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Chain extension of poly (butylene adipate-co-terephthalate) and its microcellular foaming behaviors

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ABSTRACT

A facile chain extension and solid-phase batch foaming method was proposed to prepare microcellular poly (butylene adipate-co-terephthalate) (PBAT) foams in the presence of supercritical CO_2. Branching structure and micro cross-linking structure were generated in modified PBAT with styrene-acrylonitrile-glycidyl methacrylate terpolymer (SAG) as chain extender, which was confirmed by Fourier transform infrared spectra, gel permeation chromatography and gel fraction measurements. The intrinsic viscosity and branching degree of modified PBAT increased as well as their viscoelasticity was improved respectively, with the SAG content increasing. The crystallization temperature and crystallinity of various PBAT samples increased and then decreased slightly due to the heterogeneous nucleation effect of branching points and the generation of cross-linking structure. An interesting complex cellular structure was observed in modified PBAT foams with the SAG content of 1 and 3 wt%, owing to the different rheological properties in branching molecular chain regions and linear molecular chain regions.

1. Introduction

In general, microcellular polymer foams possess the average cell diameter in the range of 1–10 μm and the cell density higher than 10^9 cells/cm^3 [1,2], which exhibit a large number of unusual properties such as good mechanical performance, high thermal and acoustic insulation, excellent dielectric properties, and so on [3]. As a consequence, microcellular polymer foams are used widely in the fields of thermal and building insulation materials, packaging materials, and auto parts [4].

Compared with that of microcellular amorphous polymer foams, the preparation of most microcellular semi-crystalline polymer foams faced with three big difficulties [5,6]. Firstly, foaming processing window for preparing microcellular semi-crystalline polymer foams was narrow due to the relative high crystallization rate and low melt strength. Secondly, the crystalline regions were hard to plastic deformation during the foaming process, which could not support the cell growth. Thirdly, the solubility and diffusibility of blowing agent gas in the crystalline regions is very low. In other words, the crystalline region was an obstacle in the passageway of blowing agent gas during the foaming process.

Semi-crystalline biodegradable polyesters such as poly (lactic acid), poly (butylene adipate-co-terephthalate) (PBAT), and so on, have good biocompatibility and mechanical properties, which also present low melt strength for foaming due to their low molecular weight and linear architecture [7,8]. Many approaches such as blending [9], filling [10], cross-linking [11], and chain extension [12,13] were often used to improve the foamability. Among these, the chain extension method is very effective to enhance the foamability by adjusting the molecular chain structure and increasing the molecular weight. In the chain extension of biodegradable polyesters reported previously, chain extenders (ADR-4368 and ADR-4370) are used widely, which were provided by BSAF Company [12,13]. However, numerous gels were usually generated during the chain extension, which is adverse to the degradability and the cell growth of biodegradable polyesters. It was significant to seek a modified method for preparing chain extended biodegradable polyesters with micro cross-linking structure and excellent viscoelasticity.

Supercritical CO_2 ($ScCO_2$) possesses many unique properties such as nontoxic, environmental, cheap, relatively large solubility in polymers, and so on, which has attracted a lot of attention of

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researchers engaged in polymer foams [14,15]. However, the diffusivity of $scCO_2$ in polymers is higher than that of other common physical blowing agents such as supercritical N_2, leading to the cell coalescence and large cells easily [16]. Therefore, it was still a big challenge to prepare the microcellular semi-crystalline biodegradable polyester foams using $scCO_2$ as physical blowing agent.

Consideration on its low temperature processibility and toughness, semi-crystalline biodegradable PBAT was chosen and employed to prepare microcellular foams. First, PBAT was modified by styrene-acrylonitrile-glycidyl methacrylate terpolymer (SAG) as chain extender to improve its thermal behaviors, rheological properties, and foaming performances. Subsequently, the solid-phase batch foaming method was employed to prepare the microcellular semi-crystalline PBAT foams. The effect of the SAG content and foaming temperature on the microcellular morphology evolution of various PBAT foams was studied systematically.

2. Experimental

2.1. Materials

PBAT (C1200) was supplied by BASF (Ludwigshafen, Germany) with the mass density of 1.25–1.27 g/cm^3 and the melt flow rate of 2.7–4.9 g/10min (190 °C, 2.16 kg), under the trade name of Ecoflex. SAG (product grade of SAG-008) is a random styrene-acrylonitrile-glycidyl methacrylate terpolymer with the epoxy content of 8 ± 0.5 wt%, which was provided by Fine-Blend Compatibilizer Jiangsu Co., China.

2.2. Preparation of torqued PBAT and PBAT-SAG samples

Pure PBAT was dried in an oven at 80 °C for 6 h before melting mixing to minimize the effect of moisture. PBAT and SAG with different blending ratios (99/1, 97/3, 95/5, 93/7) were fed into a Haake internal mixer at 140 °C for 15 min with a rotor speed of 60 rpm, according to the formula shown in Table 1. The corresponding sample names were denoted as torqued PBAT, PBAT-SAG1, PLA-SAG3, PLA-SAG5, and PLA-SAG7, respectively.

2.3. Foaming process of torqued PBAT and PBAT-SAG samples

To research the effect of SAG content on the foaming behavior of various PBAT samples (torqued PBAT sample and PBAT-SAG samples), various PBAT foams (torqued PBAT foam and PBAT-SAG foams) were prepared in a stainless-steel autoclave with the batch foaming technique using $scCO_2$ as physical blowing agent under the same conditions. In detail, the resultant various PBAT samples were placed in the autoclave [17], and then the foaming system was heated to different temperatures (80 °C, 83 °C, 86 °C and 89 °C) and soaked in $scCO_2$ for 6 h to ensure all the PBAT samples were fully saturated with CO_2. Finally, the pressure of the foaming system released rapidly from 20 MPa to 0.1 MPa and the depressurisation time was less than 3 s, which provided a driving force for cell nucleation and cell growth to obtain various PBAT foams.

2.4. Characterizations

2.4.1. Fourier transform infrared spectra (FTIR)

The FTIR spectra were recorded at room temperature using a Nicolet IZ10 spectrometer. Various PBAT samples were placed on sample stand and measured with 32 scans at a resolution of 2 cm^{-1}. Each spectrum was obtained within the range of 4000–400 cm^{-1}.

2.4.2. Gel permeation chromatography (GPC)

The weight-averaged molecular weights (M_w) of various PBAT samples were determined by GPC measurements at 25 °C using chloroform as the eluent at a flowing rate of 1.0 mL/min. The solution of dissolved PBAT samples was filtered through a nylon membrane with the pore diameter of 0.45 μm to remove the possible existed gel in various PBAT samples.

2.4.3. Gel fraction measurement

The gel fraction of various PBAT samples was determined by the Soxhlet extraction with chloroform until the weight didn't change anymore. Subsequently, various PBAT samples were dried in the oven for 6 h at 80 °C. The gel fraction of various PBAT samples could be calculated by equation (1):

$$\text{Gel fraction} = \frac{W_g}{W_0} \times 100\% \quad (1)$$

Where W_0 and W_g were the original weight and the dried insoluble part of various PBAT samples, respectively.

2.4.4. Differential scanning calorimetry (DSC)

DSC analysis was carried out on a TA Instrument (DSC-Q20) equipped with a liquid nitrogen cooling system to investigate the thermal properties of various PBAT samples. About 5–10 mg of each PBAT sample was tested under a nitrogen flow of 50 mL/min. Various PBAT samples were quickly heated from room temperature to 190 °C and maintained for 3 min to eliminate thermal history, then cooled to 20 °C at a rate of 10 °C/min, and finally reheated to 190 °C at the same rate. The crystallization temperature (T_c) and melting temperature (T_m) of various PBAT samples were determined. The relative crystallinity (χ_c) of various PBAT samples was calculated using the following equation (2):

$$\chi_c = \frac{\Delta H_m}{\Delta H_m{}^0} \times 100\% \quad (2)$$

Where ΔH_m and $\Delta H_m{}^0$ were the experimental melting enthalpy of various PBAT samples and the standard melting enthalpy of the crystallized PBAT (114 J/g), respectively [18].

2.4.5. Intrinsic viscosity ([η])

Ubbelohde capillary viscometer was used to measure the [η] of various PBAT samples. To keep the temperature constant throughout the test, the viscometer was immersed in a thermostatic water bath at 30 °C. Five different concentrations of each PBAT sample were prepared by volumetric flask of 25 mL. The flowing time measurements for each concentration were repeated for five times to ensure the accuracy of the results. Branching degree and [η] of various PBAT samples were calculated using the

Table 1
Formula of torqued PBAT and PBAT-SAG samples.

Sample name	Torqued PBAT	PBAT-SAG1	PBAT-SAG3	PBAT-SAG5	PBAT-SAG7
PBAT/wt.%	100	99	97	95	93
SAG/wt.%	0	1	3	5	7