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The effect of nanosized carbon black on the morphology and sc-CO_2 foaming behavior of LLDPE/PS blends at semi-solid state

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ABSTRACT

The influences of nanosized carbon black (CB) on the morphology of immiscible cocontinuous LLDPE/PS blends and their foaming behavior under the sc-CO_2 batch foaming was studied. The morphologies and cellular structures of LLDPE/PS blends and LLDPE/PS/CB nanocomposites were characterized by scanning electron microscope (SEM). The results indicated that the introduction of CB nanoparticles could effectively improve foaming ability of LLDPE/PS = 50/50 blends, when enough amount of CB nanofillers was added. This was ascribed to the morphology transformation from cocontinuous structure to sea-island structure due to the presence of CB nanofillers. Furthermore the critical amount of CB for dramatically improving the foaming capacity depended on the foaming temperature. In contrast, the addition of CB in the LLDPE/PS blends with spherical dispersed phase (such as 80/20 or 20/80, by weight) did not dramatically change the foaming behavior of the blends.

1. Introduction

Polymer foams have been applied widely in various applications. Now the foaming behavior of polymer with sc-CO_2 as physical blowing agent, especially polymer blends and nanocomposites, is a hot topic [1,2]. Compared to single polymer, polymer blends and nanocomposites show different foaming behavior due to the intervention of morphology and interfacial regions [3–7]. More interestingly, how will the foaming behavior of polymer blends change when some nanofillers are added into the blends? As we know, the distribution of nanofillers is a critical issue to the microstructure and properties of the final materials in polymer blends [8]. The introduction of nanoparticles might result in the change of physical properties, such as crystallinity, melt strength and interfacial interaction, which would influence the foaming process and finally the cellular structure. Depending on the mixing process and the interaction strength of nanofillers with two components, the added nanofillers can be distributed in the interfacial region or polymer bulks, which will affect the foaming behavior of polymer blends. Han et al. [9] have found that the added nanoclays are distributed along the PS/PMMA interface, where the nanoclays serve as heterogeneous nucleation sites because of the abundant CO_2 from the PMMA phase and the low interfacial tension on the clay surface, resulting in smaller cell size and increased cell density in the final composite foam.

As we know, the properties of polymer blends strongly depend on their morphology. Among possible morphologies of blends, cocontinuous blends are very interest due to their unique characteristic of possessing two continuous phases, which results in the formation of polymer materials with specific properties, such as strong conductive plastics [10]. Considering the special morphology of cocontinuous blends, how about is the influence of blend morphology on the foaming behavior under the physical foaming conditions? In a previous work [11], we have demonstrated that, immiscible LLDPE/PS blends with cocontinuous phase structure do not well foam under the suitable physical foaming conditions for LLDPE and PS alone, but the addition of PE-*g*-PS (as a compatibilizer) can dramatically improve the foaming behavior of these blends, although the phase structure of compatibilized LLDPE/PS blends was still cocontinuous. This results from that the interfacial interaction between LLDPE and PS is strongly increased in the compatibilized blends, blocking the release of CO_2 from the interfacial region. However, we wonder if the introduction of some nanofillers can remarkably enhance the foaming ability of immiscible cocontinuous LLDPE/PS blends. So far, most of previous reports are

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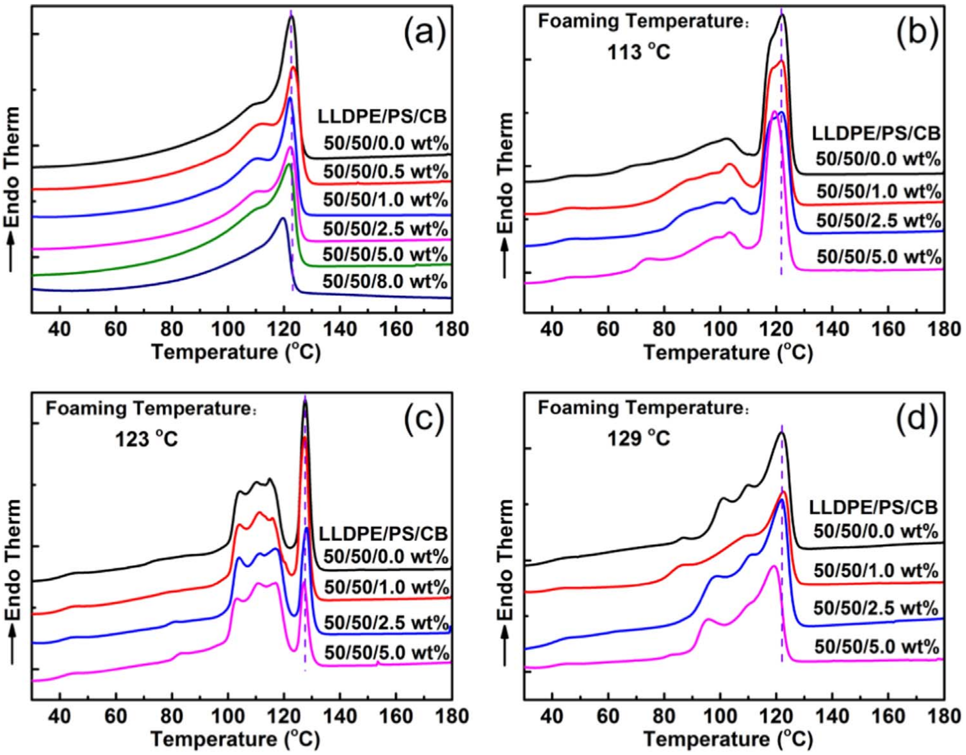

Fig. 1. DSC curves of LLDPE/PS blend and LLDPE/PS/CB nanocomposites before (a) and after foaming ((b)-(d)).

focused on the mediation of the phase morphology in polymer blends, there is no report relating to the influence of the dispersion state and distribution of the fillers on the foaming behaviors of immiscible cocontinuous blends. In this work, nanosized carbon black (CB) was used to adjust foam behaviors of immiscible cocontinuous LLDPE/PS blends (LLDPE/PS = 50/50 as an example) under sc-CO_2 physical foaming conditions. The influence of added nanofillers on the foaming behaviors of the blends was investigated.

2. Experimental section

2.1. Materials

Linear low density polyethylene (LLDPE, MI = 2.0 g/10 min, M_w = 141k, PDI = 3.36) was supplied by Sinopec Maoming Company, China. Polystyrene (PS, MI = 2.2 g/10 min, M_w = 372k, PDI = 1.78) was provided by Zhenjiang Chi Mei Chemical. Co., Ltd. Carbon black (CB) with the primary particle diameter of 17 nm (purity > 99%) was purchased from Linzi Qishun Chemical Co., Shandong, China.

2.2. Preparation of polymer blends and nanocomposites

LLDPE/PS = 50/50 and corresponding nanocomposites were prepared via melt compounding method. Briefly, LLDPE, PS and predetermined amounts of CB nanoparticles were mixed in a torque rheometer (XSS-300, Shanghai Kechuang Rubber Plastic Mechanical Equipment Co., Ltd., China) with 100 rpm at 180 °C for 10 min. The obtained samples were cooled to room temperature, and then the samples for test and foaming were molded into disks with a diameter of 25 mm and a thickness of 1 mm by compression-molding at 180 °C for 3 min under 10 MPa. Then, the samples were quenched at room temperature under 10 MPa.

2.3. Batch foaming

A stainless steel high-pressure vessel was used in batch foaming process. After the high-pressure vessel containing samples was purged with low-pressure CO_2, a given amount of CO_2 was pumped into the vessel. The vessel was heated to the predetermined foaming temperature and continuously charged with CO_2 to the fixed pressure. The samples were saturated for 4 h to ensure equilibrium adsorption of CO_2. Thereafter, the valve was rapidly opened to release the CO_2. Then the high-pressure vessel was opened up, and the foamed samples were taken out for subsequent analyses.

2.4. Characterization methods

Both the morphology of polymer blends and cell morphology of the foamed samples were characterized by a XL 30 ESEM FEG scanning electron microscope (SEM). The compression-molded samples and foamed samples were cryofractured in liquid nitrogen. A representative micrograph containing 100–200 bubbles was obtained and the number of bubbles n in the micrograph was determined. The cell diameter was the average of the sizes of more than 100 cells on the SEM micrograph. The cell density (N_0), the number of cells per cubic centimeter of unfoamed polymer, was determined from Eq. (1):

$$N0 = \left[\frac{n}{A}\right]^{3/2}\frac{\rho}{\rho f} \tag{1}$$

where n is the number of cells seen in the SEM micrograph, A is the area of the micrograph (cm^2), calculated according to the scale bar, ρ and ρ_f are the mass densities of samples before and after foaming treatment, respectively, which was measured by water displacement method.

Transmission electron microscopy (TEM) measurements were performed on a TEM (JEM-1011, JEOL) operated at an acceleration voltage of 100 kV. The samples were ultra-microtomed in liquid nitrogen by a microtome (Leica Ultracut ME_1-057) equipped with a glass knife.

All the samples were measured using DSC (Mettler Toledo Star system (DSCI)) under a nitrogen atmosphere, operating at a heating rate of 10 °C/min from 25 to 200 °C, held at 200 °C for 5 min, subsequently cooled at a rate of 10 °C/min and heated again at a rate of 10 °C/min.