Materials and Design 45 (2013) 198–205

Contents lists available at SciVerse ScienceDirect

Materials and Design

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

Thermal, mechanical and rheological properties of polylactide toughened by expoxidized natural rubber

Chunmei Zhang [a], Weiwei Wang [a], Yun Huang [a], Yonghao Pan [a], Long Jiang [a], Yi Dan [a,*], Yongyue Luo [b], Zheng Peng [b]

[a] State Key Laboratory of Polymer Materials Engineering of China (Sichuan University), Polymer Research Institute of Sichuan University, Chengdu 610065, Sichuan, China
[b] Chinese Agricultural Ministry Key Laboratory of Tropical Crop Product Processing, Agricultural Product Processing Research Institute, Chinese Academy of Tropical Agricultural Sciences, Zhanjiang 524001, China

ARTICLE INFO

Article history:
Received 12 July 2012
Accepted 12 September 2012
Available online 23 September 2012

Keywords:
Polylactide
Crystallization
Interfacial adhesion
Epoxidized natural rubber
Rheological properties

ABSTRACT

This paper concerns on the use of epoxidized natural rubber (ENR) as toughening agent for polylactide (PLA). ENR with epoxidation content of 20 mol% (ENR20) and 50 mol% (ENR50) were separately melt blended with PLA using an internal mixer. DSC results suggested that PLA/ENR blends were amorphous after melt blending while they were crystalline and revealed two melting peaks in the thermograms after being annealed at 100 °C. Mechanical tests showed that the introduction of ENR reduced the tensile modulus and strength but enhanced the elongation and the impact strength of PLA. The impact strength of the 20 wt% ENR20/PLA and ENR50/PLA blends increased to 6-fold and 3-fold, respectively, compared to that of pure PLA. This enhancement was due to a good interfacial adhesion between ENR and PLA. Both ENR20/PLA and ENR50/PLA blends performed very strong shear thinning behavior, and the complex viscosity, storage and loss modulus of the blends also increased after blending with ENR.

1. Introduction

Polylactide (PLA) is a thermoplastic polymer that is producible from renewable resources such as starch and sugar. It exhibits high strength and modulus that is comparable to polystyrene (PS). Together with its biodegradable and compostable properties, PLA in principle holds great potential as an alternative to petroleum-based polymers [1–3]. However, some of its applications are limited by its low elongation at break and poor toughness. PLA has a glass transition temperature ranging from 55 °C to 65 °C, and it is brittle at room temperature, fracturing via a crazing mechanism [4]. To modify the mechanical brittleness of PLA, many strategies such as processing manipulation, copolymerization and blending have been employed [5–7]. Among these methods, blending it with other biodegradable polymers is probably the most extensive and effective methodology for toughening PLA.

Our interest in toughening PLA has focused on the use of natural rubber (NR), a renewable resource obtained from Hevea brasiliensis [8]. Owing to its advantages of abundant availability, biodegradability, high toughness and outstanding mechanical strength, NR seems to be an ideal candidate for toughening PLA [9]. As we know, the rubber ought to be phase separated with plastic to serve as impact modifier [10]. This criterion could be easily fulfilled due to the non-polarity of NR and polarity of PLA. However, precisely because of this different polarity, compatibility between the two polymers has yet to be improved. Fortunately, NR is an unsaturated polymer consisting of 91–94 wt% cis-1,4-polyisoprene, there are a large number of double bonds in the backbones that are reactive [11]. For such a scenario, natural rubber grafted with poly(butyl acrylate) (NR-g-PBA) was prepared to toughen polylactide (PLA), which has been reported in our previous work [12]. The results showed that NR-g-PBA is compatible with PLA, and the elongation at break and the impact strength were significantly improved.

Epoxidized natural rubber (ENR) has been commercially prepared in latex stage by reacting natural rubber with peroxide [13]. Epoxy groups of ENR would improve the polarity of rubber and hence promoting compatibility with PLA. In fact, Nghia et al. [14] investigated the compatibility of the ENR/PLA solution blend; they concluded that the reaction occurs between the epoxy groups of ENR and the ester groups of PLA. Saito et al. [15] established quantitative analysis of the reaction between ENR and PLA through ^{1}H NMR spectroscopy. However, to the best of our knowledge, the melt blend of PLA and ENR, as well as mechanical properties of the blend has not been investigated. Tanrattanakul et al. [16] used ENR as toughening agent for nylon 6. In that report, they mentioned that the epoxy groups in ENR could interact with the terminal carboxylic groups in PLA. In relation to our study, ENR could act as a good toughening agent for PLA after melt blending with PLA.

* Corresponding author. Tel.: +86 28 85407286; fax: +86 28 85402465.
E-mail address: danyi@scu.edu.cn (Y. Dan).

0261-3069/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.matdes.2012.09.024

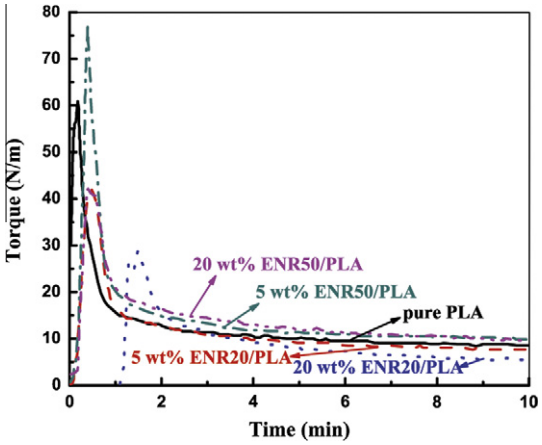

Fig. 1. Torque–time curves of pure PLA, ENR20/PLA and ENR50/PLA blends.

Based on our knowledge, the mechanical properties of ENR have much to do with its epoxidation content. Only those ENR with epoxidation content ranging from 10 mol% to 50 mol% are widely applicable [17]. Therefore, epoxidized natural rubber containing 20 mol% (ENR20) and 50 mol% (ENR50) of epoxidation were melt blended with PLA and investigated in detail.

2. Experimental details

2.1. Materials

Polylactide (PLA) pellets, type 2002D, were obtained from NatureWorks LLC (USA), with melt flow rate of 5–7 g/(10 min) (2.16 kg, 210 °C) and density of 1.24 g/cm^3. Epoxidized natural rubber (ENR) containing 20 mol% (ENR20) and 50 mol% (ENR50) of epoxidation were kindly supplied by the Key Laboratory of Tropical Crop Products Processing (Ministry of Agriculture, China).

2.2. Preparation of the blends

Prior to blending, the PLA and two types of ENR were separately dried at 80 °C and 40 °C for at least 8 h in a vacuum oven. ENR20/PLA and ENR50/PLA blends were both prepared at various ENR contents (1%, 3%, 5%, 10% and 20%, by weight based on PLA, respectively) in a Haake internal melt mixer (Rheocord 90, Germany) at a rotor speed of 60 rpm, 170 °C for 10 min. The well mixed blends were cut into small granules. Pure PLA was treated with the same procedure for comparison.

2.3. Morphology observation

The morphology of the pure PLA, ENR20/PLA and ENR50/PLA blends was investigated with an INSPECT F scanning electron microscope (SEM). Before the SEM observation, samples were submerged in liquid nitrogen and broken to expose the internal structure for SEM studies, and all the surfaces were sputtered with gold.

2.4. Thermal analysis

The thermal properties of PLA, ENR20/PLA and ENR50/PLA blends were measured by a differential scanning calorimeter (Netzsch DSC-204F1). Samples of 6–7 mg were taken in an aluminum pan and sealed tightly with an aluminum cover. Firstly, the samples were heated from 0 °C to 200 °C. Secondly, (1) cooled down to 0 °C or (2) cooled down to 100 °C and annealed at this temperature for isothermal crystallization for 60 min and then cooled down to 0 °C. Finally, the samples were reheated up to 200 °C. All the heating and cooling rates were 10 °C/min. The glass transition temperature, cold crystallization and melting temperatures denoted as T_g, T_{cc} and T_m, respectively, were obtained from the DSC curves. The crystallinity ($\%X_C$) of PLA in the ENR/PLA blend was evaluated from the DSC data by using the following equation:

$$\%X_C = [(\Delta H_m - \Delta H_{cc})/\Delta H_m^0]/\Phi_{PLA} \times 100 \quad (1)$$

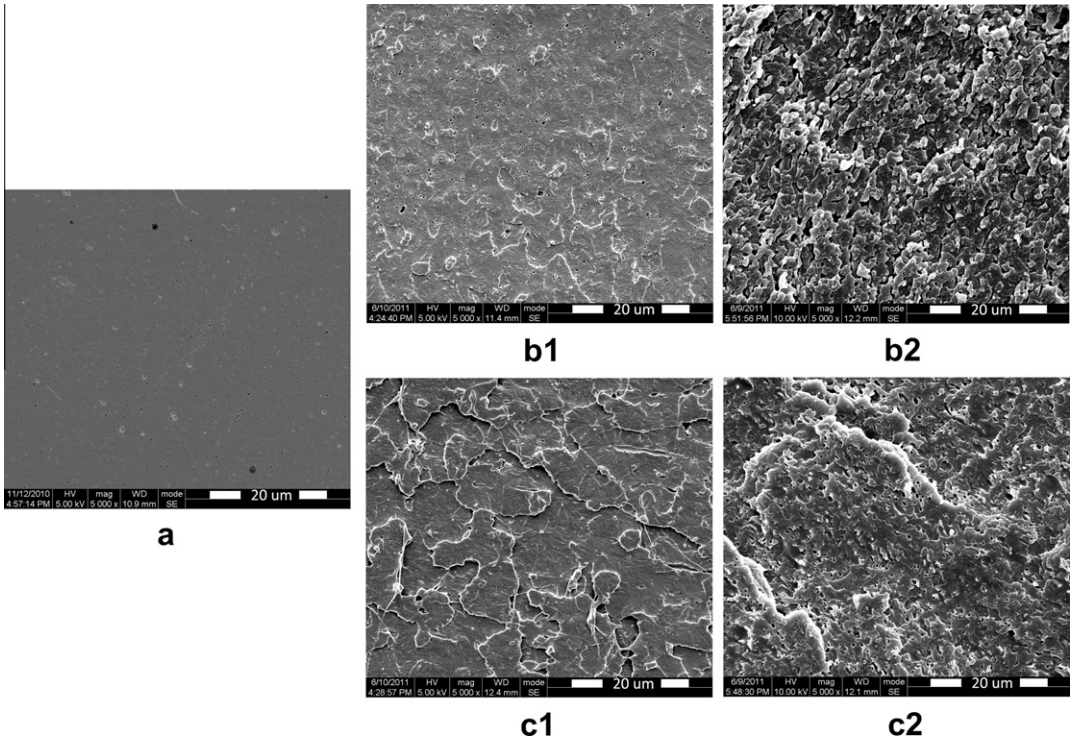

Fig. 2. SEM micrographs of cryofracture surfaces for (a) pure PLA, (b1) 5 wt% and (b2) 20 wt% ENR20/PLA blends, and (c1) 5 wt% and (c2) 20 wt% ENR50/PLA blends.