), a specific inhibitor of the nitrification process. It was found a reduction of the biodegradability of polymers and blends in the presence of ATU, as depicted in Table 3.3. These results suggested that in the present study biodegradability determined in the absence of ATU is overestimated. In view of these findings, the use of ATU or the adjust of the C/N ratio present in the mineral medium to minimise oxygen consumption in the oxidation of ammonium ions in the BOD method was proposed.

Table 3.3 Biodegradation (BOD/ThOD) of polymers and blends (40 d essay) determined by the BOD method with and without nitrification inhibitor (values listed in the table are the average ± 95% confidence interval).

Sample inhibitor	BOD (mg/L O_2)		ThOD (mg/L O_2)	BOD/ThOD	BOD/ThOD
	Without	With		Without	With
HDPE	103±66	87±36	4477	0.02	0.02
PCL	2522±397	1683±99	2527	1.00	0.66
PLA	597±115	228±99	1601	0.37	0.14
PLA 60	547±132	427±291	2527	0.22	0.17
PCL 60	1486±175	1128±695	3126	0.48	0.36
SPLA 50	1009±133	388±99	3050	0.33	0.13
SPLA 70	716±289	506199	2401	0.30	0.21
SPCL 70	1446±497	1169±99	2766	0.52	0.42

To evaluate the extent of biodegradation of polymers (Figure 3.3) and blends (Figure 3.4) FTIR spectra of unbiodegraded and biodegraded samples were compared. FTIR spectra of PLA (Figure 3.3 (b)) and PCL (Figure 3.3 (c)) before and after biodegradation showed major changes that were not observed in the case of HDPE (Figure 3.3 (a)). Transmittance data, on a common scale, showed that all peaks in FTIR spectra of PLA (Figure 3.3 (b)) decreased in size after biodegradation. Reduction in the CH-assymetric (2920 cm^{-1}) and CH-symmetric (2850 cm^{-1}) stretches indicated a decrease in PLA molar mass while the reduction of peaks related to carbonyl (1800 cm^{-1} and 1700 cm^{-1}) and ether (1100 cm^{-1}) suggested chain scission. A reduction of the peak at 1460 cm^{-1} was associated with the decrease of CH_3 side groups. A considerable change in the PCL backbone took place during the biodegradation process (Figure 3.3 (c)) resulting in a reduction of peaks related to CH bonds (3000 cm^{-1} to 2800 cm^{-1}), carbonyl (1800 cm^{-1} and 1700 cm^{-1}) and ether (1100 cm^{-1}).

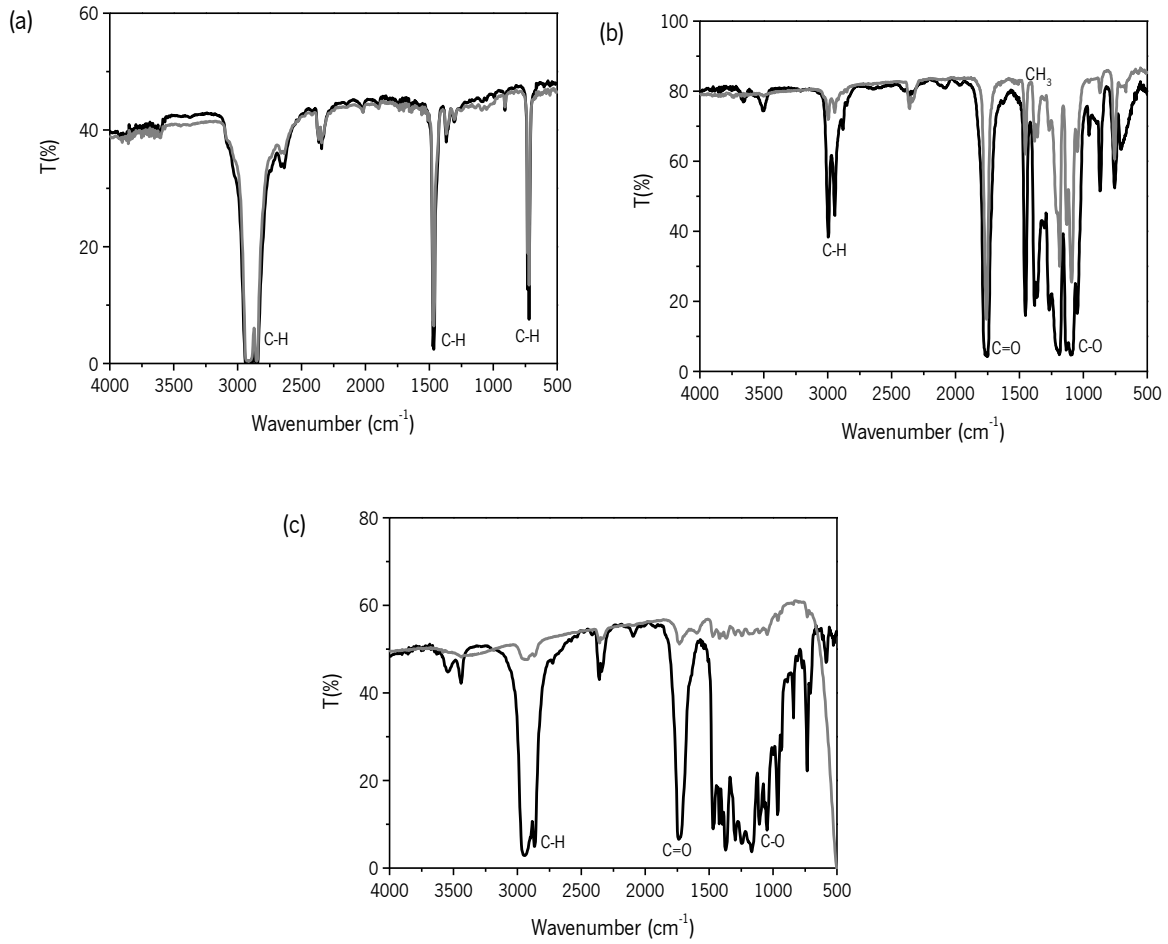


Figure 3.3 FTIR spectra of undegraded (black line) and biodegraded (gray line) polymers: (a) HDPE, (b) PLA, and (c) PCL.

These results indicated chain scission and consequently a strong reduction of PCL molar mass. Differences between unbiodegraded and biodegraded samples were noticed by visual analysis of the prepared films, the biodegraded was very brittle. FTIR spectra of PLA 60 (Figure 3.4 (a)) showed a significant reduction in all peaks related to PLA (as previously described) while the ones associated to HDPE, mainly the peak connected to CH_2 groups (720 cm^{-1}), were still present indicating that no major changes occurred in this polymer. In the case of PCL 60 (Figure 3.4 (b)) similar results were obtained. The spectra of undegraded blends containing similar amounts of starch, SPLA 70 (Figure 3.4 (c)) and SPCL 70 (Figure 3.4 (d)), showed the presence of OH peaks (3600 cm^{-1} and 3200 cm^{-1}) that decreased in the spectra of biodegraded blends indicating bound scission probably due to a hydrolysis reaction [33]. As expected, a significant decrease of all peaks related to PLA and starch in SPLA 70 or PCL and starch in SPCL 70 were observed during the biodegradation process with the exception of the peak related to the CH_2 group of HDPE (720 cm^{-1}).

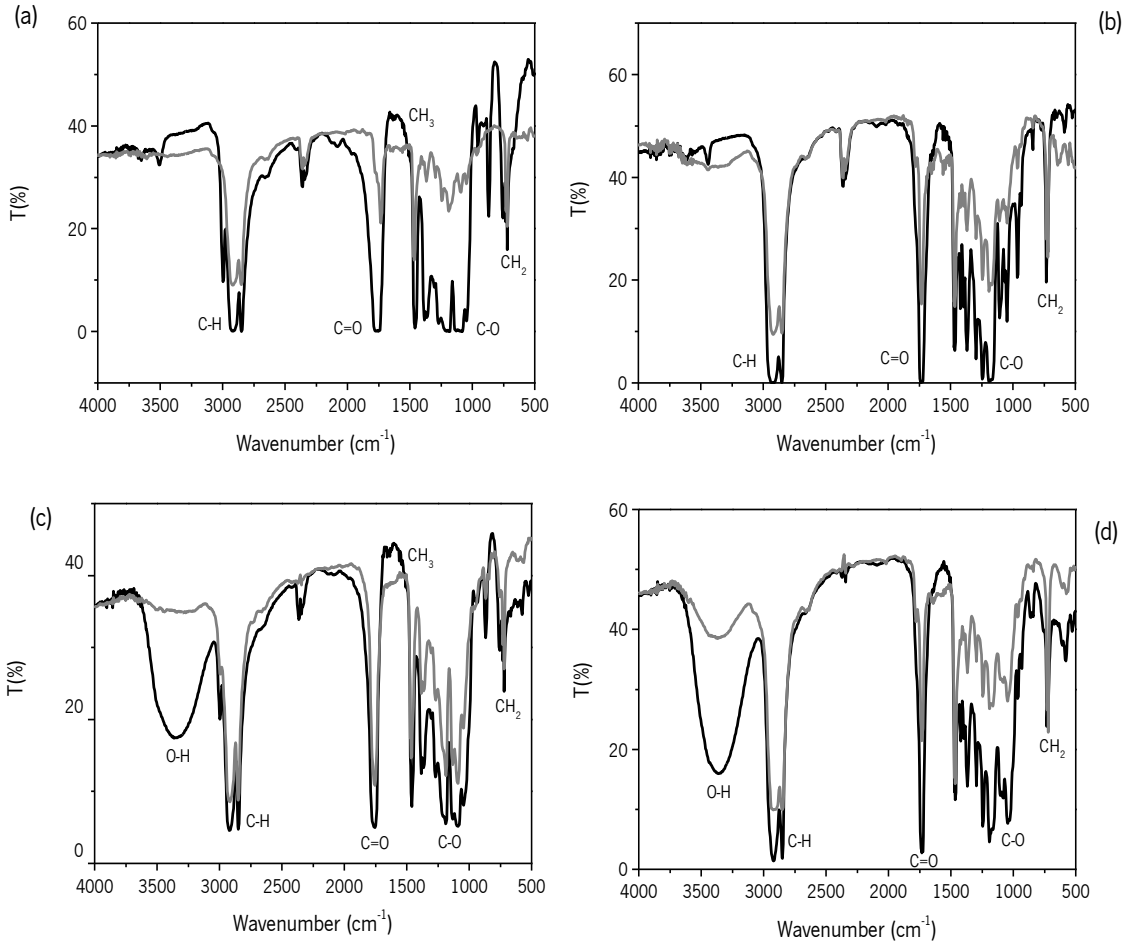


Figure 3.4 FTIR spectra of undegraded (black line) and biodegraded (gray line) blends: (a) PLA 60, (b) PCL 60, (c) SPLA 70 (18% starch), and (d) SPCL 70 (18% starch).

The extent of biodegradation increased with the amount of starch present in SPLA blends (data not shown). In summary, the spectra of polymers and blends, after biodegradation, presented a significant reduction in the intensity of the peaks corresponding to the groups C-H, C=O, C-O and O-H. This reduction might have been due to the metabolism of oxygen consumption microorganisms, as suggested by the BOD test. FTIR spectra of polymers and blends biodegraded in the presence of ATU showed a smaller reduction of the intensity of all peaks compared to one obtained in the absence of the nitrification inhibitor (data not shown). These results are complementary to the biodegradability data obtained for polymers and blends by the BOD method.

FTIR spectrum of PCL biodegraded in the presence of ATU presented a broad band at 3450 cm^{-1}, which is associated to O-H bonds (Figure 3.5). A possible explanation for this result might be the formation of acid and alcohol groups due to PCL hydrolysis and reaction with protons (H^+) existing in the reactional medium.

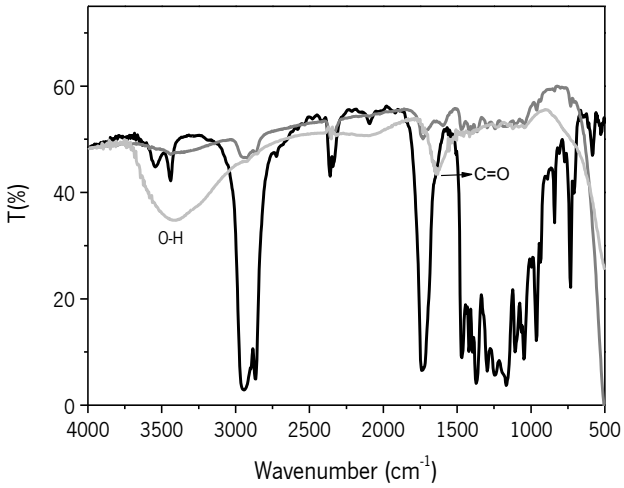


Figure 3.5 FTIR spectra of PCL undegraded (black line), biodegraded (dark gray line) and biodegraded in the presence of ATU (bright gray line).

3.3.3 Comparison with Literature Data

Table 3.4 summarizes several studies performed to evaluate the biodegradability of PCL and PLA polymers.

It is interesting to note that different shapes of polymers, biodegradability methods, experimental conditions, and length of the assays were used complicating the direct comparison of biodegradability data. For instance, values of 38% [18] and 80% [34] are presented for the biodegradability of PCL particles by the Aquatic Test done at 30 °C. In the present study, using the same test and grinded samples, almost 100% was obtained without the addition of nitrification inhibitor and 66% with inhibitior at the same temperature. One of the several possible explanations for these highly variable results might be related to polymer properties: physical form (film or power) molar mass, molar mass distribution and degree of crystallinity [35]. These data are usually not mentioned in literature studies. The data obtained in the present study also suggests that the occurrence of nitrification (oxygen consumption in the oxidation of ammonium to nitrate and carbon dioxide production) might overestimate biodegradability results. The biodegradability essays done under composting conditions presented very distinct results, 4.3% for PCL with molar mass of 80.000 $g.mol^{-1}$ [36] and 21.6% for the one with 50.000 $g.mol^{-1}$ [18], suggesting that biodegradability decreases with the increase of molar mass.

Table 3.4 Summary on literature values of PCL and PLA biodegradability.

Polymer	Method	Biodegradability	References
PCL particles (188-200 μm) $\overline{Mn}$ = 43.000 g.mol^{-1}	Aquatic test – ASTM D-5209 (CO_2 evolution)	80% at 30°C after 11 d	34
PCL particles $\overline{Mn}$ = 80.000 g.mol^{-1}	Composting conditions – ASTM D-5338 (CO_2 evolution)	4.3% [a] at 58°C after 54 d	36
PCL particles $\overline{Mn}$ = 50.000 g.mol^{-1}	Composting conditions – ASTM D-5338 and ISO 14855 (CO_2 evolution)	21.6% [a] at 58°C after 46 d	8
PLA film starch powder	Composting conditions – ASTM D-5338 and ISO 14855 (CO_2 evolution)	64.2% PLA at 58°C for 63 d	38
PLA film PCL film and particles	Aquatic test – ISO 14843 (O_2 consumption)	3.7% PLA film 34.8% PCL film 37.7% PCL particles at 30°C after 28 d	18
PLA film	Composting conditions – ASTM D-5338 and ISO 14855 (CO_2 evolution)	86% at 58°C after 58 d	39
PLA film	Composting conditions - ISO 14855 (CO_2 evolution)	55% PLA at 58°C after 90 d	37

[a] - Calculated from the mass of CO_2

Despite of the higher temperature used in the biodegradation test under composting conditions (58 °C), the biodegradability of PCL particles reported in literature was lower than the one obtained by the Aquatic Test above mentioned. Conversely, literature studies indicated that PLA films were more biodegradable under composting conditions at higher temperatures (58 °C), 55% [37], 64% [38], and 86% [39], than at lower temperatures (30 °C), 3.7% [18] used in the Aquatic Test. The fact that higher temperatures favour nonenzimatic hydrolysis of ester bonds [40, 41] support the results obtained for PLA films. As a main conclusion the present study suggested that PCL is more biodegradable than PLA by the Aquatic Test.

Guidelines from the Organization for Economic Co-operation and Development (OECD) established that a test substance is regarded as "readily biodegradable" if the degree of biodegradation based on dissolved organic carbon removal is higher than 70% (OECD 1992). In the case of BOD determination or CO_2 production, 60% of the theoretical values have to be reached. This removal is required to occur in a specific assay with the test material as the sole carbon source, and within 10 days after the initial

lag phase. According to the results obtained in the present study, only PCL may be considered "readily biodegradable" according to the OECD standard, presenting an 83% removal within 10 days in the absence of inhibitor. However, these results do not comply with the definition of "readily biodegradable" established by the OECD guidelines. If a chemical does not pass the "ready"-level test, either degradation starts too late or it occurs too slowly. The results from the O_2 consumption test (Figure 3.2) seem to indicate that biodegradation of the polymeric blends is a slow process.

3.4 CONCLUSIONS

The results obtained have shown that the blend containing PCL is more biodegradable than the blend containing PLA based on the microbial growth (ASTM G 22-76) and biochemical oxygen demand (ISO 14851:1999). Addition of starch increased the biodegradability of the PLA blend. The biodegradability of the blends evaluated in the presented study by the biochemical oxygen demand method ranged from 22% (PLA 60) to 52% (SPCL 70). Therefore they may not be considered "readily biodegradable" according to the OECD standard. The qualitative results of FTIR spectroscopy of unbiodegraded and biodegraded polymeric blends are in agreement with the ones obtained in the standard biodegradability tests.

Biodegradability of fine grinded polymeric blends was tested using the biochemical oxygen demand. It is important to point out that the surface area of the polymeric material sample available to microbial attack in the present study was increased considerably compared to film samples. Thus, the biodegradation under these conditions was enhanced when compared to tests performed in real environment.

3.5 REFERENCES

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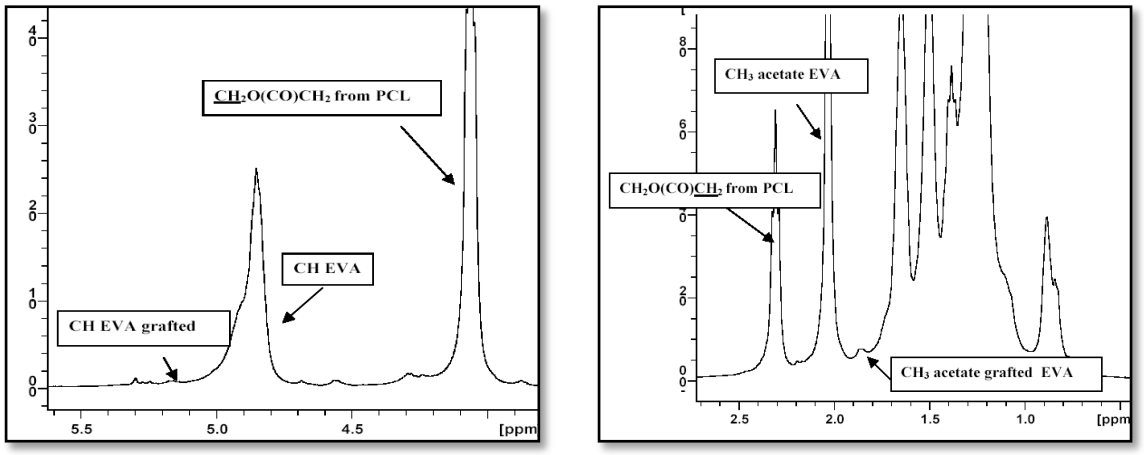
4 | BIO-BASED GRAFTED POLYESTERS PREPARED BY *IN SITU* RING OPENING POLYMERIZATION



Moura, I. Nogueira, R. Bounor-Legare, V. Machado, A.V. 2011. Reactive and Functional Polymers 71: 694-703.

4.1 INTRODUCTION

In recent years, much concern increased on the deterioration of our environment due to solid waste pollution [1]. Nowadays, the challenge is to replace conventional plastics by biodegradable ones to design materials with good performance, which after use can be susceptible to microbial and environmental degradations, using adequate solid waste management disposal practices, without any adverse environmental impact [2]. The easiest way to solve this problem would be to replace commodity synthetic polymers by biodegradable polymers. However, most biodegradable polymers by itself do not have the performance specifications required for a given application [3]. Thus, it is necessary to develop new routes to enhance the properties of biodegradable polymers.

Aliphatic polyesters are one of the most promising biodegradable materials because they are readily susceptible to biological attack [4]. One example is polylactide (PLA), which has melting temperature around 160-180 °C, has received much attention as alternative biodegradable polymer [5]. PLA can be obtained from renewable agricultural sources, because lactic acid monomers can be extracted from the fermentation of crop like corn starch and sugar feed stocks [6]. Its production consumes carbon dioxide, providing significant energy savings and is recyclable and compostable [7-9]. Therefore, PLA presents advantages over other synthetic materials. Other is poly(ε-caprolactone) (PCL), which can be degraded aerobically by a large number of microorganisms in various microbiological environments [10] and it is compatible with a variety of the polymers. However, the high cost of PCL and low melting temperature have prevented its widespread industrial use [11].

Since blending 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 polymers have been studied for a variety of industrial applications [12]. Natural and synthetic biodegradable polymers (for example, starch, poly(ε-caprolactone) and polylactic acid) have been blended with non-biodegradable synthetic polymers [13, 14, 10, 15]. The results showed that even though biodegradability can increase, due to polymer incompatibility the specified final properties are not achieved. An alternative approach to produce these materials with enhanced properties would be the synthesis of grafted copolymers. Reactive extrusion based on chemical modification by post polymerization is an attractive way to synthesize these types of copolymers [16, 17]. The amount of grafted copolymer formed depends on many factors: i) choice of the initiator, that is one of the main controlling factors in the grafting reaction through post-living polymerization ii)

processing conditions (temperature and time), iii) polymers molar mass, iv) nature of the reaction and v) monomer miscibility in the molten matrix [18, 19].

Ethylene vinyl acetate (EVA) copolymers have a broad range of industrial applications [20], such as packaging, adhesives, wire, cable and health care. Due to the mechanical properties, these copolymers are used perhaps, in a broadest spectrum of applications of any synthetic polymeric material [21]. Since these copolymers have good properties and high resistance to biodegradation, it would be a challenge to develop new materials based on copolymers of EVA and biodegradable polymers.

In previous studies dedicated to the polymerisation of ε-caprolactone and the synthesis of EVA-g-PBT grafted copolymers from *in situ* polymerization of cyclic butylene terephthalate monomer (cBT) in the presence of molten EVA, the advantages of the specificity of the ring-opening polymerization initiator was taken. First the study of the ring-opening polymerization of the ε-caprolactone initiated by the titanium phenoxide evidenced that, on average, one phenoxide ligand initiates the ring-opening polymerisation [17]. Second, an increase of the polymer molar mass was observed after complete monomer conversion, with a decrease of phenoxyl ester end groups concentration. Actually, this phenomenon is due to transesterification reactions favoured with end groups in case of polymerization with $Ti(OPh)_4$. Actually, the C-O bond of phenoxyl ester terminal is more prone to nucleophilic substitution than the C-O bond in repetitive unit due to the influence of phenyl group on electronic delocalisation. This leads to more selective transfer reactions and consequently to more efficiency for grafting reactions. Due to the aromatic character of this titanium derivative, the transfer reaction of the PBT chain onto the EVA backbone was enhanced as described in a recent paper of Bahloul et al. [16]. The copolymer structure and amount was carefully accessed and then precisely characterized by ^1H NMR study.

Thus, the present work aims to prepare grafted copolymers of EVA/PLA and EVA/PCL using *in situ* polymerization of lactide (LA) and ε-caprolactone (ε-CL) in the presence of molten EVA. This process will take the advantage of a specific exchange reaction between PLA or PCL end-chain groups and the acetate groups of EVA to increase the probability of grafting and consequently the concentration of the formed copolymer. For the ring-opening polymerization, the length of the polymer chains depend directly on the $[M]/[I_0]$ ratio, where [M] and $[I_0]$ are the monomer and the initiator concentration, respectively. Titanium phenoxide ($Ti(OPh)_4$) was used for its specificity action in the grafting reactions.

The prepared samples were characterized using several analytical techniques, such as, ^1H NMR, GPC, FTIR, rheology, SEM, DSC, TGA and mechanical tests. Biochemical oxygen demand (BOD) was carried out to evaluate the biodegradability.

4.2 EXPERIMENTAL

4.2.1 Materials

Ethylene vinyl acetate copolymer (EVA 28-03) with 28 wt.% of vinyl acetate ($\overline{Mn}$ = 18.000 g.mol^{-1}), supplied by ARKEMA, was used as a synthetic polymer. Polylactide ($\overline{Mn}$ = 22.000 g.mol^{-1}), poly(ε-caprolactone) ($\overline{Mn}$ = 10.000g.mol^{-1}), lactide (M = 144 g.mol^{-1}) and ε-caprolactone (M = 114 g.mol^{-1}) were supplied from Sigma Aldrich. Titanium phenoxide ($Ti(OPh)_4$), used initiator, was prepared according to procedure developed by Cayuela et al. [17]. The sample composition is presented in Table 4.1. For specific comparison, the $[M]/[I_0]$ ratio, where [M] and $[I_0]$ are the monomer and the initiator concentration were chosen to target an *in situ* PCL and PLA molar mass similar to the commercial polymers used.

Table 4.1 Samples composition.

Sample	EVA (wt.%)	PLA (wt.%)	PCL (wt.%)	LA (wt.%)	ε-CL (wt.%)	$Ti(OPh)_4$ (wt.%)	$[M]/[I_0]$
1	60	40	0	0	0	0	0
2	60	0	40	0	0	0	0
3	59.5	0	0	39.5	0	1.0	117
4	59.5	0	0	0	39.5	1.0	141

4.2.2 Reactive Blending

Polymer pellets were dried in a vacuum oven at 25 °C for 12 hours before use.

Blends of EVA with PLA and EVA with PCL and *in situ* polymerization of LA with EVA and ε-CL with EVA were performed in a Haake batch mixer (Rheocord 90; volume 60 mL), equipped with two rotors running in a counter-rotating way. The rotor speed was 50 rpm and the set temperature was 160 °C. To prepare the blends, the dried components were pre-mixed and introduced together in the mixer. For the *in situ* polymerization the following procedure was adopted, first the EVA pellets were introduced into the hot mixer, after melting, the monomer and initiator were added simultaneously. Titanium phenoxide was collected in an argon atmosphere, to prevent hydrolysis reaction. In both cases, blends and *in situ* polymerization, the rotors were stopped after 15 min of mixing and the total sample was removed.

4.2.3 Material Characterization

4.2.3.1 Extraction of Copolymer

The EVA-g-PCL and EVA-g-PLA copolymers produced through *in situ* polymerization were isolated from the homopolymers according to the following method described below and summarized in Figure 4.1. Solubility tests showed that EVA was soluble in hot toluene, but insoluble in acetone. Conversely, PLA and PCL were 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. After, the suspension obtained was filtered. The clear solution was precipitated in methanol and the resulting precipitate was dried until constant mass. This product is referred to as fraction 1 (PLA or PCL). The insoluble fraction of the first filtration was extracted in hot toluene during 3 days. The solution obtained was filtered, then evaporated, in a rotational evaporator, and dried. The fraction obtained is referred to as fraction 2 (EVA). The residue of this second extraction was washed with methanol and subsequently dried. This residue composes the third fraction, i.e., the copolymer.

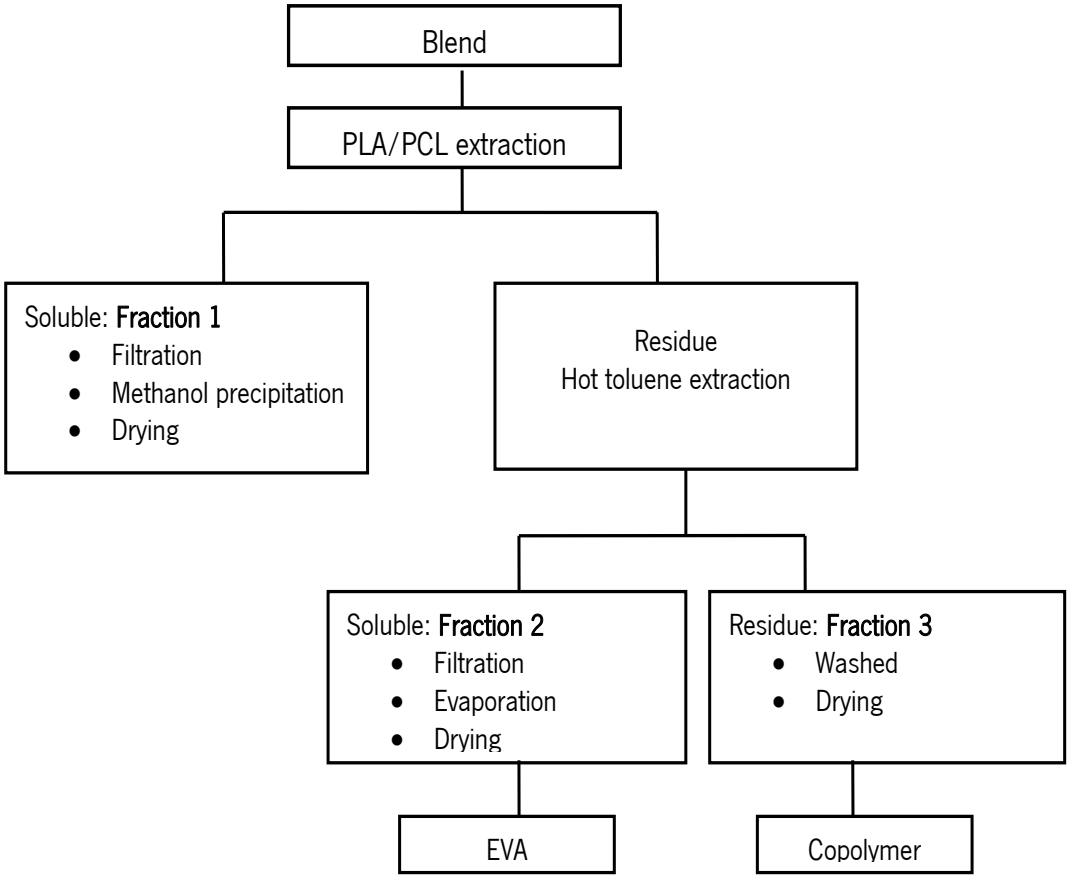


Figure 4.1 Extractions scheme of EVA-g-PLA and EVA-g-PCL copolymers.

4.2.3.2 Structural Characterization

4.2.3.2.1 ^{1}H NMR

High resolution liquid ^{1}H NMR spectroscopy was carried out with a Bruker AC 250 instrument at 250 MHz for ^{1}H. Deuterated chloroform, $CDCl_3$ was used as solvent for analysis. Chemical shifts values (δ) are in ppm with reference to internal tetramethylsilane (TMS).

4.2.3.2.2 Rheological Properties

Oscillatory rheological measurements of original 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 4.0 cm, respectively. A frequency sweep from 0.01 to 100 Hz under constant strain was performed for each sample.

4.2.3.2.3 TGA and DSC

All samples were analyzed using a TA Q500 thermobalance operating under a nitrogen flow atmosphere (50 mL/min). Samples were heated from 30 °C to 600 °C at a heating rate of 10 °C/min.

Thermal properties of all samples were measured using TA Instruments differential scanning calorimeter (DSC 2920). Samples were heated from 25 °C to 200°C at a heating rate of 10 °C/min, cooled from 200 °C to room temperature at the same rate, under liquid nitrogen. The crystallinity degree (X_c) was calculated by the ratio of ΔH_f (the apparent melt enthalpy indicated in DSC curves as melting enthalpy per gram) corresponding to the component and ΔH_f° (the melt enthalpy per gram of the component in its theoretically completely crystalline state).

4.2.3.2.4 SEC

The number average molar mass ($\overline{Mn}$), the mass average molar mass ($\overline{Mw}$) and the polydispersity (Ip) were measured by size exclusion chromatography. Solutions were prepared in chloroform (99,9%) and prefiltered on filter plate (hydrophobic polytetrafluoroethylene, 0.45μm pore size) before injection. The SEC apparatus was equipped with 2 Waters Ultrastyragel columns (HR1 and HR4; inner diameter = 7.8mm, length = 300 mm and particle size = 5μm) and a Waters R410 refractometer detector. Chloroform was used as eluent with a flow rate of 1 mL/min and at 22 °C. The calibration curve was previously obtained with polystyrene standards.

4.2.3.2.5 SEM

After fracture of the samples in liquid nitrogen and gold plating, the morphology of the samples was studied using a Jeol JSM 6310F Scanning Electron Microscope

4.2.3.2.6 Mechanical Properties

Mechanical experiments were performed in a MINIMAT apparatus using a test speed of 0.5 mm/min, at room temperature and relative humidity of 50%. The tests were performed on 2.5 cm x 0.5 cm rectangular samples in a longitudinal direction. At least 6 specimens of each sample were tested. Prior to mechanical measurements, films with a thickness of 1.5 mm were prepared by compression moulding using the samples that were removed from the mixer.

4.2.3.2.7 Biodegradability Assessment

Biodegradation tests were carried out in aqueous environment under aerobic conditions according to the standard ISO 14851:1999 (Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium) [22, 23] which specify a method for determining the biochemical oxygen demand (BOD) in a closed respirometer. Polymers were reduced to powder to create a suspension of the polymer in the test system. The Oxitop system used in the determination of BOD contains an individual number of reactors consisting of glass bottles with a carbon dioxide trap (sodium hydroxide) in the headspace. The bottles are supplied with a magnetic stirrer and sealed with a cap containing an electronic pressure indicator. BOD determinations were carried out in 510 mL bottles containing 62.5 mg of the test blend, 2 mL of inoculum and 50 mL of mineral medium. The mineral medium contained 40 mL/L of solution A (28.25 g/L KH_2PO_4, 146.08 g/L K_2HPO_4), 30 mL/L of solution B (3.36 g/L $CaCl_2.2H_2O$, 28.64 g/L NH_4Cl), and 30 mL/L of solution C (3.06 g/L $MgSO_4.7H_2O$, 0.7 g/L $FeSO_4.7H_2O$, 0.4 g/L $ZnSO_4$). The source of inoculum was activated sludge freshly sampled from a municipal sewage treatment plant. The BOD of the inoculum was determined in blank tests performed only with mineral medium and inoculum. These values were subtracted from the BOD values of the blends to obtain exact values of the degradation activity. Test bottles were incubated at 30 °C in the dark with stirring for 20 days. All experiments were carried out in triplicate. The amount of O_2 consumed in polymer's biodegradation (after correction with the blank test) was expressed as a percentage of the theoretical oxygen demand (ThOD). The ThOD expressed as mass of O_2 per mass of polymer was determined by calculating the amount of O_2 necessary for aerobic mineralization of the

polymer, i.e. complete oxidation of C to CO_2 [23]. The ThOD of the polymer $n(C_cH_hO_o)$, with a relative molar mass M_r (per monomer), was calculated according to equation (1), defined in the fourth chapter
The values of theoretical oxygen demand were calculated based on elemental analysis of each sample (see table 4.7).

4.2.3.2.8 FTIR

FTIR spectra of all samples before and after biodegradation were recorded using a Perkin Elmer 1720 spectrometer in the range of 500-4000 cm^{-1}, using 16 scans and a resolution of 4 cm^{-1}. Non-degraded and biodegraded samples were dissolved in chloroform at 5.0% (w/v) and stirring during an hour. Subsequently, an aliquot of this solution was removed and a portion of it (some drops) was deposited in a sodium chloride cell. After solvent evaporation (approximately three minutes) a thin film was obtained and it was analyzed using a solid film support.

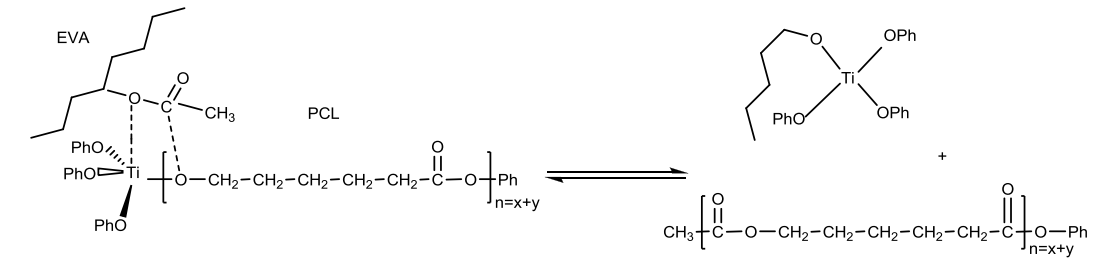
4.2.3.2.9 Elemental Analysis

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

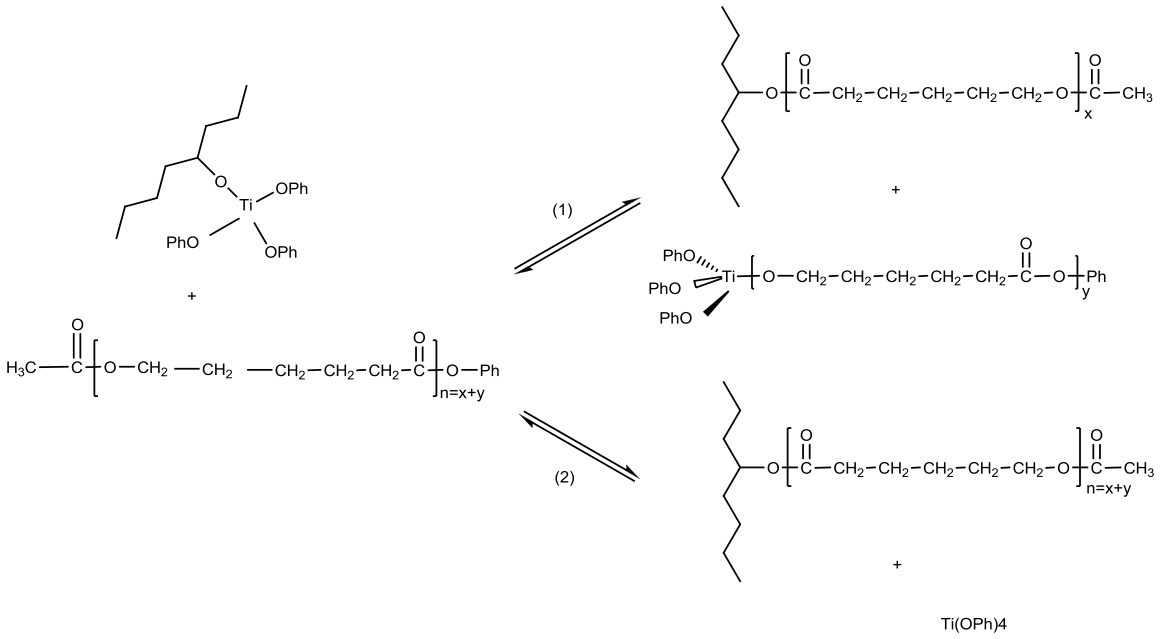
4.3 Results and Discussion

4.3.1 Copolymer Identification

In the present work, authors want to take advantage of the specific exchange reaction between the polyester end-chain and the EVA acetate groups, to increase the probability of grafting and consequently the formation of the copolymer in the blend. Therefore, enhancement of the biodegradability character of these copolymers would be expected.
As described previously when polymerization of the cyclic monomer initiated by the titanium phenoxide takes place in the presence of molten EVA, two transfer reactions may be observed leading to the grafting process as shown in Figure 4.2 for ε-CL (the mechanism is the same for LA). A transfer reaction between the acetate group of the EVA and the Ti-O-Polyester bond results in EVA chain functionalized by $Ti(OPh)_3$ and polyester functionalized by an acetate group (Figure 4.2 (a)). Another transfer reaction between this new titanate species and either an ester function of polyester chain (Figure 4.2 (b)-1), or on the phenoxyl ester end-group (Figure 4.2 (b)-2), this latter reaction being favored according to the previous explanations, lead to the formation of grafted species.



4.2 (a)



4.2 (b)

Figure 4.2 Reaction mechanism of EVA-g-PCL copolymer formation (similar mechanism is obtained with the lactide instead of ε-caprolactone monomer).

After extraction, the fraction amount of each polymer for all the samples is summarized in Table 4.2. All fractions were analysed by ^{1}H NMR to get information on its composition. The spectra obtained for fractions 1 and 2 confirmed that only PLA or PCL and EVA were extracted. It also confirms the efficiency of the extraction methods and the solvents choice. As expected for the physical blends, i.e., mixing both homopolymers without any initiator, the homopolymer percentage is in agreement with the theoretical amount.

Table 4.2 Fractions amounts extracted.

Sample	Fraction 1	Fraction 2	Fraction 3
	(wt.%)	(wt.%)	(wt.%)
1	40	60	0
2	40	60	0
3	36	56	8
4	35	54	11

Sample 3 and 4 obtained by *in situ* polymerization of LA and ε-CL monomers in the presence of molten EVA exhibit an amount of fraction 3 around 8 and 11 wt.% for sample 3 and 4, respectively. The characterization of fraction 3 by ^{1}H NMR, which corresponds to the insoluble compound in acetone and in hot toluene, gives the following information. On the ^{1}H NMR spectrum of EVA-CL (Figure 4.3), the resonance of both EVA and PCL specific protons are easily detectable. The peaks of CH and CH_3 of EVA are at 4.85 and 2.05 ppm and the peaks of the CH_2 of the CH_2-O(CO)CH_2 repetitive unit of PCL are at 2.30 and 4.05 ppm. Besides these main contributions, others new resonance peaks can also be observed by zooming the regions around 4.0 ppm and 2.0 ppm, respectively. One new peak at 5.15 ppm can be detected, which is associated with a –CH- protons resonance and other one at 1.85 ppm, which is associated to an acetate –CH_3- protons resonance. The appearance of these signals, which are not presented in the spectrum of $Ti(OPh)_4$, are consistent with the proposed mechanism. The new acetate groups corresponds to the one created through a transfer reaction between the acetate group of the EVA and the Ti-O-Polyester end bond (Figure 4.2 (a)) and the CH corresponds to the grafted PCL on the EVA backbone. These results are in agreement with our previous work dedicated to the synthesis of EVA-PCL grafted copolymer [24] and EVA-PBT grafted copolymer [16].

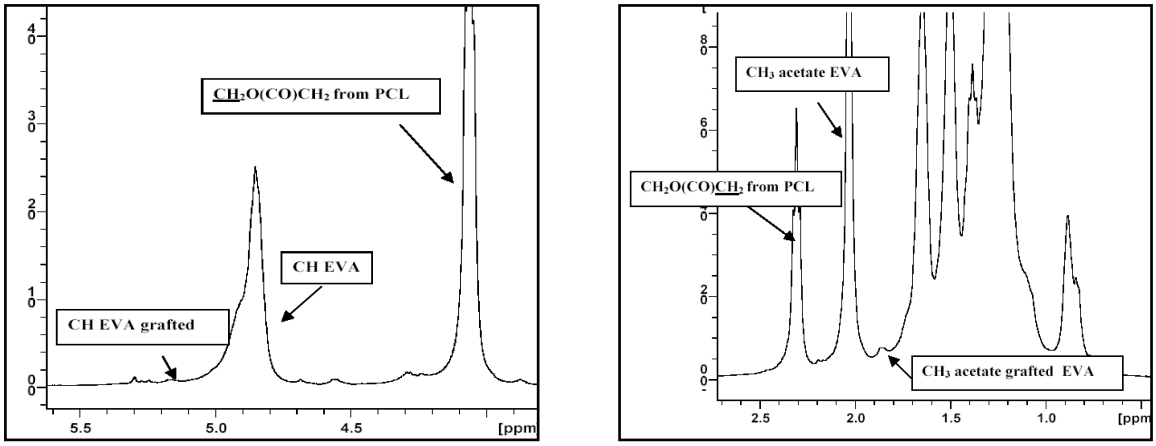


Figure 4.3 ^{1}H NMR spectra of EVA-g-PCL.

Since oscillatory rheological measurements are very sensitive to molecular changes, the rheological behaviour of all prepared samples was characterised using this technique. From the viscosity values at low frequency (0.1 Hz) presented in Table 4.3 it is possible to observe that PLA presents the highest value. This can be explained by the low temperature (160 °C) selected for the rheological measurements, which is very close to the PLA melting temperature. The addition of a biodegradable polymer to EVA promotes significant changes of viscosity, but, as expected, the samples with PLA have higher values than the ones with PCL. Comparing the viscosity values of the blends and the samples resulting from the *in situ* polymerization, one can noticed that the values are higher for samples obtained by *in situ* polymerization. The difference between the values of sample 1 and 3 and sample 2 and 4 can be associated with copolymer formation, which is in agreement with the extractions. As explained by the ^{1}H NMR results, the copolymers formed in samples 3 and 4 are grafted copolymers, resulting from the reactions between the ester groups of EVA and the ester groups of the *in situ* polymerized LA or ε-CL. As these copolymers have a branching structure, its presence increases the sample viscosity at low frequencies.

Table 4.3 Complex viscosity of initial polymers and prepared samples at a frequency of 0.1 Hz at 160 °C.

Sample	η (Pa.s)
EVA	105
PLA	1000
PCL	11
1	165
2	52
3	204
4	81

Figure 4.4 depicts the thermal behaviour (weight loss and correspondent derivative) of EVA, PLA, PCL and prepared samples when heated from 30 °C to 600 °C at a heating rate of 10 °C/min, under nitrogen flow atmosphere. EVA exhibits a first mass lost (18.5%) at around 325 °C, which can be attributed to the decomposition of the acetate groups due to the release of acetic acid [25]. At approximately 400 °C, a second weight lost (81.5%) can be noticed, corresponding to the degradation of the olefinic part of the copolymer (C-C and C-H bonds).

PLA presents a one-step decomposition profile with a single decomposition temperature. This polymer has lower thermal stability than EVA, because its degradation peak is around 346 °C and it decomposes completely (0% char residue) at 380 °C. Samples 1 and 3 show two degradation transitions, corresponding to the degradation of the two components of the sample. Sample 1, has an intermediate behaviour of EVA and PLA, being the first decomposition temperature (361.68 °C) close to the one of PLA and second (380 °C) close to the one of EVA. Even though, the thermal behaviour of sample 3 is similar to sample 1, a slight shift to higher decomposition temperatures can be noticed from the derivative curves. This might be associated with the amount of grafted polymer present in this sample, its branching structure seems to result in a slight increase of the thermal stability [26].

Compared to EVA, PCL also has lower thermal stability, its first decomposition temperature is around 284 °C and it is completely decomposed (0% residue) at 450 °C (see Figure 4.4 (b)). Samples 2 and 4 exhibit an intermediate behaviour between EVA and PCL. The first decomposition temperature of the blend is similar to the one of PCL and it has a second decomposition temperature similar to the second degradation temperature of EVA. However, as it can be observed from the derivative curves, sample 4 presents a slight increase in decomposition temperatures, which, as in the case of sample 3, might be associated with the presence of the grafted copolymer.

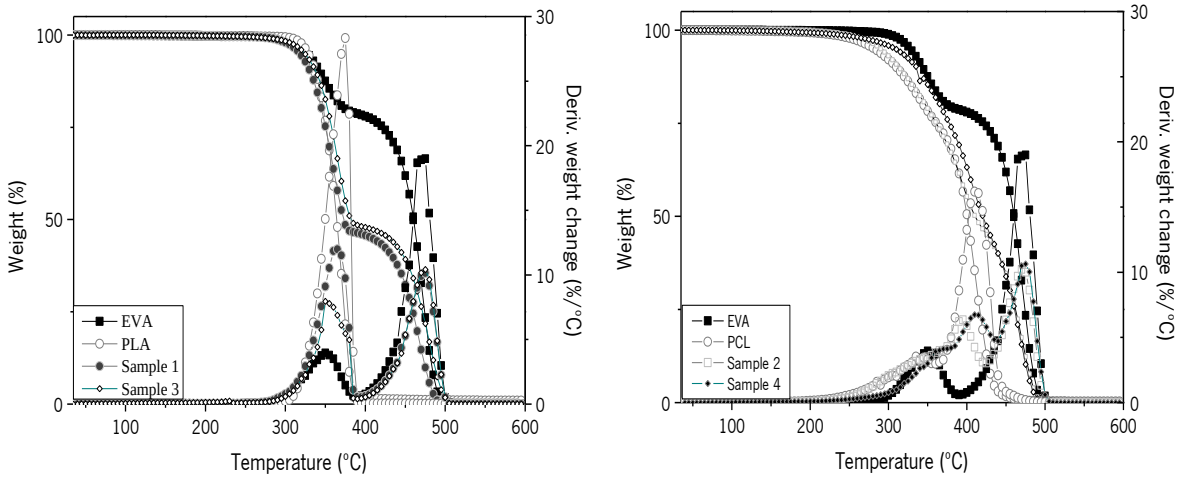


Figure 4.4 Thermograms and derivative curves of neat polymers and prepared samples.

SEC analysis of all prepared samples and extracted copolymers were performed to confirm copolymer formation. Figure 4.5 depicts chromatograms of the neat polymers (EVA, PLA and PCL). Each polymer has a single peak at a certain elution time being the elution time different for all. The results obtained for samples 1 and 2 (Figures 4.5 (a) and 4.5 (b)) are similar, each analyzed samples presents only one

peak. This can be due to the similarity of the molar mass of the neat polymer (18.000, 22.000 and 10.000 g.mol^{-1} for EVA, PLA and PCL, respectively), which after blending are impossible to separate under the conditions used for SEC analyses. Additionally, overlaying sample 1 and 2 with the individual components shows that both samples cover the retention volume of both individual polymers, which indicates that no degradation occurred during blending.

In order to prove that PLA and PCL were grafted onto EVA, SEC data of samples 3 and 4 were overlaid with EVA (Figures 4.5 (c) and 4.5 (d)). A shift to lower retention volume can be observed for samples 3 and 4, which is due to an increase of molar mass. These results corroborate the proposed mechanism, the reaction takes place between the ester groups of both copolymers.

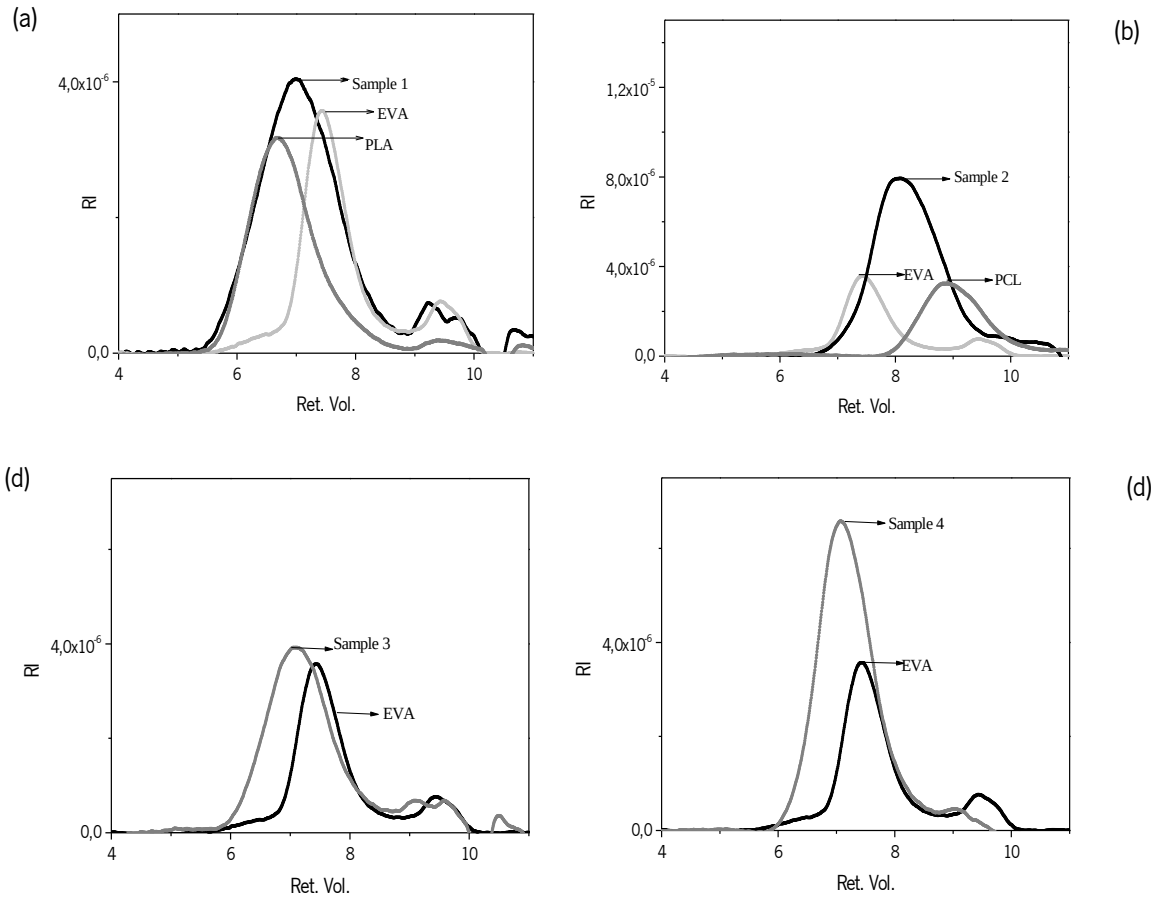


Figure 4.5 SEC analysis of neat polymers and prepared samples.

4.3.2 Morphology and Physical Properties

Figure 4.6 depicts the morphology of all the samples analysed by SEM after fracture in liquid nitrogen. The morphology of the polymer blends (Figures 4.6 (a) and 4.6 (b)) and the samples obtained by *in situ*

polymerization (Figures 4.6 (c)) and 4.6 (d)) consists in a dispersion of particles in the EVA matrix, but significant differences can be noticed among them. Figure 4.6 (a), EVA/PLA blend, which has the lowest magnification, exhibits a coarse morphology, big particles of PLA dispersed in the EVA matrix. The low interfacial adhesion can be perceived from the separation between the blend components. Even though PCL is also dispersed in the EVA matrix, the size of the dispersed phase is much smaller. Since the viscosity of the individual components play an important role on morphology of polymer blends, the differences observed can be associated with differences in melt viscosity. As seen in Table 4.3, the melt viscosity of PCL is more close to the melt viscosity of EVA than PLA. Another possible explanation can be some compatibility between EVA and PCL.

The dispersed phase of the samples obtained by *in situ* polymerization is very small when compared to the physical blends morphology, being less pronounced for sample 4. This decrease can be explained by the copolymer formed during reaction, which acts as compatibilizer decreasing the interfacial tension between blends components and consequently the size of the dispersed phase. The morphology of sample 4 can be attributed to the higher copolymer amount.

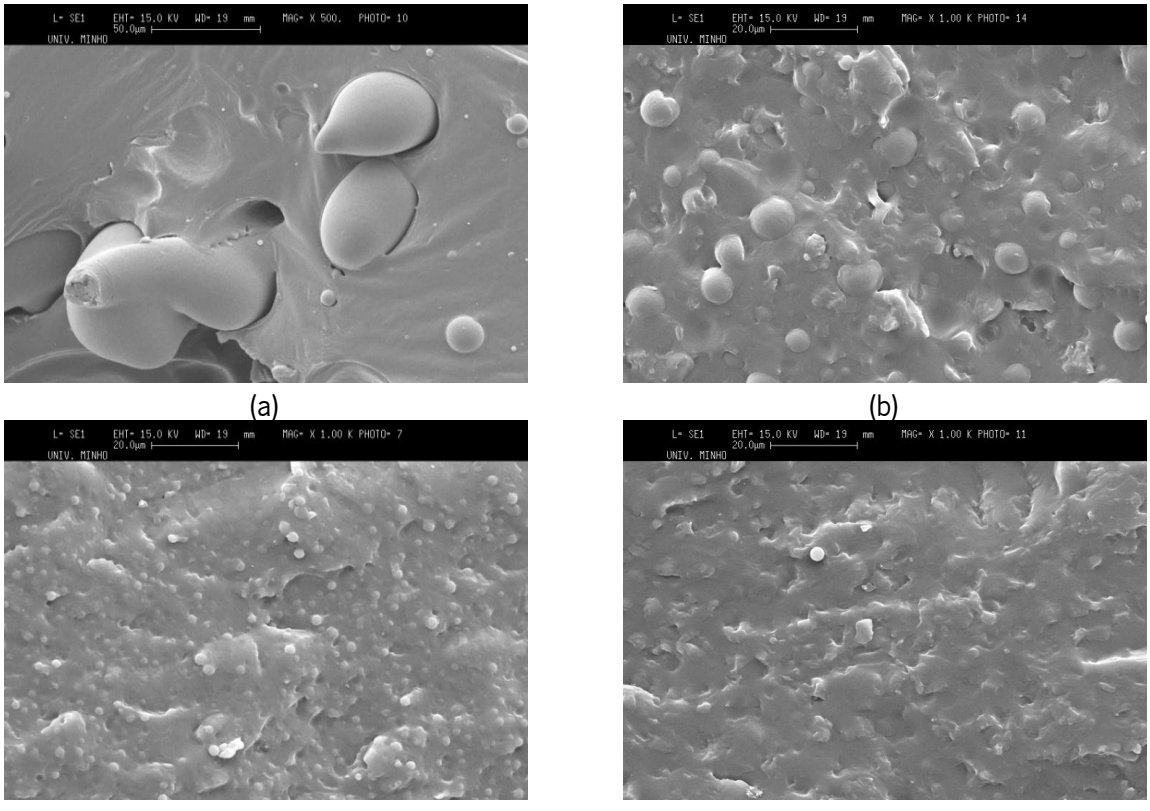


Figure 4.6 SEM micrographs of (a) sample 1, (b) sample 2, (c) sample 3 and, (d) sample 4.

Table 4.4 and 4.5 presents the melting temperature and degree of crystallinity, obtained from DSC measurements of neat polymers and prepared samples. The melting temperature and the degree of crystallinity of EVA and PLA of sample 1 is practically the same as the values obtained in the individual measurements. Due to the immiscibility between EVA and PLA, it would be expected that both polymers kept their thermal properties. In sample 2, the melting temperature of EVA changes slightly from 52.1 °C to 51.3 °C and the melting temperature of PCL changes from 64.4 °C to 62.4 °C and the degree of crystallinity of both polymers decrease. This small difference could be related with some compatibility between EVA and PCL, as it was observed by SEM. The results of samples 3 and 4 present considerable changes in melting temperature and degree of crystallinity when compared to individual blend components or samples 1 and 2. This indicates that EVA/PLA and EVA/PCL samples obtained by *in situ* polymerization present an enhanced affinity. The decrease of degree of crystallinity of samples 3 and 4 is related with the transfer reactions, from which result covalent bonds between PLA or PCL and EVA segments and lead to a lower regularity of the molecular structure. The significant crystallinity decrease observed for PLA in sample 3 is probably due to the PLA structure. This polymer has methyl side groups, which might inhibited the chains connected to EVA to pack and therefore a lower crystallinity degree is achieved. The occurrence of reactions and copolymer formation leads to changes of molecular structures of the polyesters, which promotes changes in melting temperature and crystallinity.

Table 4.4 Melting temperature (Tm, °C), melting entalphy (**ΔH**, J/g) and degree of cristallinity (X_c, %) of neat polymers.

Polymer	T_m	ΔH	ΔH°	X_c
	(°C)	(J/g)	(J/g)	(%)
EVA	52.1	10.4	44	27.2
PLA	154.6	25.7	93.6	27.5
PCL	64.4	77.1	146	52.8

Table 4.5 Melting temperature (Tm, °C), melting enthalpy (ΔH, J/g) and degree of cristallinity (X_c, %) of all samples.

Sample	EVA			PLA or PCL		
	T_m (°C)	ΔH (J/g)	X_c (%)	T_m (°C)	ΔH (J/g)	X_c (%)
1	52.1	10.8	24.6	154.7	27.4	26.6
2	51.3	9.4	25.1	62.4	60.8	45.1
3	50.3	11.2	25.6	150.0	17.6	18.8
4	50.7	10.1	23.0	60.4	61.4	42.1

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. Tensile strength, modulus and elongation at break of EVA and prepared samples obtained according to the procedure explained in the experimental part are depicted in the Table 4.6 and Figure 4.7. The values for PLA and PCL are not present because under the conditions used to test the samples, these two polymers were very brittle. As it can be observed, the addition of biodegradable polymers to EVA promotes an increase in the tensile strength, i.e., increases of stiffness. Moreover, this enhancement was more pronounced for samples obtained by *in situ* polymerization than for physical blends. Comparing the physical blends, it can be observed that sample 2, which is slightly more crystalline than sample 1, exhibits slightly higher tensile strength (0.27 MPa). This would be expected since it is well know that crystallinity in polymers is associated with their mechanical properties [28]. This effect can also be seen for samples obtained by *in situ* polymerization. Sample 4 exhibits a tensile strength of 0.47 MPa while sample 3 has 0.42 MPa and sample 4 is more crystalline than sample 3.

Table 4.6 Tensile strenght and elongation at break of EVA and prepared samples.

Sample	σ	ε	*E*
	(MPa)	(%)	(MPa)
EVA	0.17±0.02	568±14	1.61±0.49
1	0.10±0.07	361±12	3.98±1.24
2	0.27±0.02	375±24	5.05±2.99
3	0.42±0.03	452±11	11.35±1.63
4	0.47±0.05	611±10	13.23±1.10

Conversely, the addition of biodegradable polymers to EVA leads to a decrease of the elongation at break, especially for physical blends. This result can be explained by the formation of two phases with poor compatibility. Nevertheless, this property increases slightly from EVA (568%) to sample 4 (611%). This enhancement can be attributed to the formation of EVA-g-PCL copolymer and its compatibility effect. The effect was less noticeable for sample 3, where EVA-g-PLA where formed, the value in this case was only 452%. The small differences in mechanical properties of the samples prepared by *in situ* polymerization, can be related with the chemical structure of the copolymer formed and its effect as compatibilizer.

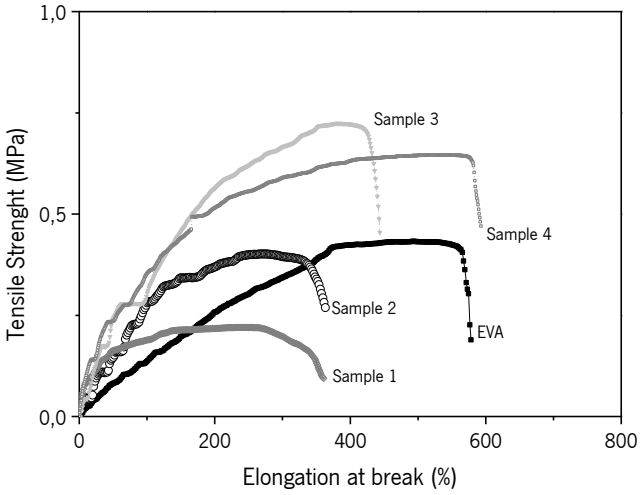


Figure 4.7 Tensile properties, at room temperature, of EVA and prepared samples.

SEM micrographs (Figure 4.6) clearly show this effect. The enhancement of mechanical properties between samples 1 and 3 and 2 and 4 follows morphology improvement.

4.3.3 Biodegradability Assessment

The biodegradability of the neat polymers and prepared samples (physical blends and grafted copolymers) was characterized by the biochemical oxygen demand (BOD) method done in a closed respirometer (ISO 14851: 1999). The results obtained during 20 days of biodegradation are depicted in Figure 4.8. Among the neat polymers, EVA showed the lowest degree of biodegradability (6.6%), PCL the highest (99.8%), and PLA was in between (37.3%).

According to previous studies, reporting that aliphatic polyesters, PCL and PLA, are biodegradable in a wide variety of ecosystems [29], these results were expected. Based on physico-chemical characteristics of both polyesters, it is difficult to explain the fact that PCL was more biodegradable than

PLA. On the one hand, the melting temperature of PCL is lower than the one of PLA. As described in literature, polymers with lower melting temperatures are more susceptible to biodegradation because the polymer chains are more flexible and the enzymes can fit more easily into active sites [30]. Also, PCL had a lower molar mass than PLA, which also favored biodegradation [31]. On the other hand, PLA was more amorphous than PCL and based on this parameter PLA was expected to be more biodegradable than PCL, which just did not happen. Thus, prevision of biodegradability based on physico-chemical analyses of the polymers is complex because it depends on several parameters and can lead to wrong results.

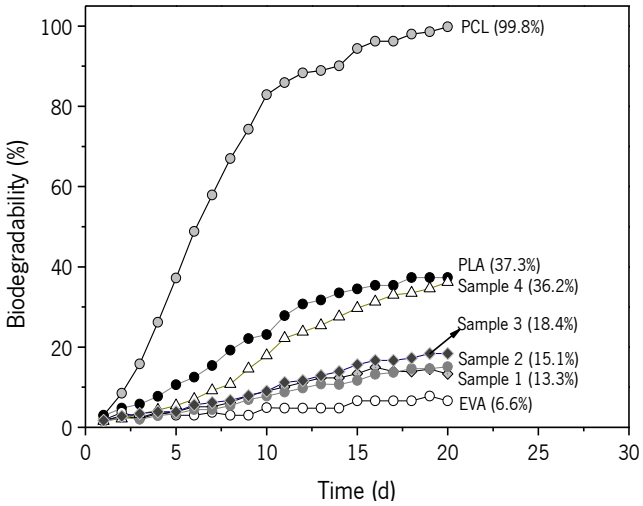


Figure 4.8 Biodegradability of polymers and all samples according to ISO 14851:1999.

Table 4.7 Elemental analysis of all samples.

Sample	Carbon (%)	Hydrogen (%)	Oxygen (%)	Chemical formula
1	65.3	9.2	25.5	C_4H_6O
2	71.5	11.0	17.5	$C_6H_{10}O$
3	66.0	9.5	24.5	C_4H_6O
4	66.7	10.2	23.2	C_4H_7O

It is complex to compare biodegradability results obtained with different methods, using polymers with distinct molar mass. As an example, the biodegradability of PCL under composting conditions (58 °C), 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 (99.8%) [32]. A possible explanation for the differences observed derives from the fact that the molar mass of the PCL used in the present study

was lower, 10.000 g.mol^{-1}, which enhanced microbial attack. Unfortunately it not possible to compare our PLA data with data from literature because, either the biodegradation were performed at different temperature or the molar mass was unknown. A relatively high biodegradability result for PCL with a molar mass of 43.000 g.mol^{-1}, 80%, was reported in literature obtained with a similar method to the one used in the present study [33]. Blending PLA or PCL with EVA had a positive effect on the biodegradability of the blends obtained, sample 1 (13.3%) and sample 2 (15.1%), compared to EVA (6.6%). Even better biodegradability results were obtained with grafted copolymers, namely sample 3 (18.4%) and sample 4 (36.2%). An increase of biodegradability of grafted copolymers (samples 3 and 4) compared to physical blends (sample 1 and 2) was probably due to the simultaneous decrease of crystallinity, melting temperature, and molar mass [34, 35].

FTIR analyses of neat polymers were performed to monitor main changes in polymers' backbone after biodegradation. Major changes occurred in the FTIR spectra of PLA (Figure 4.9 (a)) and PCL (Figure 4.9 (b)) but not in the one of EVA (data not showed). Regarding PLA, transmittance data on a common scale showed that all peaks decreased in size after biodegradation. The reduction in the CH-assymetric (2920 cm^{-1}) and CH-symmetric stretches (2850 cm^{-1}) indicated degradation of PLA chains. The decrease of peaks related to carbonyls (1800 cm^{-1} and 1700 cm^{-1}) and ethers (1100 cm^{-1}) indicated chain scission. A reduction of the peak at 1460 cm^{-1} was associated with a decrease of CH_3 side groups. The FTIR spectrum of PCL after biodegradation showed a dramatic change in the polymer backbone evidenced by the reduction of peaks related with CH bonds (3000-2800 cm^{-1}), carbonyl (1800 cm^{-1} and 1700 cm^{-1}) and ethers (1100 cm^{-1}) indicating chain scission and, as a consequence, reduction of polymer's molar mass.

FTIR spectra of synthesized PLA polyesters, sample 1 (physical blend, data not showed) and sample 3 (grafted copolymer, Figure 4.9 (c)), showed a similar decrease in the intensity of all peaks after biodegradation suggesting a reduction in the molar mass of the polymers. Spectra presented a significant reduction in the intensity of the peaks corresponding to the groups C-H, C=O, and C-O. This reduction might have been caused by the metabolism of oxygen consuming microorganisms, as suggested by the biodegradability tests. The FTIR spectrum of sample 2 (physical blend, data not showed) and sample 4 after biodegradation (grafted copolymer, Figure 4.9 (d)), showed a reduction in all peaks related to PCL while no major changes were observed in the peaks related to EVA. The decrease in the intensity of the peaks was more pronounced in samples 3 and 4 (containing the grafted copolymers) than in samples 1 and 2 (physical blends), which is in agreement with the biodegradability results. FTIR spectra of biodegraded samples, present a peak at 3500 cm^{-1}, which is associated with O-

H bonds. A possible explanation for this result is the formation of an alcohol end-groups resulting from polymers biodegradation [36].

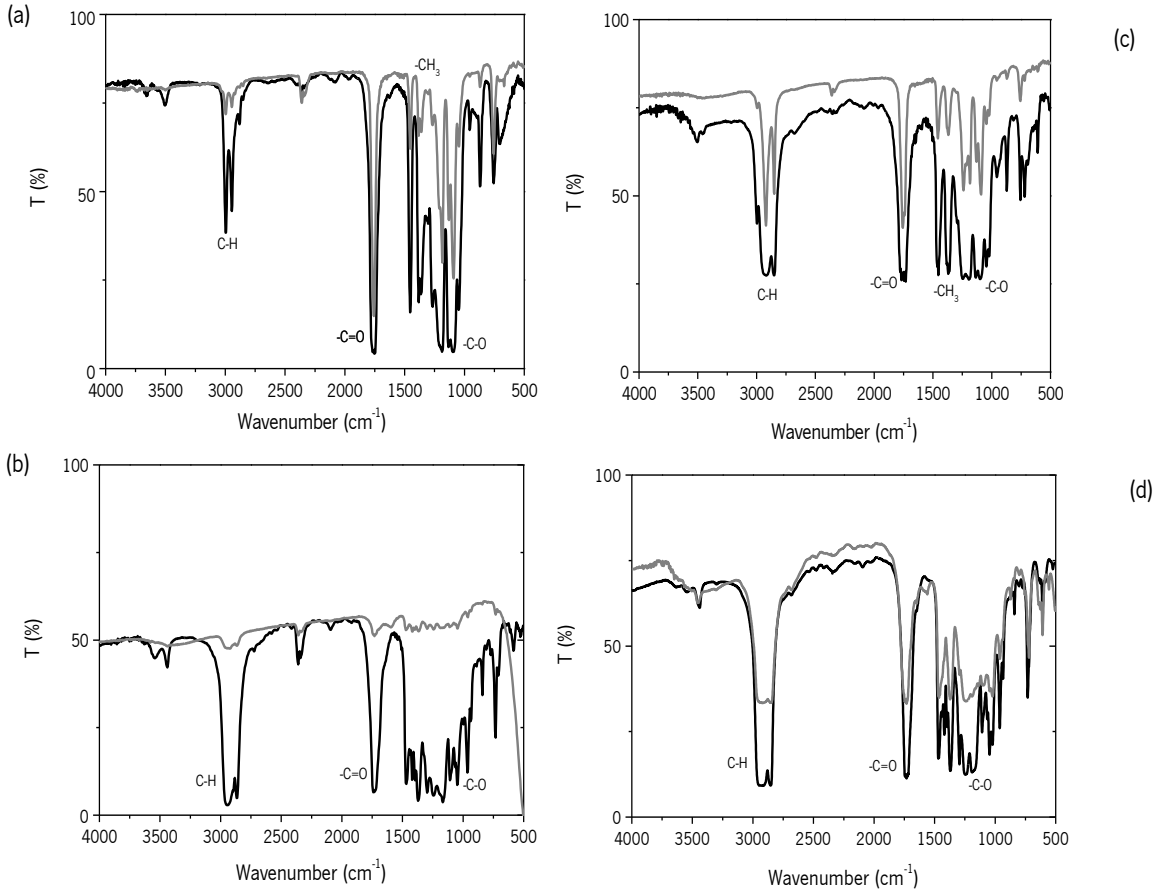


Figure 4.9 FTIR spectra of undegraded (black line) and biodegraded (gray line) blends: (a) PLA, (b) PCL, (c) sample 3, and (d) sample 4.

4.4 Conclusions

Synthesis of EVA-g-PLA and EVA-g-PCL copolymers was investigated by *in situ* polymerization of ε-caprolactone and lactide in the presence of molten EVA copolymer using as initiator titanium phenoxide. The copolymer structure was characterized by ^{1}H NMR after selective extraction. An amount of approximately 11 wt.% for EVA-g-PCL and 8 wt.% for EVA-g-PLA was obtained. SEM micrographs showed that the size of the dispersed phase decreased as the amount of copolymer increased, being almost undetectable for the EVA-g-PCL sample. The samples prepared by *in situ* polymerization, mainly for the EVA-g-PCL sample, exhibit the better mechanical performance.

Biodegradability results, showed that PCL is more biodegradable than PLA, and both more biodegradable than EVA, based on biochemical oxygen demand (ISO 14851:1999). Differences in biodegradability behaviour were observed between the physical blends and the samples prepared by *in situ* polymerization. Moreover, EVA-g-PCL sample was the more biodegradable one. The qualitative results of FTIR spectroscopy of biodegraded polymeric samples confirmed the ones obtained by the standard biodegradability test.

The method used allowed copolymer formation, which even in small amount, promote an enhancement of thermal and mechanical properties of EVA matrix properties and an increase of its degradability. Therefore, *in situ* polymerization is a promising route to produce biodegradable/bio-based materials with good mechanical properties, which could be used in technological applications.

4.5 Acknowledgments

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4.6 Rereferences

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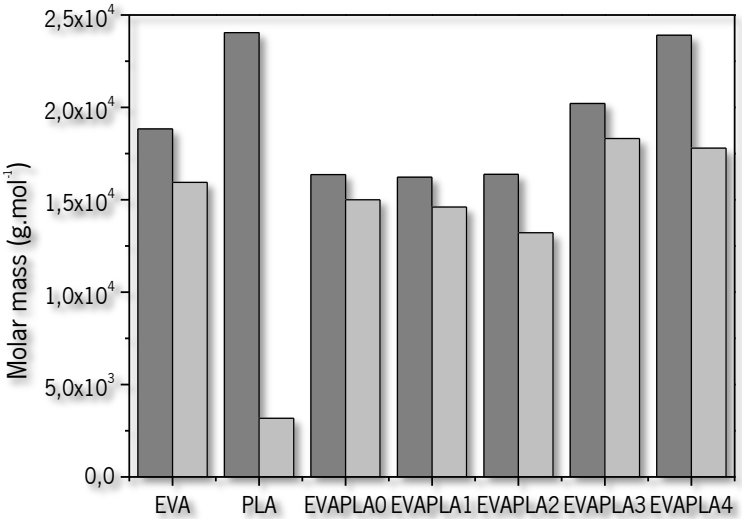
5 | Synthesis of Eva-g-Pla Copolymers Using Transesterification Reactions



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5.1 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 [1]. A way to overcome this problem would be the use of biodegradable polymers. However, they did not prove yet to be useful for commercial applications due to their high price or limitations in terms of thermal and mechanical properties [2].

In the recent years, a lot of effort has been made to develop low-cost and environmentally friendly materials through blending and modification of biodegradable polymers [3, 4]. The use of blends or copolymers of biodegradable and non-biodegradable polymers called bio-based polymers, could be an alternative to conventional non-biodegradable plastics and contribute to the solution of the environmental problem. Even though these polymers are not completely biodegradable, they have economic advantages and better properties than biodegradable ones.

Blends of natural and synthetic biodegradable polymers (starch, poly(ε-caprolactone) and polylactide) and non-biodegradable synthetic polymers (polyolefins, polystyrene, ethylene vinyl acetate) have been widely studied for a variety of industrial applications [5, 6].

Since polyolefins present a combination of physical properties that are ideally suitable to a wide variety of applications, many studies have been carried out blending them with biodegradable polymers [5, 7-9]. Contat-Rodrigo et al. [8] and Matzinos et al. [9] blended polyethylene and biodegradable polymers (polylactide and poly(ε-caprolactone)) to increase the mechanical properties. Matzinos et al. [9] found out that the mechanical properties of the blends depend not only on its content but also on the final morphology. Machado et al. [5] investigated the mechanical properties and biodeterioration of blends of high density polyethylene (HDPE) and poly(ε-caprolactone), polylactide and starch. It was observed that while the blend containing PLA had higher Young's modulus and lower elongation at break than HDPE, the blend containing PCL had the opposite behavior. The biodeterioration was higher for blends containing PCL.

Since the morphology of the blends has a major effect on mechanical properties, another approach to prepare polymers with biodegradable potential is by synthesis of copolymers of non-biodegradable and biodegradable polymers [10]. Within one copolymer different repetitive units can be present and 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 enhanced performance. The source of interest for these materials is linked to the *in situ* compatibilization of polymer blends [11], where a graft copolymer is formed during blending and reduces the surface tension, avoid droplets coalescence and consequently generate polymer blends with enhanced properties.

Moura et al. [12], synthetized copolymers of EVA-g-PLA and EVA-g-PCL through *in situ* polymerization of lactide and/or ε-caprolactone in presence of EVA using titanium phenoxide ($Ti(OPh)_4$ as catalyst. The obtained materials exhibited better mechanical properties and higher biodegradability than the correspondent blends of EVA and PLA or EVA and PCL.

The present work aims to prepare copolymers of EVA-g-PLA through transesterification reactions between ethylene vinyl acetate (EVA) and polylactide (PLA) catalysed by $Ti(OPh)_4$ and $Ti(OPr)_4$. The effect of the amount of grafted copolymer (EVA-g-PLA) on biodegradability, mechanical properties and other physical properties was investigated.

5.2 EXPERIMENTAL

5.2.1 Materials

Ethylene vinyl acetate copolymer (Escorene Ultra Lot. 61E466) with 28 wt.% of vinyl acetate ($\overline{Mn}$ = 18.000 g.mol^{-1}), supplied from Exxon was used as a non-biodegradable polymer and polylactide (PLA) ($\overline{Mn}$ = 22.000 g.mol^{-1}) supplied by NatureWorks® was used as a biodegradable polyester. Titanium propoxide ($Ti(OPr)_4$ from Aldrich and titanium phenoxide ($Ti(OPh)_4$), prepared according to a procedure published elsewhere, [13] were used as a transesterification catalyst.

5.2.2 Synthesis of EVA-g-PLA graft copolymers

The composition of the prepared samples is shown in Table 5.1. The pellets of both polymers were dried in a vacuum oven at 60 °C for 24 hours before use. Samples 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 the catalyst were added. Both catalysts were collected and carried to the mixer under argon atmosphere, to prevent hydrolysis reaction. After 20 min the rotors were stopped and the total sample was removed.

Table 5.1 Composition of the prepared samples.

Sample	EVA	PLA	$Ti(OPh)_4/Ti(OPh)_4$
	(wt.%)	(wt.%)	(wt.%)
EVAPLA0	60.0	40.0	0.0
EVAPLA1	59.5	40.0	0.5
EVAPLA2	59.5	39.8	0.7
EVAPLA3	59.5	39.6	0.9
EVAPLA4	59.5	38.6	1.9

5.2.3 Copolymer Identification and Characterization

The synthesized graft copolymers, EVA-g-PLA, were characterized by several analytical techniques described below.

5.2.3.1 Extraction of Copolymer

The EVA-g-PLA copolymers produced by reactive extrusion were isolated from the other components according to the method previously described in Moura et al [12] and summarized in.Figure 5.1.

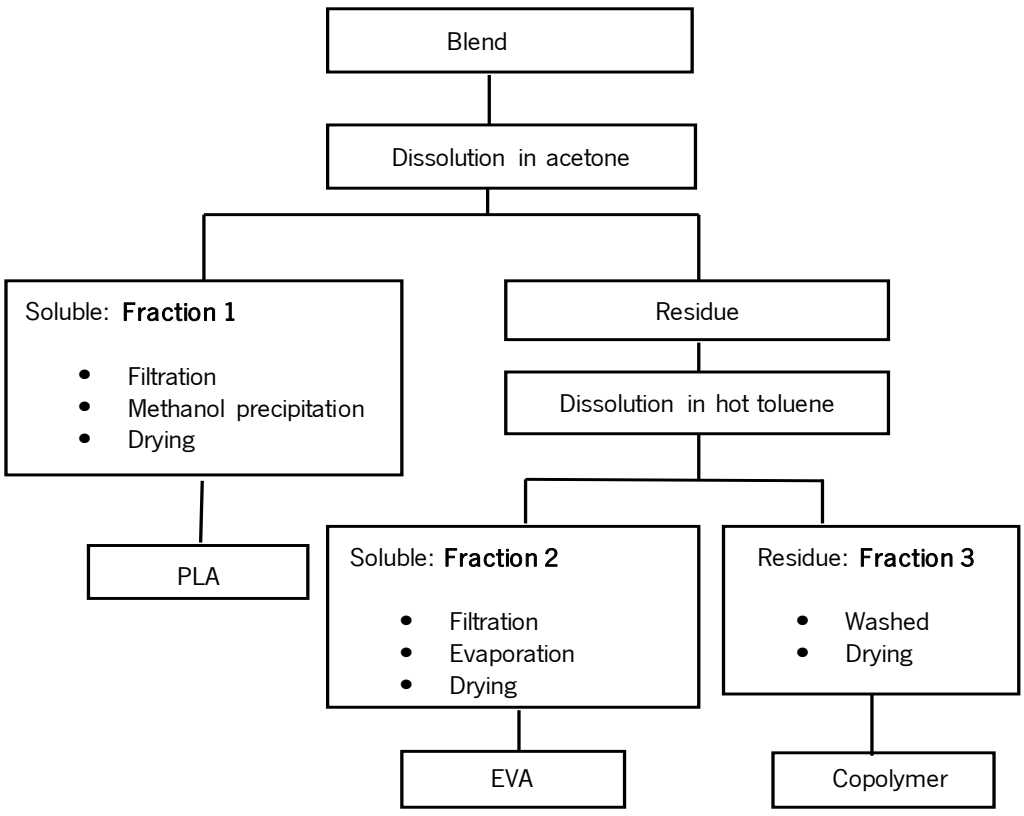


Figure 5.1 Scheme of polymers and EVA-g-PLA copolymers extraction.

5.2.3.2 Structural Characterization

5.2.3.2.1 X-ray Diffractometry (XRD)

Initial polymers and all prepared samples (EVAPLA0 to EVAPLA4) were subjected to XRD analysis. The X-ray diffractograms were performed in an automatic diffractometer, Philips Analytical X-ray PW 1710 BASED, using kα radiation of a copper ampoule (I=1.54056 A), operating at a cathode current of about 30 mA and a voltage around 40 kV. The diffractograms were performed between 0° and 60° (2q) with a scanning speed of 2ϴ min^{-1}. The standard calibration was made using a silicon standard. Films of the samples were placed in an aluminium samples holder.

5.2.3.2.2 Rheological Properties

Oscillatory rheological measurements of original polymers and produced samples 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.

5.2.3.2.3 TGA and DSC

All samples were analyzed using a TGA 2950 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.
Thermal properties of all samples were measured using TA Instruments differential scanning calorimeter (DSC 2920). Samples were heated from 25 °C to 200 °C at a heating rate of 10 °C/min, cooled down to room temperature at the same rate, under liquid nitrogen, in order to eliminate the thermal history of the material. Then, they were heated again until 200 °C and cooled to room temperature at the same heating rate. The degree of crystallinity (X_c) was calculated by ratio of ΔH_f (the apparent melt enthalpy measured from the DSC curves as melting enthalpy per gram) corresponding to the component and ΔH_f^o (the melt enthalpy per gram of the component in its completely crystalline state).

5.2.3.2.4 SEC

The number average molar mass ($\overline{Mn}$) and polydispersity (Ip) were measured by size exclusion chromatography. Solutions were prepared in chloroform (99,9%) and prefiltered on filter plate (hydrophobic polytetrafluoroethylene, 0.45μm pore size) before injection. The analysis was performed

in a SEC Waters 150-CV apparatus equipped with 3 Waters Ultrastyragel columns (HR1 and HR4; inner diameter = 7.8 mm, length = 300 mm and particle size = 5μm) and with a viscometer and refractometer detectors. Chloroform was used as eluent with a flow rate of 1 mL/min and at 23 °C. The calibration curve was previously obtained with polystyrene standards with narrow molar mass distribution.

5.2.3.2.5 SEM

The morphology of the samples was analyzed with a FEI Quanta 400 Scanning Electron Microscope (SEM), after fracturing the samples in liquid nitrogen and coating with a gold thin film.

5.2.3.2.6 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 x 0.8 cm rectangular samples in a longitudinal direction. At least 6 specimens of each sample were tested. Prior to mechanical measurements, films were prepared by compression moulding using the samples that were removed from the mixer.

5.2.3.2.7 Biodegradability Assessment

Biodegradation tests were carried out in aqueous environment under aerobic conditions according to the standard ISO 14851:1999 (Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium) [14], which specify a method for determining the biochemical oxygen demand (BOD) in a closed respirometer. This procedure was previously described in Moura et al. [12].

5.2.3.2.8 FTIR

FTIR spectra of all samples before and after biodegradation were recorded using a Perkin Elmer 1720 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-moulding and analyzed directly using a solid film support.

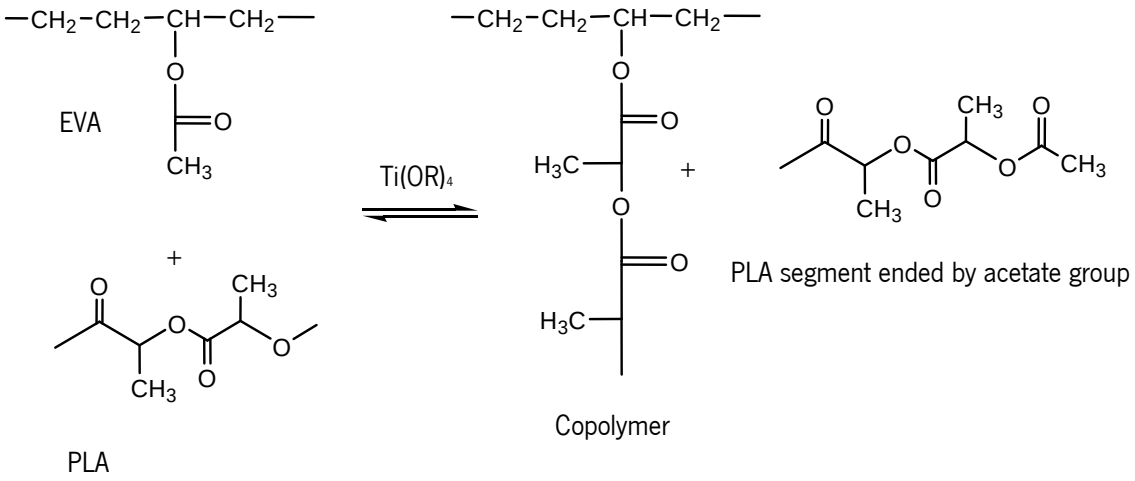
5.2.3.2.9 Elemental Analysis

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

5.3 Results and Discussion

5.3.1 Structural Characterization

Table 5.1 gives the composition of the prepared samples, amount of polymers (EVA and PLA) and catalyst. The amount of PLA and titanium propoxide/phenoxide was varied in order to investigate the effect of catalyst type and amount on the copolymer formation. Therefore, a physical blend (without catalyst) and blends containing four different amount of catalyst were prepared. The expected copolymers was obtained through a transesterification reaction according to the following mechanism [15] and catalyzed by the titanium alkoxide derivative:



First, as expected, the amount of each polymer extracted in the physical blend (EVAPLA0) is the same as the amount of polymer used and no copolymer is formed (Table 5.2). In addition the amount of copolymer extracted for all the samples prepared using titanium phenoxide as catalyst was nil. This means that no reaction occurred between PLA and EVA esters groups when this catalyst was used. This is due to the steric hindrance of phenyl groups bringing by the titanium phenoxide as already noticed in our previous works dedicated to cyclic ester ring-opening polymerization initiated by this titanium derivative [12,13,15].

On the contrary, Table 5.2 shows the amount of polymers and copolymers extracted for each sample prepared using titanium propoxide as catalyst. Three different fractions were obtained: fraction 1 and 2, corresponding to PLA and EVA and fraction 3 corresponding to the copolymer (EVA-g-PLA) formed during the reaction. All fractions were analysed by ^{1}H NMR to get information on its composition (data not shown). The spectra obtained for fractions 1 and 2 confirmed that only PLA and EVA were

extracted. As expected, the highest amount of copolymer, around 25 wt.%, was obtained for EVAPLA4 with the highest amount of catalyst followed by EVAPLA3, EVAPLA2 and EVAPLA1.

Table 5.2 Fractions amounts of polymers and copolymers extracted.

Sample	Fraction 1	Fraction 2	Fraction 3
	(wt.%)	(wt.%)	(wt.%)
EVAPLA0	40	60	-
EVAPLA1	39	59	2
EVAPLA2	39	58	3
EVAPLA3	37	55	8
EVAPLA4	29	46	25

X-ray measurements were performed to analysed structural changes due to copolymer formation. The X-ray diffraction spectra of EVAPLA0 and EVAPLA4 samples are presented in Figure 5.2. While EVAPLA0 sample has a sharp diffraction peak at 21.35°, similar to EVA, and a few small peaks around 23.6°, sample EVAPLA4 exhibits the same peaks as EVAPLA0 and a new peak at around 15°. This new peak can be attributed to a different crystalline phase, which can be due to the presence of the copolymer. Moreover, these results indicate that titanium propoxide is not in polymorphous form, but connected to the structure, where acts as a template (structuring agent) and consequently promotes not only the appearing of the new peak, but also the angle shifts for low values, due the changes occurred in the plans orientation [16].

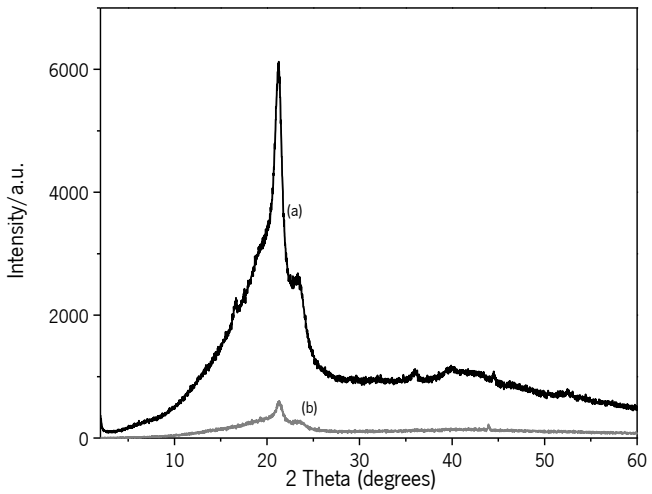


Figure 5.2 XRD diffraction patterns of (a) EVAPLA4 and (b) EVAPLA0.

To investigate the influence of the formed copolymer on the rheological behaviour, oscillatory rheological measurements were carried out. The complex viscosity and storage modulus as a function of frequency are shown in Figure 5.3 (a) and 5.3 (b), respectively. Despite all samples show a non-Newtonian behaviour, significant differences exist among them. With the exception of the samples with the highest amount of copolymer (EVAPLA4), the viscosity and the modulus of the other samples are between the curves of PLA and EVA. The sample without catalyst (physical blend), presents, as expected, the lower complex viscosity (1.8E4 Pa.s) and elastic modulus (7.8E2 Pa) at low frequency (0.01Hz). As the amount of catalyst increases, i.e., increase of amount copolymer formed, the complex viscosity and elastic modulus at low frequencies shifts to higher values, in agreement with the extractions results. The complex viscosity and the elastic modulus of sample EVAPLA4 is higher than for EVA (7.2E4 Pa.s and 3.2E4 Pa, respectively at f=0.01Hz). Moreover, the slope of this curve is different from the other samples, which can be associated with more branched structure of the copolymer formed in this case. Since this blend has a higher amount of copolymer it is expected that it has higher number of ester groups of EVA linked to PLA chains.Therefore, it will behave as a branched structure, which explains the high complex viscosity and elasticity at low frequencies. These results corroborate that the amount of copolymer obtained for EVAPLA4 was higher.

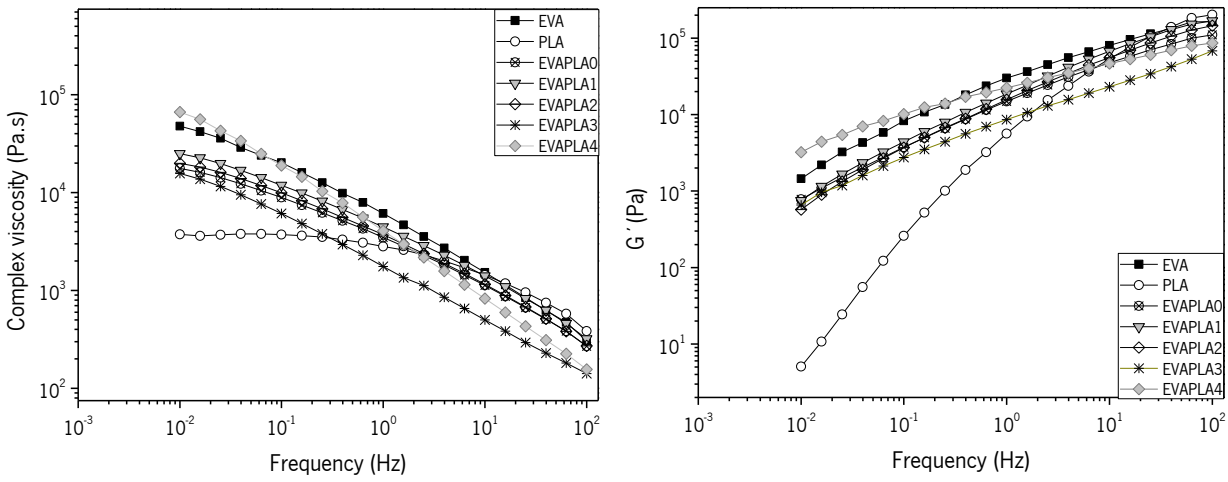


Figure 5.3 Rheological behaviour of the individual components and prepared materials (a) complex viscosity and (b) elastic modulus.

Figure 5.4 depicts the thermal behaviour of EVA, PLA, and prepared samples when heated from 35 °C to 600 °C at a heating rate of 10 °C/min. In the case of EVA two weight lost steps can be observed. A first one at around 300 °C (12.44%), attributed to the decomposition of the acetate groups, attributed

to the release of acetic acid [17]. At approximately 370 °C, a second weight lost (86.94%) can be noticed, corresponding to the degradation of the olephinic part of the copolymer (C-C and C-H bonds). PLA presents a one-step decomposition profile with a single decomposition temperature. This polymer has lower thermal stability than EVA, because its degradation peak is around 250 °C and it decomposes completely (0% char residue) at 300 °C.

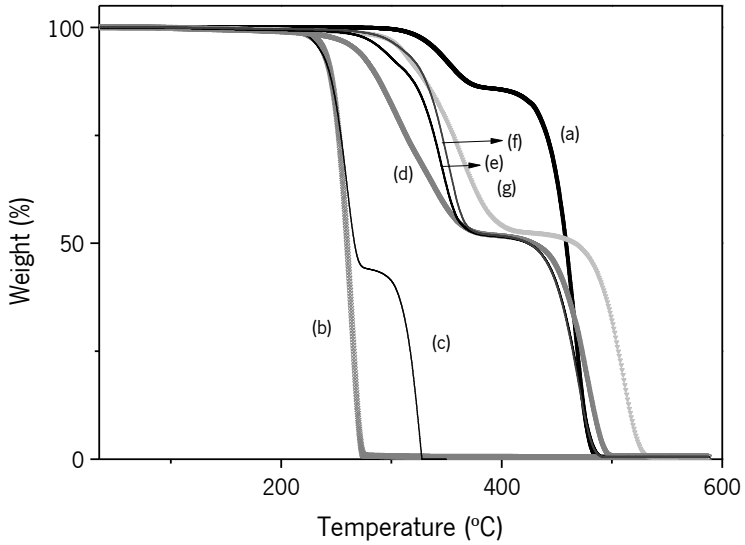


Figure 5.4 Thermograms of (a) EVA, (b) PLA, (c) EVAPLA0, (d) EVAPLA1, (e) EVAPLA2, (f) EVAPLA3 and (g) EVAPLA4.

All the prepared samples also show two steps degradation, corresponding to the degradation of the individual components. EVAPLA0 sample has an intermediate behaviour between EVA and PLA, being the first decomposition temperature (251.8 °C) close to the one of PLA and the second (290 °C) close to the one of EVA. Since this sample is a physical blend of EVA and PLA, this behaviour would be expected. Even though, the thermal behaviour of the all other samples is similar to EVAPLA0, a shift to higher decomposition temperatures can be observed, which increases as the amount of catalyst increases. This might be associated with the amount of grafted polymer present in each sample, its branching structure seems to contribute to an increase of the thermal stability.

SEC analysis of polymers and all prepared samples were performed to confirm copolymer formation and its effect on molar mass. Figure 5.5 depicts chromatograms of the neat polymers (EVA and PLA) and prepared samples. Each initial polymer has a single peak at a certain elution time, being the elution time slightly different. Even though, the EVAPLA0, EVAPLA1 and EVAPLA2 present only one peak, which can be explained by the similarity of the molar mass of neat polymers (18.000 and 22.000 $g.mol^{-1}$ for EVA and PLA respectively), some differences can be noticed among them, which can be related to the

amount of copolymer present. EVAPLA3 and EVAPLA4 exhibit a different behaviour, the chromatograms of both samples have a different shape, two peaks with a retention time of 22.1 and 24.7 min can clearly be noticed in EVAPLA4. This suggests that molecules with different molar mass are presented in the sample. Moreover, overlapping these chromatograms with the individual components, it can be observed that they do not cover the elution time of both individual homopolymers, which indicates that some degradation also occurs during processing. These results corroborate the proposed mechanism, i.e., the transesterification reaction takes place between the ester groups of both polymers.

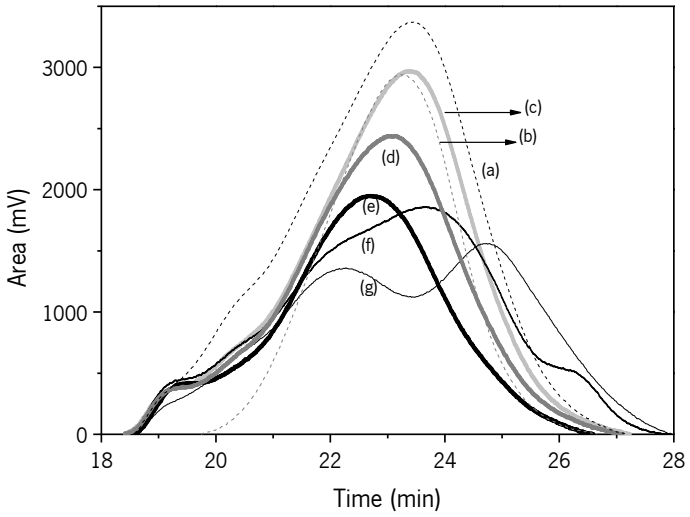


Figure 5.5 SEC chromatograms of (a) EVA, (b) PLA, (c) EVAPLA0, (d) EVAPLA1, (e) EVAPLA2, (f) EVAPLA3 and (g) EVAPLA4.

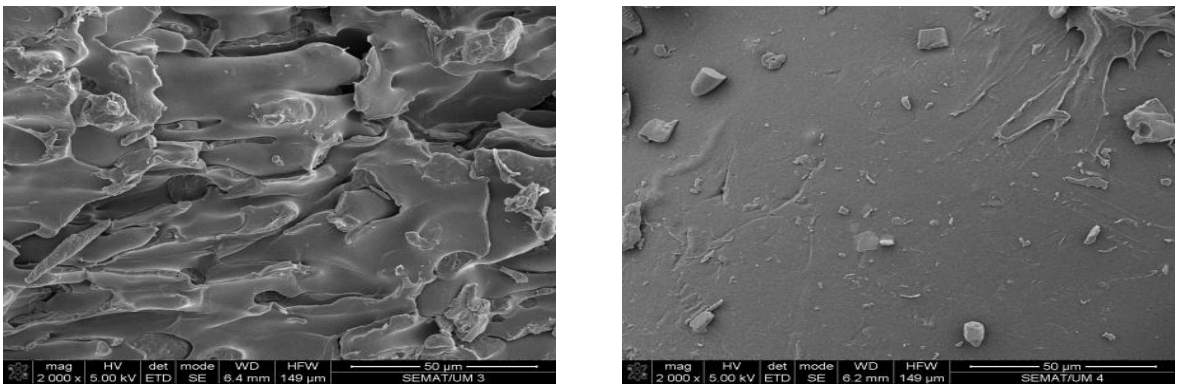
The number average molar mass ($\overline{Mn}$) measured for neat polymers (Table 5.3) exhibit negligible differences when compared to the values given by the supplier. With the exception of EVAPLA4, which has a slightly higher number average molar mass, the values of the other prepared samples are similar among them.

Table 5.3 $\overline{Mn}$ obtained from SEC measurements for neat polymers and prepared samples before and after biodegradation.

Sample	$\overline{Mn}$ (g.mol^{-1}) (From the datasheet)	$\overline{Mn}$ (g.mol^{-1}) (Before degradation)	$\overline{Mn}$ (g.mol^{-1}) (After degradation)
EVA	18.000	18.831	15. 943
PLA	22.000	24.046	3.171
EVAPLA0	-	20.122	19.288
EVAPLA1	-	20.235	19.245
EVAPLA2	-	20.741	18.885
EVAPLA3	-	20.814	18.310
EVAPLA4	-	23.900	17.000

5.3.2 Morphology and Properties

Figure 5.6 depicts the morphology of the samples analysed by SEM after facture in liquid nitrogen. The morphology of all prepared samples consists in dispersed PLA particles in the EVA matrix, but significant differences can be observed among them. While sample EVA/PLA0 (Figure 5.6 (a)) exhibits a coarse morphology, the PLA particles are almost undetectable in EVA matrix of sample EVAPLA4 (Figure 5.6 (b)). This change in morphology can be explained by the copolymer formation during reaction, which acts as compatibilizer decreasing the interfacial tension between blend components and consequently the size of the dispersed phase.



(a) (b)

Figure 5.6 SEM micrographs of samples (a) EVAPLA0 and (b) EVAPLA4.

Tables 5.4 and 5.5 present the melting temperature and degree of crystallinity, obtained from DSC measurements of neat polymers and prepared samples. The melting temperature and the degree of crystallinity of EVA and PLA of the physical blend is practically the same as the values obtained for

individual components. Due to the immiscibility between EVA and PLA, it would be expected that both polymers kept their thermal properties.

Table 5.4 Melting temperature (Tm, °C) melting entalphy (ΔH, J/g) and degree of cristallinity (X_c, %) of neat polymers.

Polymer	T_m	ΔH	ΔH°	X_c
	(°C)	(J/g)	(J/g)	(%)
EVA	85.4	11.6	44.0	26.4
PLA	150.0	25.7	93.6	27.5

The results of EVAPLA1 and EVAPLA2 present small changes in melting temperature and crystallinity degree when compared to individual blend components or physical blend. However, EVAPLA4 presents considerable changes, the melting temperature of EVA changes slightly from 85.4 °C to 85.0 °C, the melting temperature of PLA changes from 150.0 °C to 140.2 °C and the crystallinity degree of both polymers decrease. This difference could be related with the increase in compatibility between EVA and PLA, as it was observed by SEM.

Table 5.5 Melting temperature (Tm, °C), melting enthalpy (ΔH , J/g) and degree of cristallinity (X_c, %) of prepared samples.

Sample	EVA			PLA		
	T_m (°C)	ΔH (J/g)	X_c (%)	T_m (°C)	ΔH (J/g)	X_c (%)
EVAPLA0	86.7	8.8	20.0	149.0	23.2	24.8
EVAPLA1	86.0	8.3	18.9	143.5	24.6	26.2
EVAPLA2	85.7	8.2	18.6	143.3	23.8	25.4
EVAPLA3	85.2	7.7	17.5	141.3	22.8	24.3
EVAPLA4	85.0	7.5	17.0	140.2	20.2	21.5

The decrease of degree of crystallinity, namely for EVAPLA3 and EVAPLA4 is related with the transesterification reactions and its extent, from which result covalent bonds between PLA and EVA segments and lead to a lowered regularity of the molecular structure. Also, the occurrence of transesterification reactions leads to changes of molecular structures of the polyesters, which promotes changes of crystallinity.

Elongation at break and young modulus as a function of copolymer amount are depicted in Figure 5.7. The addition of PLA (ε=8.0%) to EVA (ε=329.2%) leads to lower flexible materials, i.e., a decrease of the elongation at break was observed, namely for physical blends, where the copolymer amount was zero. This result can be explained by the immiscibility of the blend components. Nevertheless, increasing the copolymer amount increases the elongation at break. A similar trend was observed for young modulus (Figure 5.7), increases and it is higher for samples with the higher amount of copolymer.

This enhancement can be attributed to the formation of EVA-g-PLA copolymer and its compatibility effect, as observed by SEM (Figure 5.6).

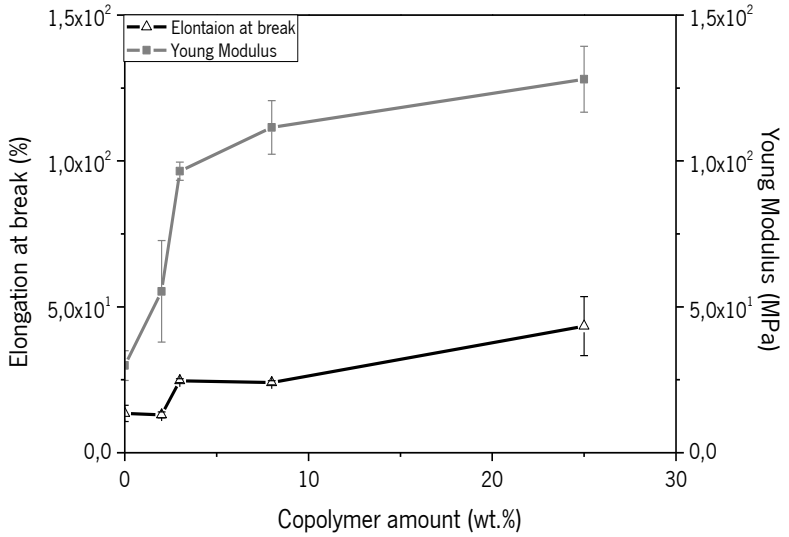


Figure 5.7 Young modulus and elongation at break as function of copolymer amount.

5.3.3 Biodegradability Assessment

The biodegradability of the prepared samples was characterized by biochemical oxygen demand, where biodegradability is expressed as the amount of O_2 consumed during biodegradation divided by their theoretical oxygen demand (ThOD), using the elemental analysis data of Table 5.6. The values of the theoretical oxygen demand were calculated based on elemental analysis of each sample.

Table 5.6 Elemental analysis of all samples.

Sample	Carbon (%)	Hydrogen (%)	Oxygen (%)	Chemical formula
EVAPLA0	66.7	9.5	23.9	C_4H_6O
EVAPLA1	67.5	9.7	22.7	C_4H_7O
EVAPLA2	67.6	9.7	22.7	C_4H_7O
EVAPLA3	68.3	10.0	21.7	C_4H_7O
EVAPLA4	69.1	10.0	20.9	C_4H_8O

The results during 60 days of biodegradation are presented in Figure 5.8. Among the neat polymers, EVA shows the lowest degree of biodegradability and PLA the highest. This would be expected because it is well known that aliphatic polyesters are biodegradable in a wide variety of ecosystems [18]. Several studies performed to evaluate the biodegradability of PLA indicated that PLA films were more biodegradable under composting conditions at higher temperatures (58 °C), 55% [19], 64% [20], and 86% [21], than at lower temperatures (30 °C), 3.7% [22] in the aquatic tests. The fact that higher temperatures favour non-enzymatic hydrolysis of ester bonds support the results obtained for PLA films [23, 24]. These values cannot be directly compared with the value obtained in the present study, around 52.9% (30 °C), once the molar mass, biodegradability methods, experimental conditions and length of the assays used were different.

Blending PLA with EVA had a positive effect on biodegradability of the latter, as EVAPLA0 (10.7%) exhibited slightly higher biodegradability than EVA (8.9%). Samples containing grafted copolymers showed higher biodegradability, being EVAPLA4 the sample with higher value (24.2%). Literature studies reported that grafting reactions favour the formation of branched/crosslinked structures, promoting the increase of the amorphous zones concentration in the polymer [24]. Furthermore, it seems that the microbial accessibility to ethylene vinyl acetate groups increases when higher amount of PLA are grafted to EVA. Comparing samples with copolymers to physical blend, it is possible to observe that the crystallinity decreases (see Tables 5.4 and 5.5), which is followed by a decrease of the melting temperature. Therefore, the increase in the concentration of amorphous regions increases the biodegradability, because of the higher mobility of the chains and their higher mobility to the microorganisms.

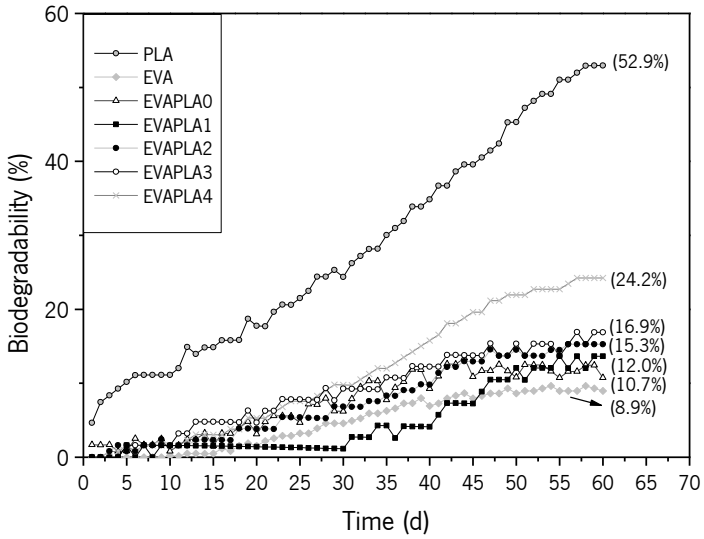


Figure 5.8 Biodegradability of the copolymers and blend according to ISO 14851:1999.

To evaluate the extent of biodegradation of all samples, FTIR spectra of initial and biodegraded samples were recorded (Figure 5.9). Each Figure contains two spectra, corresponding to initial and biodegraded material. As expected, in the case of EVA no significant changes occurred (data not shown), because EVA is a non-biodegradable synthetic polymer. The major changes occurred for PLA spectrum (Figure 5.9 (a)). Concerning PLA, transmittance data on a common scale showed that all peaks decreased after biodegradation. The reduction in the CH-assymetric and CH-symmetric stretches at 2920 cm^{-1} and 2850 cm^{-1}, respectively, indicated a reduction of the molar mass of the PLA. The decrease of peaks related to carbonyls (1800 cm^{-1} and 1700 cm^{-1}) and ethers (1100 cm^{-1}) indicated chain scission. A reduction of the peak at 1460 cm^{-1} was associated with decrease of CH_3 side groups.

FTIR spectra of EVAPLA0 (Figure 5.9 (b)) show that no major changes occurred during biodegradation. The small differences are probably related to PLA consumption in the physical blend, during the metabolism of microorganisms, resulting in a small reduction of molar mass, since EVA is a non-biodegradable polymer, as previously described. Even though similar results were obtained for EVAPLA4 (Figure 5.9 (c)), the decrease in the intensity of all peaks is more pronounced, which is in agreement with the BOD results and confirmed by the reduction in the molar mass of the samples (see Table 5.3).These results can be explained based on consumption of carbon in the polymer chains by the microorganisms, i.e., presented a significant reduction in the intensity of the peaks corresponding to the groups C-H, C=O, C-O. This reduction might have been due to the metabolism of oxygen consumption microorganisms, as suggested by the BOD test.

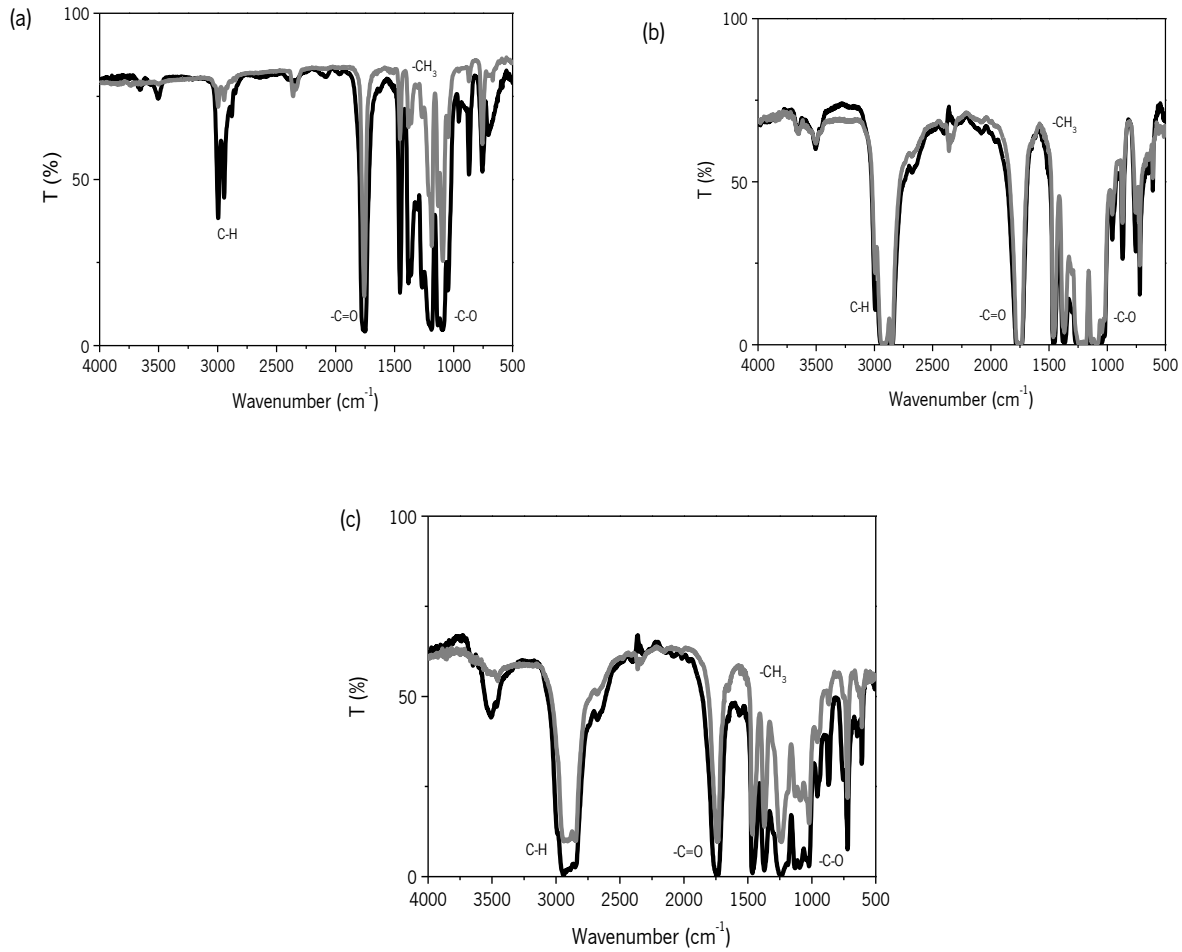


Figure 5.9 FTIR spectra of undegraded (black line) and biodegraded (gray line) blends: (a) PLA, (b) EVAPLA0, and (c) EVAPLA4.

The biodegradation was also evaluated, in a quantitative way, by SEC measurements (see Table 5.3 and Figure 5.10). PLA, as expected, suffered the highest molar mass reduction (87.0%). Among all the prepared samples, EVAPLA4, which contains higher copolymer amount, shows the highest decrease in number average molar mass (29.0%). Moreover, the main distribution peak had obviously shifted to the right side (data not shown) confirming the scission of the main chain and consequently oligomers formation. After 60 days of biodegradation the retention time increased and the intensity of peak slightly decreased.

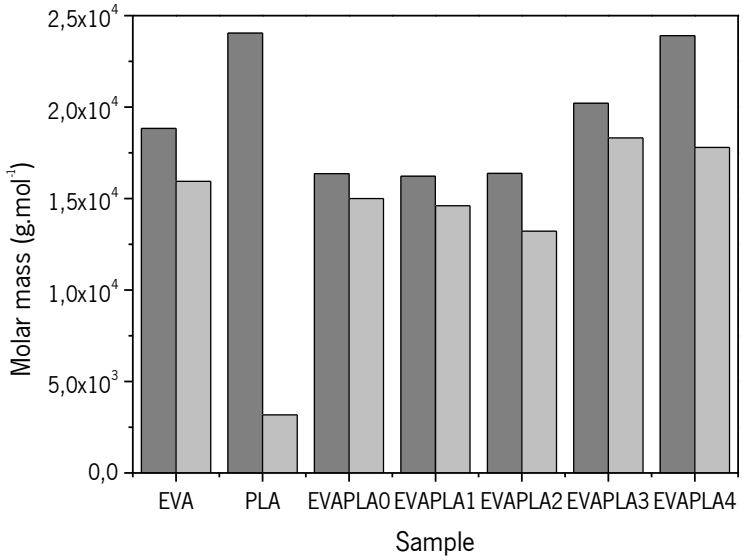


Figure 5.10 Number average molar mass of the samples before and after biodegradation.

5.4 CONCLUSIONS

Copolymers of EVA-g-PLA were synthesized using titanium propoxide and titanium phenoxide as catalysts, which were characterized by several analytical techniques.

Changing the ratio of PLA and catalyst resulted in a series of graft copolymers, which allowed to prepare materials with different rheological, thermal and mechanical properties.

Biodegradability results showed that PLA is more biodegradable than EVA based on biochemical oxygen demand. Differences in biodegradability behaviour were observed between the physical blend and the samples containing copolymers. The qualitative and quantitative, by FTIR and SEC results, showed that EVAPLA4 was the more biodegradable.

The results obtained in this work show that the method employed is a promising route to produce biodegradable/bio-based materials with good mechanical properties, which could be used in technological applications.

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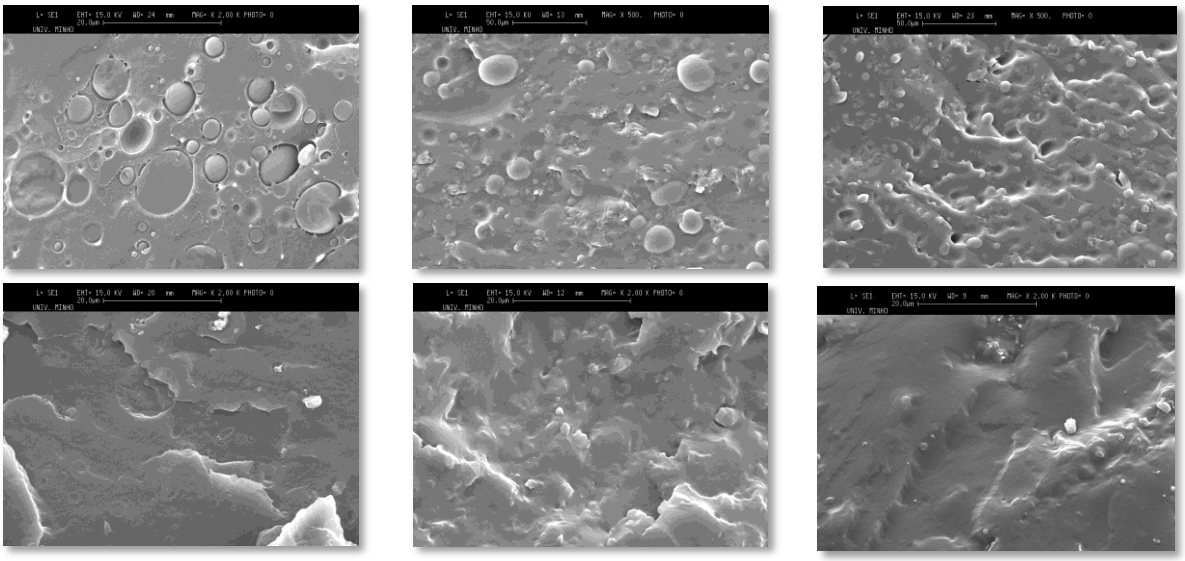
6 | Effect of PCL and EVA Molar Mass on EVA-g-PCL Copolymer Formation



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6.1 INTRODUCTION

The use of biodegradables polymers is an alternative to conventional non-biodegradable 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 best known, due to their thermoplastic and biodegradability properties, the aliphatic polyesters [3], such as, poly(ε-caprolactone) (PCL), polylactide (PLA) and other aliphatic polyesters from different lactic acid derivatives [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.

Bio-based polymers can be an alternative, these can be produced by the combination of biodegradable and cheap commodity synthetic polymers. They can be prepared by 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 [8-14]. 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, 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, exhibit better mechanical performance and enhanced biodegradability. Using a different approach, Moura et al. [23], 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 to produce biodegradable/bio-based polymers with properties similar to conventional ones.

The present work aims to prepare biodegradable polymers of EVA and PCL by transesterification reactions 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 to prepare blends. The ratio between PCL and catalyst was varied in order to obtain different amount of copolymer.

6.2 EXPERIMENTAL

6.2.1 Materials

Two grades of ethylene vinyl acetate (EVA28) (28 % of vinyl acetate (VA)) ($\overline{Mn}$ = 18.000 g.mol^{-1} and $\overline{Mn}$ = 7.900 g.mol^{-1}) supplied from ARKEMA were used as a non-biodegradable synthetic polymer and poly(ε-caprolactone) (PCL) with two different molar mass ($\overline{Mn}$ = 10.000 g.mol^{-1} and $\overline{Mn}$ = 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 6.1 shows the composition of the prepared materials.

Table 6.1 Composition of the prepared samples.

Sample	EVA1[a)]	EVA2[b)]	PCL1[c)]	PCL2[d)]	Ti(OPr)$_4$
	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(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

[a)] – EVA1 ($\overline{Mn}$ = 18.000 g.mol^{-1})

[b)] – EVA2 ($\overline{Mn}$ = 7.900 g.mol^{-1})

[c)] – PCL1 ($\overline{Mn}$ = 10.000 g.mol^{-1})

[d)] – PCL2 ($\overline{Mn}$ = 60.000 g.mol^{-1})

6.2.2 Synthesis of EVA-g-PCL graft copolymers

The pellets of both polymers were dried in a vacuum oven at 60 °C for 24 hours before use. Samples were prepared in an internal mixer (Haake Rheocord 90; volume 50 mL), equipped with two rotors

running in a counter-rotating way. The set temperature was 160 °C and the rotor speed was 50 rpm. After 20 min, the rotors were stopped and the sample was removed. The polymers 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.

6.2.3 Materials Characterization

The synthesized of EVA-g-PCL copolymers were characterized by several analytical techniques described below.

6.2.3.1 Copolymers Extraction

The EVA-g-PCL copolymers were isolated from the homopolymers according to the method previously developed by Moura et al. [22], being solubility tests of the polymers summarized in Table 6.2.

Table 6.2 Solubility of the polymers.

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

6.2.3.2 Structural Characterization

6.2.3.2.1 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.

6.2.3.2.2 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 to room temperature at the same rate, under nitrogen, in order to eliminate the thermal history. Then, samples were heated again until 120°C.

6.2.3.2.3 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.

6.2.3.2.4 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 x 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 moulding using the samples that were collected from the mixer.

6.2.3.2.5 Biodegradability Assessment

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

6.2.3.2.6 FTIR

FTIR spectra of all samples before and after biodegradation were recorded using a 4100 Jasco spectrometer in the range of 500-4000 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 moulding and analyzed directly using a solid film support.

6.2.3.2.7 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.

6.3 Results and Discussion

6.3.1 Copolymer Identification

Transesterification reactions between EVA and PCL catalysed by $Ti(OPr)_4$ lead to EVA-g-PCL formation as it is shown in Figure 6.1.

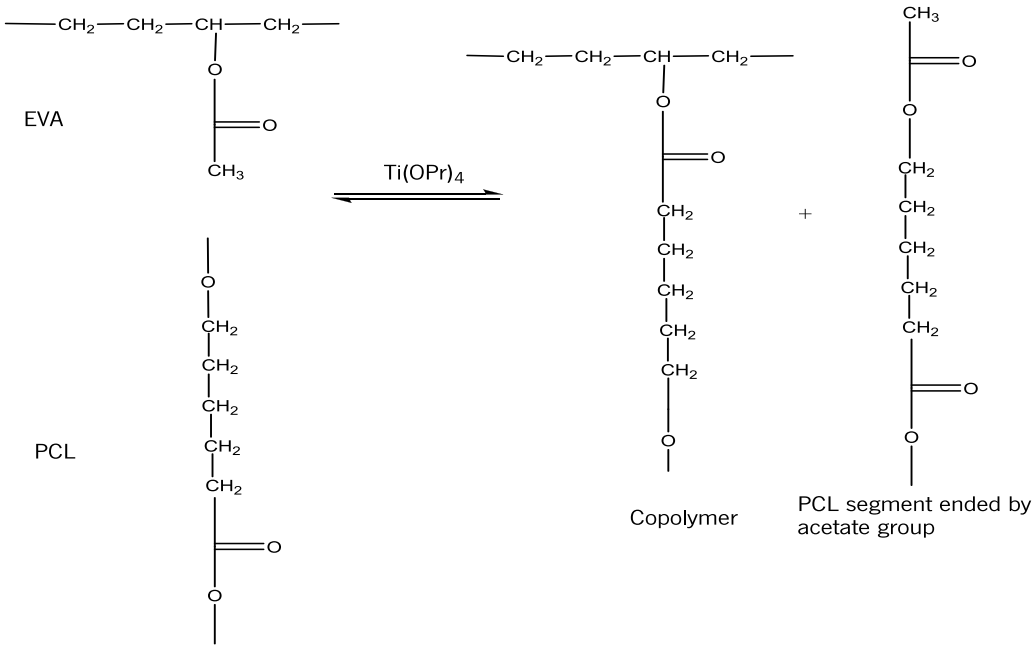


Figure 6.1 Recation mechanism of EVA-g-PCL copolymer formation by transesterification reaction.

Therefore, the solubility of EVA and PCL was explored (see Table 6.2) in order to dissolve them selectively and 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 analysed by ^{1}H NMR to get information on its composition (data not shown) and the spectra obtained confirmed that only PCL and EVA were extracted. Unfortunately, ^{1}H NMR for EVA-g-PCL copolymer was impossible to achieve, owing to the insolubility of this fraction 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 Figure 6.2. As expected, for physical blends (A1, B1 and C1) the amount of copolymer formed was nil. Its means, that

no reaction took place without catalyst. Conversely, for all other samples copolymer was formed and it amount varies with the amount of catalyst.

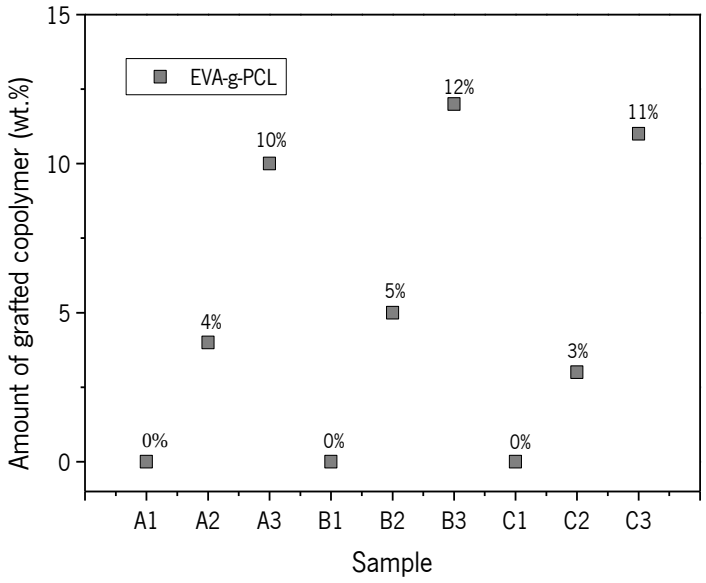


Figure 6.2 Fractions amounts of copolymers extracted.

For each serie of samples, the amount of EVA-g-PCL copolymer increases as the amount of catalyst increases. Furthermore, the difference between the copolymer amounts obtained using different EVA molar mass (A3 and B3) was very low, being slightly higher when EVA2, with lower molar mass, was used (see Figure 6.2). A possible explanation is that polymers with similar molar mass are more prone to be grafted/crosslinked in the main chain [24], EVA2 has similar molar mass to PCL1 (7.900 and 10.000 $g.mol^{-1}$, respectively).

In a similar way, when PCL molar mass changes, the difference between the copolymer amount obtained using higher PCL molar mass was also very 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].

Since oscillatory rheological measurements at low frequency are sensitive to molecular structure, the rheological behaviour of initial polymers and prepared samples was performed, using this technique. The complex viscosity of the neat polymers and prepared materials as a function of frequency, at 160°C, is shown in Figure 6.3. While PCL1, PCL2 and EVA2 exhibited a Newtonian behavior, EVA1 has a non-Newtonian behavior, in the investigated frequency range (0.01 to 100 Hz), which can be related with their molar mass. Regarding the prepared materials, A1 shows a non-Newtonian 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 due to the amount of copolymer formed (10%).

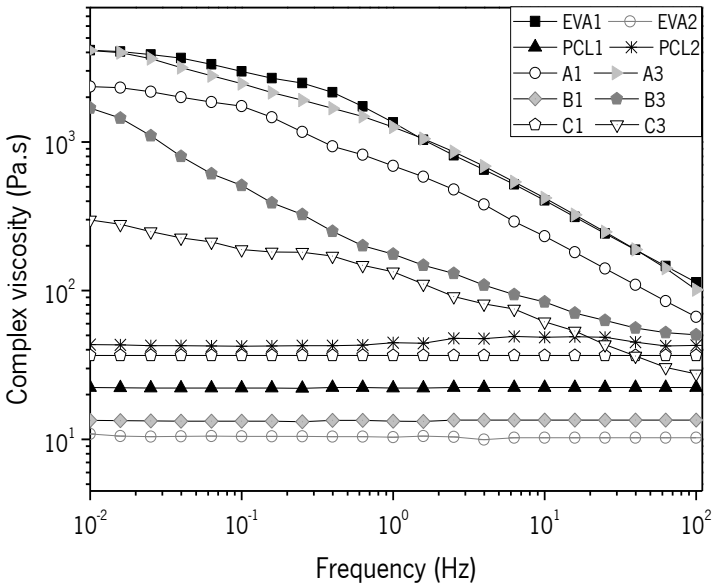


Figure 6.3 Rheological behaviour of the individual components and prepared materials.

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 it 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, i.e., shear thinning was also not noticed. Conversely, the sample containing high copolymer amount (C3) has higher viscosity (3.0E2 Pa.s) and shear thinning behavior namely at low frequencies.

Figure 6.4 (a) depicts the thermal behavior (weight loss) of EVA, PCL and Figure 6.4 (b) of the prepared samples, when heated from 35 °C to 600 °C at a heating rate of 10 °C/min, under nitrogen flow atmosphere. 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). Even though, similar decomposition occurs for EVA2 differences can be noticed. EVA2 has a lower decomposition temperature, which can be attributed to the lower molar mass. 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, only one-step decomposition profile. The difference between both, lies in the fact that thermal stability of PCL2 is higher than PCL1, which could be once more explained based on its molar mass. Comparing PCL1 to both EVAs, the former has lower thermal stability; its first decomposition temperature is around 277 °C and it is completely decomposed (0% residue) at 432 °C (Figure 6.4 (a)). Although PCL2 has higher initial thermal stability than PCL1, it decomposes completely (0% char residue) at 473 °C. Therefore, it has lower thermal stability than both EVA as well. Figure 6.4 (b) shows that sample A1 has the higher initial thermal stability and sample B1 the lowest. Since both samples were prepared with the same PCL, the difference might be related with EVA molar mass. The thermal behavior of sample C1 is between A1 and B1.

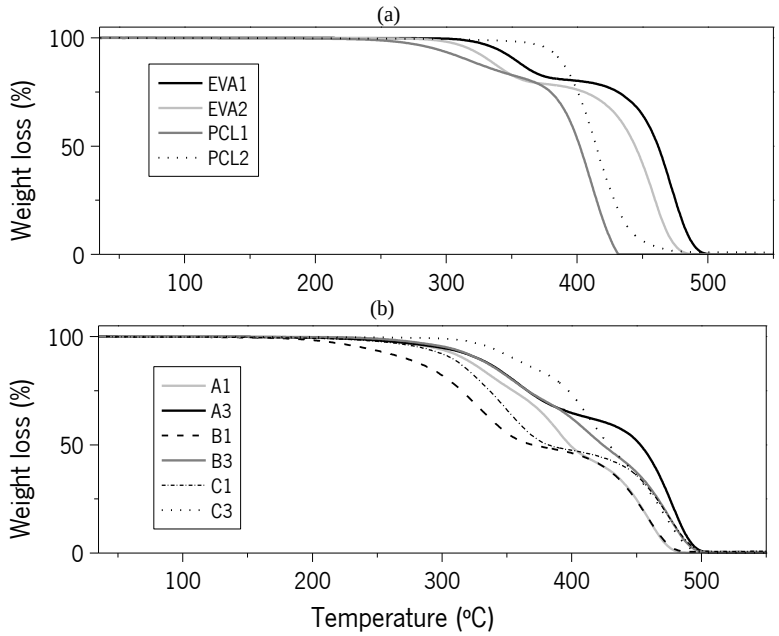


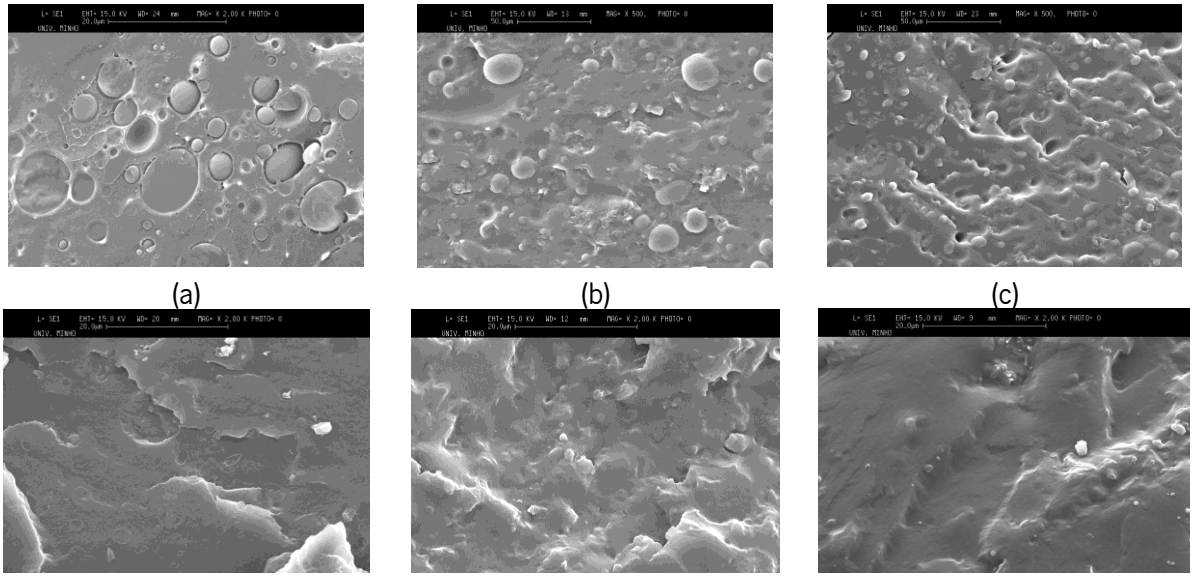
Figure 6.4 Thermograms of (a) neat polymers and (b) prepared samples.

All 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, followed by samples A3 and B3. This behavior can be explained both, by the copolymer formed and the molar mass of the initial polymer.

6.3.2 Morphology and Physical Properties

Figure 6.5 depicts the morphology of the various samples analyzed by SEM after fracture in liquid nitrogen. The morphology of the physical blends (Figure 6 (a), (b) and (c)) consists in a dispersion of PCL particles in a EVA matrix, but differences can be noticed among them. Even though the

micrographs of Figures 6.5 (b) and 6.5 (c) have lower magnification than the one presented in Figure 6 (a), it is clear that the size of the PCL dispersed phase decreases from A1 to B1 and even more for C1. This difference is associated with the polymers viscosity. As the EVA molar mass decreases between samples A1 and B1, the compatibility increases. As expected, the size of the PCL dispersed phase becomes smaller as the amount of copolymer increases, being almost undetectable for A3, B3 and C3. 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. Besides, 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.



(a) (b) (c)

(d) (e) (f)

Figure 6.5 SEM micrographs of samples (a) A1, (b) B1, (c) C1, (d) A3, (e) B3 and (f) C3.

Table 6.3 displays the melting temperature (Tm), obtained from DSC measurements for neat polymers and prepared samples. Sample A1, has a value between 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 due to similar melting temperature of neat polymers that is not possible to separate in sample A1 measurement. As the amount of copolymer increases, the melting temperature of the samples (A2 and A3) decreases. This can be associated with increase in compatibility as the copolymer amount increases, which is supported by the SEM analysis.

Changing EVA1 by EVA2, B1 melting temperature obtained is the same as for PCL1. Nevertheless, B3 (53.4 °C) presents considerable changes when compared to individual blend components and/or corresponding physical blend. Thus, melting temperature decreases, mainly for samples A3 and B3, which can be associated with the reaction that took place, from which resulted covalent bonds between PCL/EVA segments, leading to a lower regularity of the molecular structure.

Table 6.3 Melting temperature (Tm, °C) of neat polymers and prepared samples.

Sample	Tm (°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

Changing PCL1 by PCL2, the melting temperature obtained for C1, physical blend, is higher (63.7 °C). Sample C3 presents considerable changes (55.0 °C), which can be explained by the SEM results (Figure 6.5 (f)), in this case it is hard to identify two phases.

The results evidence that the presence of copolymer promotes 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 Figure 6.6. The results for PCL1 are not shown, because under the conditions used to test the samples, this polymer was very brittle. As it can be noted, blending PCL1 and EVA1

(Figure 6.6 (a)) results in a material that has lower tensile strength and elongation at break lower 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 A2 and A3, respectively) and elongation at break (171 and 409%) increase as the amount of copolymer increases, being the elongation at break of sample A3 similar EVA1 (380%). These results can be explained by the presence of copolymer at the interface, which decreases the interfacial tension and improves de adhesion. This can be seen in SEM results, the size of PCL dispersed phase decrease significantly from A1 to A3.

Adversely, blending EVA2 with either PCL1 or PCL2, results in materials with enhanced tensile strength, as it can be seen in Figure 6b and 6c. As it was observed for samples A, for samples B and C, both tensile strength and elongation at break increases as the amount of copolymer increases. 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 tensile strength and the amount of copolymer obtained (11%). Also, its elongation at break (58%), become similar to EVA2, which is a good result, since PCL2 has a very low elongation a break .

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, since it is well know that the presence of compatibilizer has a positive effect in tensile properties [28].

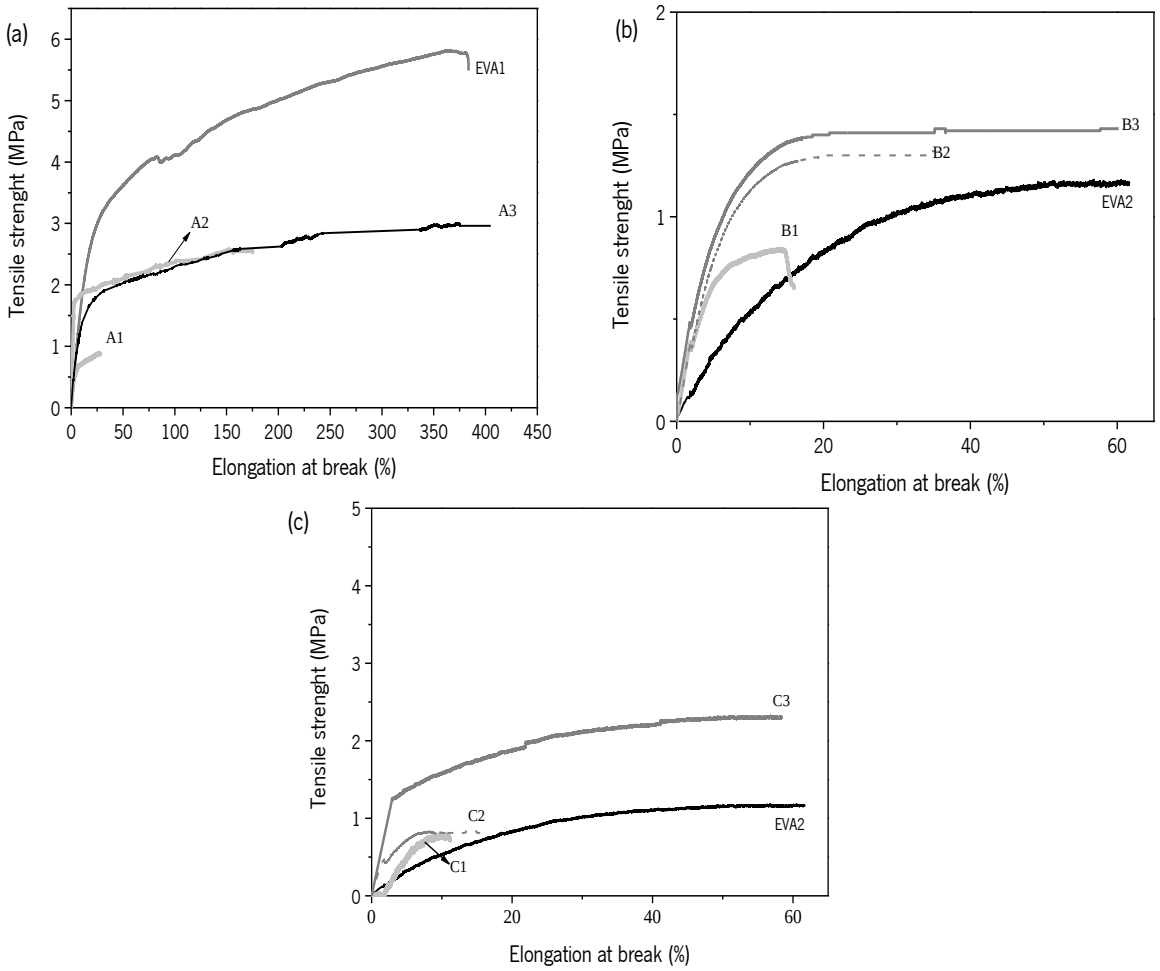


Figure 6.6 Tensile properties, at room temperature, of EVAs and prepared samples.

6.3.3 Biodegradability Assessment

The biodegradability, monitored based on biochemical oxygen demand (BOD) method, is expressed as the amount of O_2 consumed during biodegradation divided by their theoretical oxygen demand (ThOD), using the elemental analysis data (see Table 6.4) and the respective results are presented in Figure 6.7. Among the neat polymers, both EVA1 and EVA2, show the lowest biodegradability and PCL1 the highest. For EVA1 and EVA2, 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 non-biodegradable polymer.

Table 6.4 Elemental analyssis 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	$C_5H_{10}O$

Degradation of aliphatic polyesters is usually related to their molar mass, melting temperature, degree of crystallinity and chemical structure [29] Therefore, while PCL1 showed a biodegradation value around 87.0%, the value for PCL2 was much smaller (37.0%). Even though, both are aliphatic polyesters and biodegradable, PCL2 has much higher molar mass, which influence the biodegradability, as stated before. Another parameter that contributes for these biodegradation values, is the smaller melting temperature of PCL1 (55.3 °C) compared to PCL2 (59.4 °C).

Thus, prevision of biodegradability based on physico-chemical analyses of the polymers is very complex, because it depends on several parameters. 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), 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, with a similar method to the one used in the present study, a biodegradability result for PCL with a molar mass of 43.000 $g.mol^{-1}$, 80.0%, was reported in literature [31]. Comparing this result with PCL1 (87.0%), the difference obtained for PCL1 could be attributed to its lower molar mass (10.000 $g.mol^{-1}$), 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 EVA biodegradability, since the biodegradability of A1 (14.4%), B1 (26.4%) and C1 (16.7%) increased when compared to neat EVAs. The biodegradability is 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, decrease of melting temperature (Figure 6.8), [32, 33] and copolymer presence (Figure 6.2).

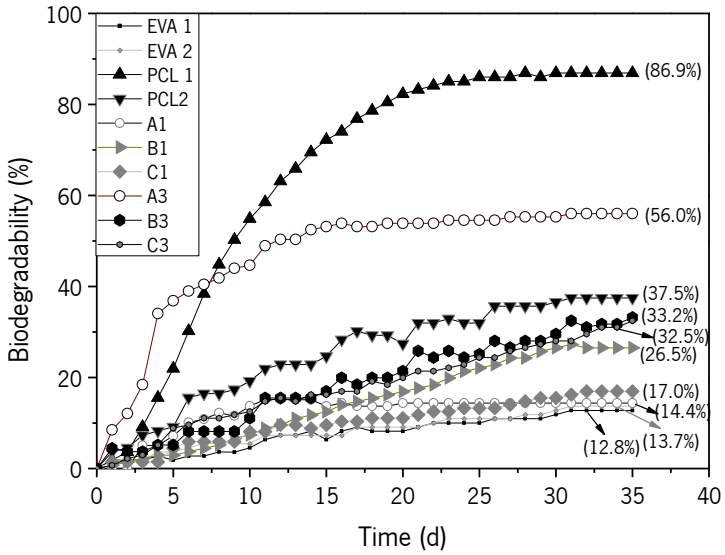
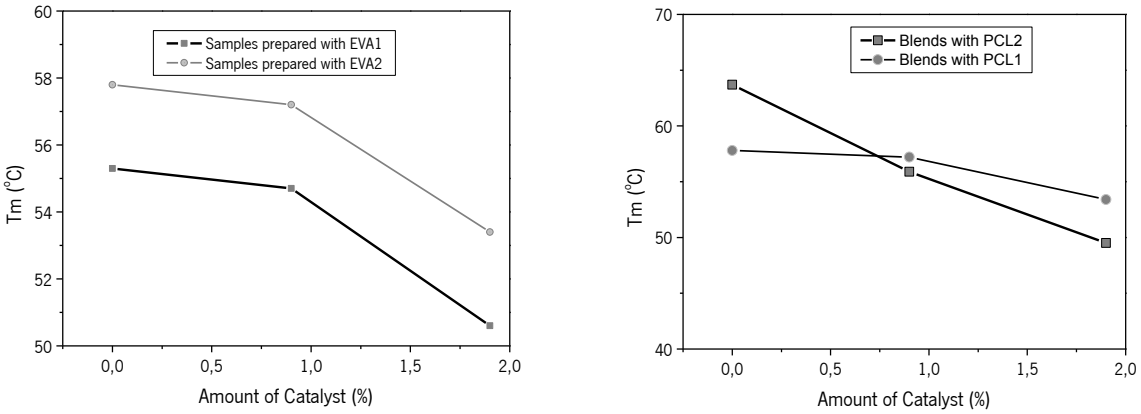


Figure 6.7 Biodegradability of the copolymers and blends according to ISO 14851:1999.



(a) (b)

Figure 6.8 Melting temperature (a) with different EVAs and (b) different PCLs molar mass.

Literature studies reported that grafting reactions favour the formation of branched/crosslinked structures, promoting the increases of the amorphous zones concentred in the polymer [34].

Furthermore, for each individual serie (A, B and C), it seems that the microbial accessibility to EVA groups increases when higher amount of PCL is grafted to EVA (Figure 6.7).

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 non-biodegradable polymer. The major changes occurred for PCL1 (data not shown).

FTIR spectra of A3 (Figure 6.9 (a)) shows that major changes occurred during biodegradation. The differences are probably related to PCL1 consumption in the blend, during the metabolism of microorganisms, resulting in a reduction of molar mass, since EVA practically does not degrade, as previously described. Even though similar results were obtained for B3 (Figure 6.9 (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., showed a small reduction in the intensity of the peaks corresponding to the groups C-H, C=O, C-O. Biodegradation was also monitored for C3 (Figure 6.9 (c)). The same trend is fallowed, since reduction in the intensity of all peaks, are in according with the biodegradation obtained from BOD test.

The remaining powder for all samples after 35 days in the sludge, under biodegradation, were collected and submitted to a scanning electron microscopy analysis. The results shown in Figure 6.10 indicated that microorganisms presented in the activated sludge degraded PCL and they could also be responsible for the hydrolytic degradation of EVA amorphous region. Although 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.

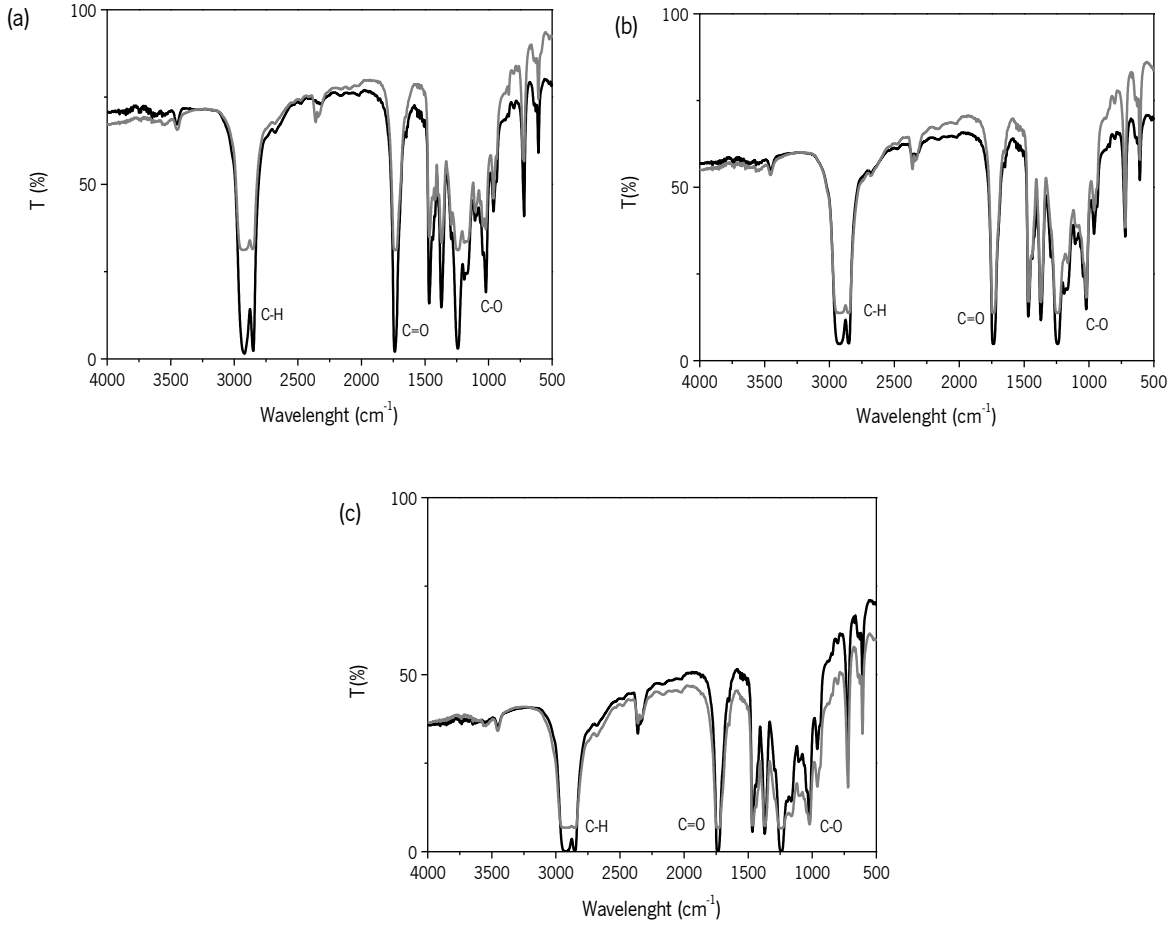


Figure 6.9 FTIR spectra of undegraded (black line) and biodegraded (gray line) blends: (a) A3, (b) B3 and (c) C3.

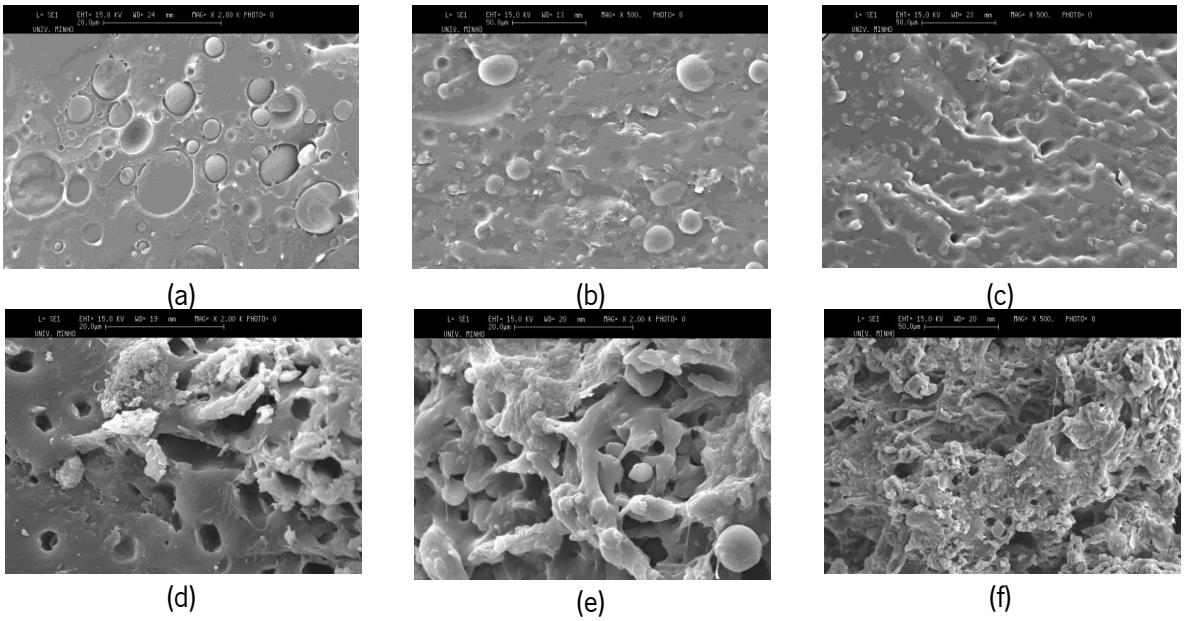


Figure 6.10 SEM surface of samples before and after 35 days of biodegradation: before (a) A3, (b) B3, (c) C3 and after (d) A3, (e) B3 and (f) C3.

6.4 Conclusions

This paper presented a method to prepare bio-based materials trough transesterification reaction. Therefore,, blends of EVA ($\overline{Mn}$ = 18.000 g.mol^{-1} and $\overline{Mn}$ = 7.900 g.mol^{-1}) and PCL ($\overline{Mn}$ = 10.000 g.mol^{-1} and $\overline{Mn}$ = 60.000 g.mol^{-1}) with different amount of catalyst were prepared by melt mixing and characterized by several techniques.

The amount of copolymer, determined by selective extractions, was similar and seems to be independent of the molar mass of the selected polymers. SEM, rheology, thermal analysis, mechanical properties and biodegradability tests were sensitive both copolymer formation and polymers molar mass. For the higher amount of copolymer, using a high molar mass EVA and PCL with low molar mass allows to prepare a material with higher thermal decomposition, better mechanical properties and higher biodegradability.

From all the results it can be concluded that A3 seems to be the sample that has better mechanical properties and higher biodegradability and it could be used for technological applications to replace EVA.

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7 | Conclusions and Suggestions for Future Work

7.1 CONCLUSIONS

The research presented in this thesis aimed to investigate routes to prepare biodegradable/bio-based polymers by reactive extrusion .Therefore, this research began (Chapter 2) by blending biodegradable polymers, PLA, PCL and starch-based thermoplastics (TPS), Mater-Bi®, with high density polyethylene and polyethylene modified with maleic anhydride (HDPE/PE-g-MA). The influence of blends composition on morphology development, physical and chemical properties and also on biodegradability was evaluated. It was shown that while blends with PLA exibithed lower elongation at break but higher Young modulus, blends with PCL had opposite behavior. The microbial growth test, carried out to evaluate the potential for biodeterioration of the blends, using a pure culture of *Pseudomonas fluorescens,* indicated that HDPE/PCL had lower resistance to bacterial attack than the blend of HDPE/PLA.

In Chapter 3, biodebradability of the blends prepared in chapter 2 were assessed by two different standard methods. The results obtained have shown that the blend containing PCL is more biodegradable than the blend containing PLA based on the microbial growth (ASTM G 22-76) and biochemical oxygen demand (ISO 14851:1999) methods. Addition of starch increased the biodegradability of the PLA blend. The biodegradability of the blends evaluated in this study by the second method ranged from 22% (PLA 60) to 52% (SPCL 70). Therefore, according to the OECD, they may not be considered "readily biodegradable". Moreover, the qualitative results of FTIR spectroscopy of non-biodegraded and biodegraded polymeric blends are in agreement with the ones obtained in the standard biodegradability tests. Biodegradability of fine grinded polymeric blends was tested using the biochemical oxygen demand. Thus, it is important to point out that the surface area of the polymeric material sample available to microbial attack in the present study was increased considerably compared to film samples. Thus, the biodegradation under these conditions was enhanced when compared to tests performed in real environment. From this study it was possible to conclude that the most sutible method to assess the biodegradability was biochemical oxygen demand (ISO 14851:1999). Therefore, this method was selected to evaluate all the polymers prepared.

The synthesis of copolymers of EVA-g-PCL and EVA-g-PLA was studied in Chapter 4. Grafted copolymers were prepared using *in situ* polymerization of LA and ε-CL in the presence of molten EVA. The process takes the advantage of the living character of PLA and PCL chains growing from LA and ε-CL monomers by ROP, to increase through the specific exchange reaction between the living PLA or PCL end-chain and the acetate groups of EVA, the probability of grafting and consequently the concentration of the formed copolymer. It was observed that the amount of copolymer formed achieved using selective

extraction combined with ^{1}HNMR, in order to verify the copolymer structure and has a great influence on materials properties. SEM results showed that the size of the dispersed phase decreased as the amount of copolymer increased. The samples prepared by *in situ* polymerization, mainly for the EVA-g-PCL sample, exhibit the better mechanical performance. Additionaly, differences in biodegradability behavior were observed between the physical blends and the samples prepared by *in situ* polymerization, being EVA-g-PCL sample most biodegradable This method allowed copolymer formation, which even in small amount, promote an enhancement of thermal and mechanical properties of EVA matrix properties and an increase of its biodegradability.

Chapter 5 describes a different approach for the synthesis of EVA-g-PLA grafted copolymers, through transesterification reaction between EVA and PLA, using titanium propoxide ($Ti(OPr)_4$) and titanium phenoxide ($Ti(OPh)_4$) as catalysts. Different materials were prepared by changing the relative amount of polylactide and catalyst. The extent of the grafting reaction was also estimated by selective extractions and other analytical techniques were used to characterize the structure, morphology and thermal and mechanical properties.

Biodegradability was assessed by biological oxygen demand, FTIR and GPC methods. The results showed that ($Ti(OPr)_4$) exhibits higher efficiency as a catalyst than ($Ti(OPh)_4$). The sample containing the higher amount of copolymer exhibits the better mechanical properties and the higher biodegradability.

In the final study of this dissertation (Chapter 6) the effect of EVA and PCL molar mass on the synthesis of EVA-g-PCL grafted copolymers was appraised applying the method described in Chapter 5, using only titanium propoxide ($Ti(OPr)_4$) as catalyst. The results acquired from this chapter deal with the expected response, i.e., for the higher amount of copolymer, using a high molar mass EVA and PCL with low molar mass allows to prepare a material with higher thermal decomposition, better mechanical properties and higher biodegradability.

Therefore, this study contributed to the development of biodegradable/bio-based polymers, using different approaches.

This knowledge can be a promising route to produce new materials with good mechanical properties and enhanced biodegradability compared to conventional polymers, that could be used in technological applications. There is no doubt that the above examples are only some illustrations of the huge potential of reactive extrusion, a solvent free melt process, in the field of the biodegradables polymers.

7.2 Suggestions for the Future Work

The research presented in this dissertation showed that it possible to prepare plastic materials of non-biodegradable and biodegradable polymers with properties similar to conventional polymers with specific properties and enhanced biodegradability. Although, a large number of studies have been published on this subject, many fundamental questions related to the structure-properties relationships and its production are still not completely understand.

In fact, this research indicated some of the complexities of the relationship between several parameters, such as molar mass, phase structure (miscibility and crystallinity), surface blend composition, molecular structure, polymer chain length and melting temperature.

Given the results and conclusions of the present research, some future work can be recommended:

- To investigate in more details copolymer formation in order to prepare nanostructured polymers with even higher biodegradability.
- To investigate chemistry and morphology development of modified polymers (copolymers) during grafting reaction made in a co-rotating twin-screw extruder, instead of using the Haake batch mixer;
- To compare for both studies (physical blends and modified polymers) biodegradability achieved from more standard methods, in order to allow a more appropriate assessment of biodegradability;
- To identify microbial populations, which represents an important tool to evaluate biodegradation assessment. However, culture-dependent or culture-independent techniques for bacteria identification have limitations. It would be interesting to compare in the same studies, in order to allow a more appropriate assessment of bacterial diversity.