



Material Properties

Bio-based polylactide/epoxidized natural rubber thermoplastic vulcanizates with a co-continuous phase structure

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ABSTRACT

A bio-based thermoplastic vulcanizate (TPV) composed of polylactide (PLA) and epoxidized natural rubber (ENR) was fabricated through dicumyl peroxide-induced dynamic vulcanization. It was found that the cross-linked ENR phase had a specific continuous structure, hence forming a bi-continuous structure in the TPV. We designed cyclic stress-strain, stress-soften and stress-relaxation tests and SEM observation to reveal the relationship between the PLA continuous phase and crosslinked ENR continuous phase. It was found that the PLA phase generated crazes to adapt the elongation of the ENR continuous phase during stretching. At the same time, the enhanced interface between PLA and ENR kept the stress transferring between the two phases. The ENR with more epoxy groups showed better compatibility with PLA, which resulted in better mechanical properties.

1. Introduction

With increasing awareness of environmental protection and crisis of petroleum supply, biodegradable polymers derived from renewable resource are of growing consideration both in industrial application and academic research [1,2]. Polylactide (PLA), a kind of aliphatic polyester with excellent biodegradability and biocompatibility, is widely considered as a promising alternative to petroleum-based materials [3]. Unfortunately, the inherent brittleness of PLA is a major drawback to restrict its applications. Among various toughening techniques [4–9], to blend PLA with elastomers is the most feasible and economic route [10,11]. Up to now, natural rubber [12,13], polyurethane [14,15], poly(ethylene-glycidyl methacrylate) (EGMA) [16], polyamide elastomer (PAE) [11] and so on, have been found to be effective tougheners for PLA. However, most of them are petroleum-based materials which compromise the biobased attribute of PLA. Natural rubber (NR), differing from the petroleum-based synthetic elastomers, is a totally bio-based toughener for PLA [13]. However, because of the great different interfacial tension, the compatibility between NR and PLA needs to be solved by adding additional compatibilizers [17–20].

In our previous studies [21], we found that in-situ compatibilization between NR and PLA could be achieved in free radical-induced dynamic vulcanization without any external modifiers due to the C=C double

bonds in the NR chains [22,23]. The enhanced interface endowed PLA/NR blends with super toughness. Considering that epoxidized natural rubber (ENR), which is commercially prepared in latex stage by reacting NR with peroxide, has potentially better compatibility with PLA than NR due to the existence of epoxy groups, we selected it to be dynamically vulcanized with PLA. There are also a few of reports on simple blends of PLA and ENR. Zhang et al. [24,25] have studied simple blending of PLA with ENR and reported that ENR hindered the crystallization of PLA while it improved the impact strength and elongation at break. Bijarimi et al. [26] also reported PLA/ENR blends by using liquid natural rubber (LNR) as a compatibilizer. To fabricate a PLA/ENR blend through dynamic vulcanization will contribute to enrich studies of this blending system.

During typical dynamic vulcanization, the rubber phase is cross-linked and sheared during melt mixing in a thermoplastic phase, which results in a thermoplastic vulcanizate (TPV) with sea-island morphology of particulate cross-linked rubber particles dispersed in the plastic continuous phase. Surprisingly, a co-continuous phase structure was found in this system. The current study thus mainly focused on the relationship between the deformation of phase structure and properties of the PLA/ENR TPV. The results confirmed that excellent interfacial adhesion was achieved in PLA/ENR TPV.

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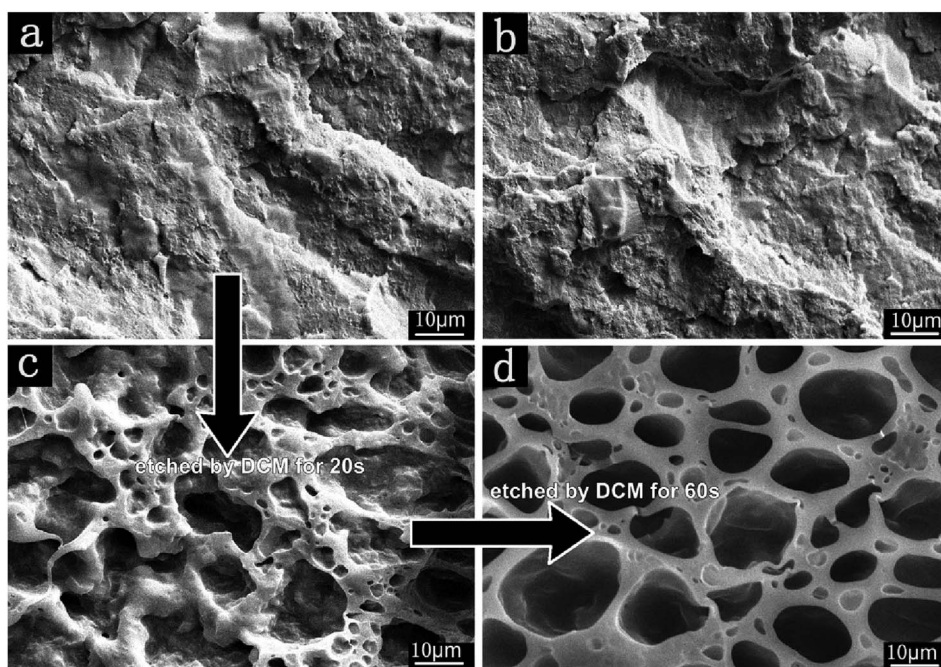


Fig. 1. SEM images of PLA/ENR TPVs: (a) cryo-fracture surface of DP3E7-30; (b) cryo-fracture surface of DP3E7-50; (c) cryo-fracture surface of DP3E7-30 etched by DCM for 20s; (d) cryo-fracture surface of DP3E7-30 etched by DCM for 60s.

2. Experimental section

2.1. Materials and sample preparation

PLA (REVODE110) was purchased from Zhejiang Hisun Biomaterials Co. Ltd (China). It has a density of 1.25g/cm^3 , MFR (190 °C, 2.16 kg) of 5–8g/10min, weight average molecular weight (Mw) of 1.5×10^5 g/mol and polydispersity of 1.7, respectively. ENR with 30mol% of epoxy groups (ENR-30) and ENR with 50mol% of epoxy groups (ENR-50), were kindly provided by Chinese Academy of Agriculture Science Institute of Tropical (China). Dicumyl peroxide (DCP) was supplied by Sinopharm Chemical Reagent Co. Ltd (China). Irganox1010 antioxidant was of industrial grade and obtained from the open market.

PLA, dried for 6 h in a vacuum oven at 80 °C, was firstly shear melted with Irganox1010 (the antioxidant for PLA) for 5–6 min in a Haake Rheomix OS (Germany) at a set temperature of 150 °C and a rotor speed of 60 rpm. Subsequently, the masticated ENR was added. 5 min later, DCP was added to initiate the dynamic vulcanization. This course lasted for 5–7 min. Finally, the TPVs were cooled to room temperature and the specimens for mechanical testing were prepared by hot molding at 150 °C.

For all TPVs, the concentration of DCP was fixed at 1.5% weight of the ENR component. The concentration of Irganox 1010 in the blend was fixed at 0.2% weight of (PLA + ENR). The sample codes were defined according to the PLA/ENR ratio and epoxy group concentration of ENR, e.g. the PLA/ENR-30 (PLA/ENR = 70/30) TPV was defined as DP7E3-30, the PLA/ENR-50 (PLA/ENR = 70/30) was defined as DP7E3-50, and the simple blend of PLA/ENR-30 (PLA/ENR = 70/30) was defined as BP7E3-30.

2.2. Mechanical properties

The tensile strength was characterized by a tensile test machine (UT-2080, U-CAN DYNATEX INC, China) according to ISO 37-2005 using dumbbell test pieces at the speed of 50 mm/min. The stress-strain curves were recorded. The average value of tensile strength and elongation at break were calculated from at least five specimens for each sample. The tear strength was determined using the same UT-2080 according to ISO 34-1:1994. Shore A hardness was determined as the

conditions given in ISO 7619-97.

2.3. Cyclic stress-strain measurements

Three consecutive cyclic stress-strain measurements were conducted in tensile mode on the UT-2080. The strain was set at 80%, in order to avoid rupture of the ENR phase at room temperature.

2.4. Stress-softening behavior

The standard dumbbell specimens were firstly stretched to a strain of 100% at room temperature, followed by annealing at 60 °C for 2 h to ensure maximum recovery of the PLA phase. Then, the recovered specimens were again elongated to 100% at room temperature. The stress-strain curves were recorded.

2.5. Stress relaxation test

The relaxation resistance of the TPVs was also investigated by using UT-2080. The samples were stretched to 100% strain and then the strain was kept unchanged at 100% for 900 s. The stress-time curves were recorded.

2.6. Scanning electron microscopy (SEM)

The phase morphology of the PLA/ENR TPVs was studied using a scanning electron microscope (Nova Nano SEM 430, FEI Company, USA). The cryo-fractured surface was obtained after the TPVs were immersed in liquid nitrogen. To expose the crosslinked ENR phase, dichloromethane (DCM) was used to etch the PLA phase. Before morphological observation, the surface of samples was sputter coated with gold to prevent electrostatic charge build-up during observation.

3. Results and discussion

3.1. The co-continuous phase structure in the bio-based PLA/ENR TPVs

The phase morphologies of the PLA/ENR TPVs are shown in Fig. 1, using DP3E7 as a typical example. As seen from Fig. 1a and b, the morphologies of the cryo-fracture surfaces of DP3E7-30 and DP3E7-50

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