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Role of high-density polyethylene in the crystallization behaviors, rheological property, and supercritical CO_2 foaming of poly (lactic acid)

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ABSTRACT

A simple and effective methodology to improve the crystallization behaviors, rheological property, and supercritical CO_2 foaming of poly (lactic acid) (PLA) using high-density polyethylene (HDPE) as modifier was proposed. PLA was blended with various content of HDPE through a melt blending method. The results demonstrated that with the blending of PLA and HDPE, the crystallization behaviors of PLA and HDPE were improved simultaneously as well as the rheological property of PLA got better gradually. The morphology of HDPE dispersion phase in the PLA/HDPE blends was irregular and its average size became larger gradually with the content of HDPE increasing. Then resultant PLA/HDPE blends were foamed using supercritical CO_2 as physical blowing agent in the autoclave. The cellular morphology evolution of PLA/HDPE blending foams had a relationship with the content of HDPE. When the content of HDPE increased from 0 wt% to 5 wt%, complex cellular structure (CCS) appeared in the PLA/HDPE blending foams. With the content of HDPE more than 10 wt %, the CCS disappeared gradually. The interface between PLA and HDPE could be acted as heterogeneous nucleation points for both the crystallization of PLA and the cell nucleation of PLA/HDPE blends. Finally, the influence of foaming temperature on the foaming behaviors of pure PLA and PLA/HDPE blends was also investigated and the foaming mechanism on pure PLA foam and PLA/HDPE blending foams with various blending ratio was presented.

1. Introduction

Biodegradable polymers have gained considerable attention in the recent years for its ecofriendly characteristic [1,2]. As one of the most popular biopolymers, poly (lactic acid) (PLA) is a promising bio-based thermoplastic polymer which displays high biocompatible, mechanical properties, and low-cost production produced from renewable resources [3,4]. PLA could be synthesized through the ring-opening polymerization of lactide and lactic-acid monomers as well as be completely biodegraded to carbon dioxide and water [5–7].

PLA foam represents unique properties such as biodegradability, biocompatibility, low density, relatively low cost and excellent physical properties, making it use in the biomedical, packaging, agriculture and transportation fields [8–11]. However, PLA foaming confronted with two big problems during the foaming process. One was the low melt strength, which was associated to poor viscoelastic and not strong enough to support the growth of the cells, resulting in bad foaming properties of PLA foams [12–14]. The other was poor crystallization properties, which caused dissolved gas in PLA escaped rapidly during the foaming process, and the cells combined, collapsed or ruptured leading to low cell density or bad cellular morphology [15–18]. These problems limited the application of PLA foams in the industrial circle.

Numerous modified methods have been studied to improve the melt strength and crystallization behaviors of PLA, such as blending with other polymers [19–23], introducing branching or cross-linking structure [24,25], and filling with different types of additives [26,27]. Among these methods, blending with other polymers is regarded as one of the most simple and practical to improve the physical properties and foamability of PLA. Generally, melt blending method could balance the respective properties of various polymeric components, improve the processability to some extent, overcome the disadvantages of certain polymeric component, reduce the cost, and develop some novel polymer products [28,29]. M. Nofar et al. found that poly (butylene adipate)-co-terephthalate and poly (butylene succinate)-co-adipate as the dispersion phase had a significant effect on the tensile properties, crystallization rate, overall processability and viscoelastic properties of

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PLA [30]. In our previous study, PLA/poly (ethylene terephthalate glycol-modified) (PETG) blends were prepared by melt blending method using multiple functionality epoxide as reactive compatibilizer. The results showed that the mechanical properties and rheological parameters such as melt viscosity and melt elasticity increased with increasing compatibilizer content. In addition, the PETG dispersion morphology in the PLA/PETG blends affected the cell structure of the PLA/PETG blending foams strongly [31].

As high-density polyethylene (HDPE) had good regularity, excellent crystallization and mechanical properties, adding 20 wt% HDPE into PLA could improve the crystallization properties and impact strength of PLA simultaneously [32]. Besides that, using HDPE as dispersion phase in PLA/HDPE blends could provide abundant interfaces between HDPE and PLA, which are potential to become the heterogeneous cell nucleation points and may improve the foaming properties of PLA foams greatly. To our knowledge, no research has been reported on the foaming behaviors of PLA/HDPE blends.

The aim of this paper is to study the effect of HDPE as dispersion phase on the crystallization behaviors, rheological properties and foaming performance of PLA. It was expected that with the addition of HDPE, the crystallization behaviors, rheological properties and foaming performance of PLA could be improved meanwhile. In detail, high crystallinity of HDPE was expected to promote the crystallization of PLA, better melt viscoelastic properties of HDPE were anticipated to improve the rheological properties of PLA, and the interfaces between HDPE and PLA as the heterogeneous bubble nucleation sites were beneficial to increase the cell density of PLA foam.

2. Experimental

2.1. Materials

Semi-crystalline PLA (Grade 2003D) in pellets form with a melt flow rate (MFR) of 3.2 g/10 min (190 °C, 2.16 kg) was supplied by Nature Works Inc. and it was reported that its D-isomer content is 4.3%, its density is 1.24 g/cm^3, its glass transition and melting temperature is 61.4 °C and 147.6 °C, respectively. HDPE (5420 GA), with a MFR of 2.3 g/10 min (190 °C, 21.6 kg) and the density of 0.95 g/cm^3, was purchased from the PetroChina Co. Ltd.

2.2. Preparation of various PLA/HDPE blends

Before melting blending, PLA and HDPE pellets were dried in vacuum at 60 °C for 4 h to remove water. PLA/HDPE blends with different blending ratios were mixed in a Haake internal mixer at 190 °C, with a mixing time of 15 min and mixing speed of 60 rpm, according to the formula shown in Table 1. The corresponding sample names were denoted as pure PLA, PLA/HDPE 5, PLA/HDPE 10, PLA/HDPE 15, and PLA/HDPE 20, respectively. Subsequently, PLA/HDPE blends were pressed into sheets with a thickness of about 2 mm by compression molding at 190 °C and 10 MPa for 10 min, and then cooled to room temperature to obtain sheet samples of 2 mm in thickness for further characterization or foaming process.

2.3. Foaming process of various PLA/HDPE blends

To investigate the effect of HDPE content on the foaming behaviors of various PLA/HDPE blends, all the foaming samples (pure PLA, pure HDPE, and PLA/HDPE blends) were prepared in the autoclave using supercritical CO$_2$ as the physical blowing agent under the same conditions. Concretely, the resultant unfoamed sheet samples were put into a stainless-steel autoclave at 170 °C and 10 MPa for 2 h to ensure the PLA/HDPE sample was fully saturated with CO$_2$. Then the temperature was cooled to various foaming temperature of 100 °C, 105 °C, 110 °C, 115 °C and 120 °C, respectively. Finally, the pressure of the stainless-steel autoclave dropped by the release of CO$_2$ from 10 MPa to 0.1 MPa in about 6 s, which provided a driving force for cell nucleation and growth to obtain the foaming samples.

Table 1
Formula of pure PLA and PLA/HDPE blends.

Sample Name	Pure PLA	PLA/HDPE 5	PLA/HDPE 10	PLA/HDPE 15	PLA/HDPE 20
PLA (wt%)	100	95	90	85	80
HDPE (wt%)	0	5	10	15	20

2.4. Characterizations

2.4.1. Differential scanning calorimetry (DSC)

The crystallization and melting behaviors of all the samples (pure PLA, pure HDPE, and PLA/HDPE blends) were investigated using DSC (Q1000, TA). The samples were heated to 190 °C rapidly under a nitrogen atmosphere and held for 5 min to remove previous thermal history. Then the samples was cooled to 20 °C and then heated to 190 °C at a cooling/heating rate of 10 °C/min to record crystallization and melting behaviors. The relative crystallinity (χ_c) of each component in all the PLA/HDPE blends was calculated by the following equations [32]:

$$\chi_{c(PLA)} = \frac{\Delta H_{m(PLA)} - \Delta H_{cc(PLA)}}{\Delta H^0_{m(PLA)} \times W_{(PLA)}} \times 100\% \tag{1}$$

$$\chi_{c(HDPE)} = \frac{\Delta H_{c(HDPE)}}{\Delta H^0_{m(HDPE)} \times W_{(HDPE)}} \times 100\% \tag{2}$$

Where $\Delta H_{m(PLA)}$ is the melting enthalpy of PLA, $\Delta H_{cc(PLA)}$ is the cold crystallization enthalpy of PLA, and $\Delta H^0_{m(\mathrm{PLA})}$ is the melting enthalpy of 100% crystalline PLA that is 93 J/g [31], $\Delta H_{c(HDPE)}$ is the crystallization enthalpy of HDPE, $\Delta H^0_{m(HDPE)}$ is the melting enthalpy of 100% crystalline HDPE that is 292 J/g [32], W is the weight fraction of each component in the PLA/HDPE blends.

2.4.2. Polarized optical microscope (POM)

Crystal morphology of pure PLA and PLA/HDPE blends was observed by POM (BX-51, Olympus, Japan). The pure PLA and PLA/HDPE blends were heated from room temperature to 200 °C at a rate of 30 °C/min, kept for 3 min to eliminate thermal history, and then cooled down at a rate of 10 °C/min to 120 °C and maintained for 40 min to observe the changes of crystal morphology.

2.4.3. Scanning Electron Microscope (SEM)

The fracture surface morphology of pure PLA and PLA/HDPE blends as well as their foams was investigated by a SEM (FEI, Quanta FEG) at an acceleration voltage of 5 kV. Before observations, the surfaces of the samples were sputter coated with Au to prevent build-up of electrostatic charge during observations.

2.4.4. Rheological properties

The dynamic rheological properties of all the samples (pure PLA, pure HDPE, and PLA/HDPE blends) were tested using a rotational rheometer (ARES Rheometer, TA, USA) at 190 °C with a pair of parallel plates (20 mm in diameter with a gap of 1.0 mm). The frequency range was 0.1–100 rad/s, and the maximum strain was fixed at 5%, in order to confirm that these conditions were within the linear viscoelastic region under nitrogen. The complex viscosity (η*), storage modulus (G′), and loss factor (tanδ) were measured at various frequencies.

2.4.5. Foaming properties

The volume expansion ratio (Φ) of pure PLA foam and PLA/HDPE blending foams was calculated by equation (3):