



# Fatty acid-based thermoplastic poly(ester-amide) as toughening and crystallization improver of poly(L-lactide)

Thomas Lebarbé<sup>a,b,c</sup>, Etienne Grau<sup>a,b</sup>, Carine Alfos<sup>d</sup>, Henri Cramail<sup>a,b,\*</sup>

<sup>a</sup> Univ. Bordeaux, Laboratoire de Chimie des Polymères Organiques, ENSCBP, 16 Avenue Pey-Berland, Pessac Cedex F 33607, France

<sup>b</sup> CNRS, Laboratoire de Chimie des Polymères Organiques, Pessac Cedex F 33607, France

<sup>c</sup> French Environment and Energy Management Agency, 20 avenue du Grésillé-BP 90406, Angers Cedex 01 F 49004, France

<sup>d</sup> ITERG, 11 rue Gaspard Monge, Parc Industriel, Pessac Cedex F 33600, France

## ARTICLE INFO

### Article history:

Received 29 September 2014

Received in revised form 4 November 2014

Accepted 6 November 2014

Available online 14 November 2014

### Keywords:

Poly(L-lactide)

Toughening

Impact resistance

Fatty acids

Crystallization

Sustainable polymers

## ABSTRACT

Poly(lactide) (PLA) is a bio-based and compostable aliphatic polyester that has gained widespread interest during the last decades due to its promising technical substitution potential. Its good mechanical properties comparable to some mainstream petroleum based thermoplastics are however counterbalanced by its inherent brittleness that limits its scope of applications. Toughening of PLA by blending with a rubber phase is the most used solution to reduce its brittleness because of economical and practical advantages that offers this modification pathway. In this study, we investigated by melt-blending, the use of a thermoplastic elastomer poly(ester-amide) (PEA), synthesized from fatty acid-based precursors, as an impact modifier of poly(L-lactide) (PLLA). This PEA demonstrated an effective rubber-toughening of PLLA. Moreover, beneficial effects of the PEA on the crystallization rate of PLLA were observed thus enlarging the scope of applications for the obtained blends.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

Nowadays, the production of biobased plastics represents nearly 1.5 million tons per year. Among them, poly(L-lactide) (PLLA), synthesized by ring-opening polymerization of L-lactide, a cyclic dimer of lactic acid derived from starch fermentation [1–3] is one of the most mature bioplastic. PLLA represents a promising polymer as substitute of petroleum-based plastics for a wide range of applications due to its high stiffness, its biobased character and its compostable behavior [4,5]. However, alike PS, PLLA is a brittle material with low values of tensile strain at break, tensile toughness and impact strength. It is currently characterized by a notched IZOD impact strength as low as

2.5 kJ/m<sup>2</sup> and the use of impact modifiers is often required to obtain acceptable toughness [6,7].

For PS, this brittleness has been overcome thanks to the development of rubber-modified high impact PS and its copolymers such as styrene-butadiene-styrene and acrylonitrile-butadiene-styrene copolymers [8,9]. These toughening strategies by adding rubber additives (low *T<sub>g</sub>* polymers) were also applied to PLLA. For efficient rubber-toughening, the rubber should be dispersed as discrete particles and be well bonded to the rigid polymer matrix. The particles can be incorporated via blending the rubber with the polymer matrix, or by copolymerizing the rubber with the polymer matrix, taking advantage of the natural segregation of immiscible polymers. Even if the copolymerization represents a powerful means to obtain properties unattainable with PLLA, most of the researches have been focusing on the melt-blending of PLLA with immiscible rubbers due to the economical advantages of this route [7]. The main

\* Corresponding author at: CNRS, Laboratoire de Chimie des Polymères Organiques, Pessac Cedex F 33607, France.

E-mail address: [cramail@enscbp.fr](mailto:cramail@enscbp.fr) (H. Cramail).

issue with respect to PLLA toughening, is the selection of the rubber. For an effective improvement of the impact strength of PLLA, the glass transition of the rubber must be at least 20 °C lower than the test/use temperature. In addition, the rubber molecular weight must not be too low, it should not be miscible with the PLLA matrix, and must be thermally stable to PLLA processing temperatures [10,11]. Based on these concepts, various types of rubber were melt-blended with PLLA. Mainstream elastomeric polymers such as olefin- [12–15], acrylic- [16,17] and styrenic-based thermoplastics [18,19] were first investigated with or without compatibilizers or reactive functions (such as glycidyl methacrylate) [20–23] in their backbone. Most of the described systems showed good enhancement in impact strength of PLLA. However, these additives do not constitute long-term and suitable solutions as they modify the compostable feature of the final PLLA material.

To improve the sustainability of high impact PLLA materials, many studies have been more recently focusing on the development of second generation impact modifiers for PLLA based on biodegradable and ideally bio-based rubbers. Main examples include blends of PLLA with poly( $\epsilon$ -caprolactone) (PCL) [11,24–27], poly(butylene succinate) (PBS) [28,29] and their copolyesters, poly(butylene adipate-co-terephthalate) (PBAT) [30,31], poly(hydroxyalkanoate)s (PHAs) [32–34], biopolyester elastomer [35], polymerized soybean oil [36]. Most of the mentioned systems showed no interactions with PLLA thus resulting

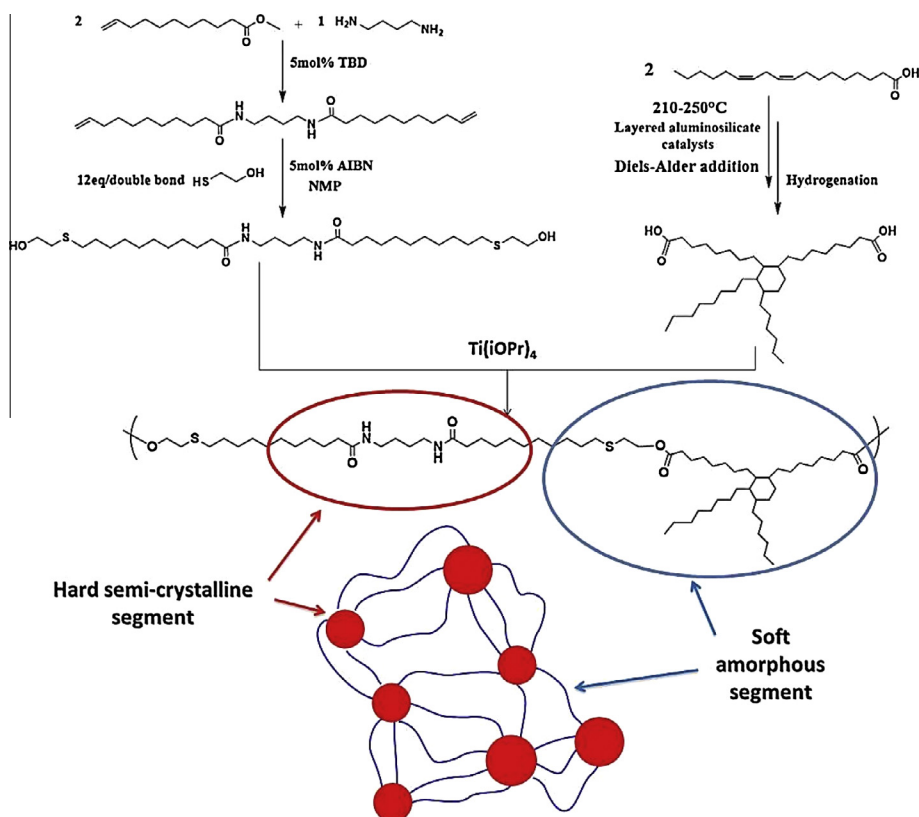
in poor interfacial adhesion. Thus, in many studies, a compatibilizer (i.e. dicumyl peroxide, epoxy functionalized compounds) was added leading to highly effective systems.

The development of bio-based rubbers remains an important challenge. Plant oils and more particularly fatty acids represent promising feedstock for aliphatic polyesters and polyamides production [37–39]. In previous studies, our group described the synthesis of various diols bearing ester and/or amide functions that were obtained from methyl 10-undecenoate, a building block issued from castor oil (pyrolysis of methyl ricinoleate) [40–43]. Such diols present a good design for the synthesis of PLLA impact modifiers. Herein we study the binary blends of a novel fatty acid-based poly(ester-amide) thermoplastic elastomer (PEA) with PLLA.

## 2. Results and discussion

### 2.1. Synthesis and properties of the poly(ester-amide) rubber

The PEA was synthesized by polycondensation of undecenoate butylene diamide diol (UndBdA-diol) with a hydrogenated dimer fatty acid (DFA) (Scheme 1). The structure of the polymer was confirmed by <sup>1</sup>H NMR spectroscopy as evidenced by ester linkages formation (peaks at 4.22 ppm and 2.28 ppm) and expected peaks integration (Fig. S1). Before melt-blending the PEA with PLLA, some requirements have to be fulfilled in order to maintain an efficient



**Scheme 1.** Synthesis of PEA rubber by polycondensation of UndBdA-diol and DFA.

Download English Version:

<https://daneshyari.com/en/article/7805533>

Download Persian Version:

<https://daneshyari.com/article/7805533>

[Daneshyari.com](https://daneshyari.com)