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Material properties

Physical blend of PLA/NR with co-continuous phase structure: Preparation, rheology property, mechanical properties and morphology

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ABSTRACT

Polylactide (PLA), a thermoplastic polymers derived from biomass, was melt-blended with natural rubber (NR). Although without any interfacial modification, the brittle-ductile transition occurred at the blend with 35wt% NR, showing impact strength of about 500 J/m, approximately 7 times that of the neat PLA. Crystallinity study results indicated that the presence of NR did not obviously influence the crystallization of the PLA phase. Rheological study results showed that the viscosity of NR was much higher than that of PLA, facilitating the coalescence of the droplets of NR during blending. This, therefore, contributed to the formation of co-continuous phase structure of the PLA/NR blends. Interestingly, scanning electron microscopy studies further conformed the continuous phase of NR, showing a “network-like” continuous structure.

1. Introduction

The interest in using polymeric materials derived from renewable resources increases by the day because of the considerably improved environmental awareness of society and concerns about the depletion of petrochemical based materials [1]. As a renewable resource derived from an aliphatic polyester with good biodegradability and biocompatibility, as well as high strength and stiffness, polylactide (PLA) has been used for bio-based products and is widely considered as a promising alternative to petroleum-based materials [2]. Unfortunately, the inherent brittleness of PLA is a major drawback to restrict its applications. As a consequence, many attempts have been made to improve the toughness of PLA by copolymerization [3,4], plasticization [5,6], blending [7] or by the production of filled composites [8].

Blending PLA with other polymers provides the most practical and economic route of toughening PLA. Elastomers have commonly been considered as an efficient toughener for plastics. The elastomer particles behave as stress concentrators enhancing the fracture energy absorption of brittle polymers and ultimately result in a toughened material. Numerous elastomers have been blended with PLA, such as thermoplastic polyurethane (TPU) [9], polyurethane [10], poly (ethylene-glycidyl methacrylate) (EGMA) [11], polyamide elastomer (PAE) [12] and so on. Although these elastomers indeed toughened PLA, most of them are synthetic rubbers which are petroleum-based materials.

Natural rubber (NR) is a renewable resource derived from latex of rubber trees. It exhibits a unique combination of toughness, biocompatibility and biodegradability that, together with its bio-based material nature, makes it an ideal candidate to modify the brittleness of PLA [13]. To the

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best of our knowledge, there are only a few reports about NR toughing PLA [13–16]. Bitinis et al. [13–15] reported a series of detailed studies of PLA/NR blends. They found that the optimal NR concentration was 10 wt% which largely improved the brittleness of PLA, and the blends showed phase separated morphology where the NR formed small droplets dispersed in PLA continuous phase. Juntuek [16] also found that the PLA/NR blend obtained the highest impact strength at a 90/10(PLA/NR) ratio, and they used glycidyl methacrylate-grafted natural rubber (NR-g-GMA) as a compatibilizer for PLA/NR blend, in which the NR domains were dispersed in the PLA matrix. It is a common cognition that the elastomer must be uniformly distributed as small domains in the polymer matrix to achieve high toughness of polymers. However, we reported a super toughened dynamically vulcanized PLA/NR blend in which the cross-linked NR had a continuous phase and excellent interfacial compatibility with PLA [17].

If the difference in the melt viscosity of PLA and NR is too large, coalescence of the droplets of NR phase may form during blending, resulting in co-continuous phases at high NR contents. To date, the physical and mechanical properties of PLA/NR blends have received extensive attention; however, there have been few studies published on the co-continuous morphology of PLA/NR blends. The current study is to investigate the rheological behaviour, mechanical properties and morphology of the PLA/NR blends, in which the blends show a co-continuous phase morphology. Although the blending of PLA and NR was simple without any interfacial modification, it is expected that the study will contribute to further understanding of the formation of co-continuous phase for PLA/NR blends.

2. Experiments and methods

2.1. Materials and sample preparation

PLA, grade REVODE101, MI(190 °C, 2.16 kg) = 5~8 g/10 min, weight average molecular weight (Mw) ≈ 150 000 g/mol, $\rho = 1.25$ g/cm^3, was provided by Zhejiang Hisun Biomaterials Co., Ltd. NR, Standard Malaysian Rubber (SMR CV60), Mooney viscosity ML(1 + 4)100 °C = 60 ± 5, was kindly supplied by Guangzhou rubber industry research institute (China). Irganox 1010, antioxidant, was of industrial grade and obtained on the open market. The other chemicals were used as received.

PLA was dried for 6 h in a vacuum oven at 80 °C prior to use. NR was masticated before use. Then, the PLA and NR were melt blended in a Haake Rheocord 90 at 150 °C and at a rotor speed of 60 rpm. PLA with the Irganox 1010 was firstly shear-melted. After reaching stable torque, the masticated NR was added and the mixing was continued until the final stable torque was reached. Subsequently, the blends were removed from the mixer and cooled to room temperature. The material was then chopped into small granules. The specimens for mechanical testing were prepared by injection molding (TTI-160F, Welltec Machinery & Equipment Co. Ltd., China). The temperature profile of the inject barrels was 165/170/170/175 °C from the first heating zone to the nozzle. The injection pressure was 35 MPa.

The PLA/NR ratios were changed from 90/10(w/w) to 60/40(w/w). For all blends, the concentration of Irganox 1010 in the blend was fixed at 0.2% weight of (PLA + NR). For convenience, the sample codes were defined according to the PLA/NR ratio, e.g. the PLA/NR (80/20) blend was defined as B80/20.

2.2. Mechanical properties

Standard tensile tests were conducted on dumbbell shaped specimens using a universal testing instrument (Shimadzu AG-1, 10 kN, Japan) in tensile mode at room temperature. Test speed was kept at 50 mm/min, according to ISO 527-2. The notched izod impact strength was used to evaluate the toughness of the samples. The notched specimens were tested with an impact test machine (ZWICK5331, Zwick/Roell, Germany) at room temperature, according to ISO 180. The hardness was tested according to ISO 868. The average value was calculated from at least 5 test specimens.

2.3. Morphology study

The morphology of the samples was observed using a Nova NanoSEM 430 (FEI Company, USA). The cryo-fractured surface was obtained after the blend was immersed in liquid nitrogen, and the impact fracture surface was obtained after impact testing. In order to observe the NR phase, the blends were subjected to dichloromethane wash (ambient temperature) to remove the PLA phase at the surface and then dried sufficiently. Before morphological observation, the surface of samples was sputter coated with gold to prevent electrostatic charge build-up during observation.

2.4. Analysis of crystallization

The crystallinity of the PLA matrix phase usually influences the mechanical properties of the blends, so thermal analysis was performed using a NETZSCH DSC 204 F1 (Germany) differential scanning calorimeter (DSC) under a nitrogen atmosphere. Samples of about 5 mg sealed in aluminum pans were heated from room temperature to 180 °C at a rate of 10 °C/min under a nitrogen atmosphere, and held at 180 °C for 5 min to eliminate the thermal history. Afterwards, the samples were cooled to −80 °C at a rate of 20 °C/min, holding about 3 min at −80 °C, and then heated again to 180 °C at a heating rate of 10 °C/min. The crystallinity of PLA (Xc) in the injection specimens was estimated from the first heating cycle using the following equation [18]:

$$X_C = \frac{\Delta H_m - \Delta H_c}{w_f \Delta H_m^o} \times 100\%$$

where ΔH_m and ΔH_c are the enthalpies of melting and cold crystallization during heating, respectively;ΔH_m^o is the enthalpy assuming 100% crystalline PLA homopolymer (93.7 J/g), [19] and w_f is the weight fraction of PLA component in the blend.