European Polymer Journal 58 (2014) 90–102

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Reactive extrusion of PLA, PBAT with a multi-functional epoxide: Physico-chemical and rheological properties

Racha Al-Itry [a,b], Khalid Lamnawar [a,c], Abderrahim Maazouz [a,b,d,*]

[a] Université de Lyon, INSA-LYON, F-69361 Lyon, France
[b] UMR 5223, Ingénierie des Matériaux Polymères IMP, CNRS, INSA Lyon, F-69621 Villeurbanne, France
[c] UMR 5259, Laboratoire de Mécanique des Contacts et des Structures LaMCoS, CNRS, INSA Lyon, F69621 Villeurbanne, France
[d] Hassan II Academy of Science and Technology, 10 100 Rabat, Morocco

ARTICLE INFO

Article history:
Received 28 November 2013
Received in revised form 14 March 2014
Accepted 19 June 2014
Available online 26 June 2014

Keywords:
Reactive extrusion
Chain extension
Branching
Linear rheology
Thermo-rheological complexity
Structural and solution viscometry

ABSTRACT

The aim of this work was to highlight the presence of long chain branching, LCB, due to the incorporation of a multifunctional epoxide, named Joncryl ®, as a chain extender, into both poly (lactic acid) (PLA) and poly (butylene-adipate-co-terephtalate) (PBAT) polymers. The modified polymers were prepared using a twin-screw reactive extrusion system. It has been demonstrated through this study that these modified biopolymers are thermo-rheologically complex. This complexity may be attributed to the formation of covalent bonds between both polymer and chain extender and leads to a failure of the time-temperature superposition (TTS). The linear viscoelastic properties were predicated on the use of the so-called Van-Gurp–Palmen plots, from which the topology of the modified PLA and PBAT has been studied and analyzed. Indeed, they exhibited a typical feature of a mixture of linear and randomly branched polymers. Furthermore, the resulting linear and branched chains, due to the reactive highly functionalized epoxide, are discussed using rheological investigations (relaxation spectra, flow activation energy) coupled with solution viscometry (solution viscometry properties, hydrodynamic radius) and physico-chemical properties (size-exclusion chromatography).

1. Introduction

Currently, most polymeric packaging materials are based on non-renewable fossil resources. Therefore, it is becoming more evident that ecosystems are disturbed considering the net contribution of these petrochemical-based polymers to the increase of carbon dioxide emission. Hence, the importance of biodegradable polymers is continuing to grow. Significant attention has recently been paid to the poly (lactic acid) (PLA) since it is compostable and renewable, made by the fermentation of corn and sugar beets. PLA is linear aliphatic thermoplastic polyester. Extensive works related to PLA synthesis, chemical, physicochemical and mechanical properties have been performed. A comparison of mechanical properties among other common polymers shows that PLA is much like polystyrene; it has relatively high modulus but is brittle. Another potential problem with PLA is that it has a lower melt strength compared to conventional polymers limiting its use in wide range of applications dedicated to blown extrusion for example [1–3].

To improve mechanical properties and processability of PLA and retain its biodegradability, blending PLA with other biodegradable polymer is used. Biodegradable polyesters generally work well in blends with PLA, starch, and natural fiber reinforcements. A broad range of

---

* Corresponding author at: Université de Lyon, INSA-LYON, F-69361 Lyon, France. Tel.: +33 472 43 63 32; fax: +33 472 438 5 15.

E-mail address: abderrahim.maazouz@insa-lyon.fr (A. Maazouz).

http://dx.doi.org/10.1016/j.eurpolymj.2014.06.013
0014-3057/

synthetic biodegradable resins based on aliphatic polyesters and aliphatic–aromatic copolyesters have been commercialized such as poly (butylene adipate-co-terephtalate) (PBAT) [4].

Several authors reported that the residual water or moisture content inside the polymer matrix activates hydrolysis reactions. Moreover, Al-Itry et al. [5] as well as Doi et al. [6] argued that thermal reactions of PLA could be generated by random chain scission reactions of the ester groups. This degradation during processing could cause a decrease of the molecular weight, which results in processing difficulties related to the limited temperature window and makes PLA un-applicable into some processes where melt strength are important and dominant, such as foaming, blow molding and film blowing [7,8,10,37]. Meanwhile, to enlarge its processing window by limiting its thermal degradation, PLA need to be melt strengthened. Some authors reported that the reactive extrusion is an attractive way to minimize the degradation effects of PLA and thus, by chain modification (creation of extended and/or branched architecture with chain extension reactions) through adding additives containing reactive groups, named chain extenders [5,11–13]. According to the literature, the different reactive pairs able to react with each other are –COOH/epoxy, –OH/epoxy, –COOH/isocyanate, –COOH/amine, –OH/–COOH, –OH/pyromellitic dianhydride PMDA and –OH/triglycidyl isocyanurate TGIC. The first related chain extension experiments of PLA were performed with an diisocyanate compound [13–16]. The bi-functional molecules have a narrow processing window. Moreover, the interest in using such molecules is limited due to its toxicity and its high volatility. Other chain extenders reported in the literature are DGEBA-based resins. Such a selective functionalization has been performed in order to increase the reactivity of specific chain extenders [17,18]. Chain extension of PLA has also been performed by initiating polymerization with either tetrol or hexol. This approach allows the synthesis of four- and six-armed PLAs [8]. In a recent study, the mechanical and rheological properties of biodegradable epoxy (epoxy-methally sorbithol and epoxy-methallyl malthytol) have been studied [19]. Recently, a multifunctional styrene–acrylic–epoxy random oligomer (Joncryl®) has been proposed as chain-extension agent for PLA during reactive extrusion [5,20–24,33,36]. Mihai et al. [9] investigated the rheology and the extrusion foaming of PLA. The improvement of shear and elongational properties of the modified PLA with Joncryl has been demonstrated recently and it is effect on the blown film extrusion has been highlighted by Mallet et al. [34]. Najafi et al. [22] compared the thermal stabilization effects of tris (nonyl-phenyl) phosphate (TNPP), polycarbodiimide (PCDI) and a multifunctional epoxide. They concluded that Joncryl was the most efficient chain extender for PLA. Meng et al. [23] reported that Joncryl showed a remarkable thermal stabilization effect on PLA/organo-modified clay nano-composites without negatively affecting the clay dispersion. Recently, Eslami et al. [26] investigated the effects of an epoxy-functionalized chain extender (CESA) on the rheological, mechanical and elongation properties of PLA. They found that the shear viscosity, the elasticity and the elongational viscosity of PLA increased as the concentration of chain extender increased. Moreover, Al-Itry et al. [5] showed an improvement of the thermal stability of PLA through reactive extrusion of PLA with various amounts of multi-functional epoxide leading to an enhancement of the visco-elastic and mechanical properties. Hence, the mechanisms of degradation, chain extending with GMA functions and their competition have been proposed. The authors should point out also, that the reactive extrusion progressed by changing residence time and the chain extender amount. Cailloux et al. [31], as well as Al-Itry et al. [5], suggested a competition between degradation, chain extension as well as branching reactions during processing with the incorporation of a styrene–acrylic multifunctional oligomeric agent on the PLA matrix. In addition, a considerable increase of the chain relaxation time was observed. However, no helps for the correlation between the structure and the final rheological properties have been devoted.

Concerning the PBAT polymer, it was reported that the introduction of aromatic polyester into the backbone chain of aliphatic polyester not only improves the mechanical properties but also the melt strength. Other authors demonstrated that under Ultraviolet (UV) exposure associated with temperature, that degradation of PBAT could occur from chain scission and crosslinking due to the recombination of the free radicals at the aromatic structures. This photodegradation promotes a reduction of mechanical properties of the polymer [41]. Furthermore, in our previous study [5], we have demonstrated that PBAT is able to degrade under specific conditions. This thermal degradation can be avoided by the incorporation of a multi-functional epoxide through the chain-extension method.

Despite the interesting nature of these researches, no efforts have been dedicated to the study of structure, neither to truly understand the thermo-rheological complexity of the modified PLA and PBAT polymers due to the incorporation of the multi-functional epoxide nor to assess their molar masses and relaxation behavior.

In this paper, the effect of a multi-functional chain extender bearing reactive epoxide groups on the rheological, solution properties and the molecular architecture of both PLA and PBAT polymers will be analyzed and discussed.

2. Experimental section

2.1. Materials and methods

2.1.1. Polymers used

The polylactide (PLA), grade 4032D, was purchased from Natureworks LLC, USA. It is a semi-crystalline material containing 2% D-lactide units. PBAT (Grade: Ecoflex FBX 7011) was obtained from BASF. A styrene–acrylic multi-functional epoxide oligomeric agent was used as a reactive agent, supplied by BASF as known under the trade name, Joncryl ADR®-4368. The polymers and Joncryl were dried in a vacuum oven at 80 °C and 40 °C respectively for 12 h and stored in a dessicator over anhydrous silica gel before use. It is accepted by the Food & Drug Administration (FDA) to be used in food packaging. Indeed, the use