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A cooling and two-step depressurization foaming approach for the preparation of modified HDPE foam with complex cellular structure

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ABSTRACT

This article reports on the fabrication of modified high-density polyethylene (HDPE) foams with complex cellular structure (CCS) using supercritical CO_2 as a physical blowing agent by a cooling and two-step depressurization method. HDPE was modified by dicumyl peroxide (DCP) and carbon nanotubes (CNTs) to improve its viscoelasticity and foaming behavior. The gel content test demonstrated that the cross-linking structure formed in the modified HDPE samples. Compared with that of neat HDPE, the viscoelasticity of modified HDPE was improved largely, which was characterized by rotational rheometer and torque rheometer. The introduction of DCP and CNTs had a slightly effect on the thermal behaviors of HDPE. The foaming properties of various HDPE samples showed that the cross-linking structure caused by DCP improved the foamability of HDPE and CNTs acted as a nucleating agent for cell nucleation. The degree of the first-step depressurization was critical to control the CCS evolution in HDPE foam.

1. Introduction

Polymeric foams with complex cellular structure (CCS) (or bimodal cellular structure) possessed merits of both large and small cell structures. Large cells could reduce the bulk density, and small cells helped to enhance the mechanical and thermal insulation properties [1,2]. For this reason, the polymeric foam with CCS had been widely applied in many fields, such as packaging materials, chemical industry, construction, and so on.

Generally, four methods for the fabrication of the polymeric foam with CCS had been reported, which were co-blowing agent method [1–3], two-step depressurization method [4–8], polymer blending system method [9–13], as well as cooling and depressurization method [14]. Polystyrene (PS) foams with CCS were prepared using water and *n*-butane as co-blowing agents in extrusion and it was found that the CCS could be tuned by *n*-butane/water/silica content and die temperature [2]. Ma et al. found that the compressive and dynamic mechanical properties of the polycarbonate (PC) foam with CCS were higher than those of PC foam with mono-porous cell structure (MCS) [5]. PS foam with CCS was prepared using a two-step depressurization method by Bao et al. They found that with the similar density, the tensile strength and modulus increased with large cells decreasing when the cell size of large cells was larger than 25 mm. When the volume fraction of large cell was more than 32%, the impact strength decreased with the large cell increasing [6]. Stearic acid (SA) and organic montmorillonite (OMMT) were added into ethylene vinyl acetate (EVA), leading to the formation of CCS in EVA/SA/OMMT foam. Compared with those of neat EVA foams, the density of EVA/SA/OMMT foam became lower, and the peel strength and elongation-at-break of EVA/SA/OMMT foam were increased [11]. The cross-linked PS/polymethyl methacrylate (PMMA) blending foam with CCS was produced by Kohlhoff et al. Two cell nucleation took place in the PS matrix and the PMMA-rich domains successively, due to the elasticity difference between the binary phase of PS and PMMA. The quantity of the small cells in the cell walls increased with the content of the MMA monomer [13]. Polypropylene (PP) foam with CCS was fabricated by Li et al. using cooling and depressurization method. The results demonstrated the rapid cooling which led to the sharp decrease of the CO_2 solubility in PP caused the first nucleation. With the eventual depressurization, these cell nucleuses grew to big cells, as well as some small cells produced, resulting in the PP foam with CCS [14].

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Table 1
Samples of various high-density polyethylene (HDPE) blends.

Samples	HDPE (phr)	DCP (phr)	CNTs (phr)
HDPE (1#)	100	0	0
HDPE/DCP (2#)	100	0.25	0
HDPE/DCP/CNTs (3#)	100	0.25	0.10

Dicumyl peroxide and carbon nanotubes are denoted as DCP and CNTs, respectively.

Through the above literatures, it could be found that the investigations about CCS were mainly focused on amorphous polymer and polymer with low crystallinity. The research on high-density polyethylene (HDPE) foams with high crystallinity was concentrated on MCS [15–19], while few studies on HDPE foams with CCS were reported. Compared with amorphous polymer and polymer with low crystallinity, HDPE possesses the lower degree of branching and the stronger crystallization ability, leading to narrower foaming processing window and lower foam ability of HDPE. Therefore, the preparation of HDPE foams with CCS was relatively difficult and a big challenge for the researchers.

In order to solve the above problem, HDPE was cross-linked by dicumyl peroxide (DCP) in this paper. Moreover, carbon nanotubes (CNTs) were introduced into the foam system acting as a nucleating agent to decrease the cell nucleated energy barrier and increase the cell density. Then, a new methodology (cooling and two-step depressurization method) was proposed for the preparation of HDPE foam with CCS. The effect of the addition of DCP and DCP/CNTs to HDPE as well as the degree of the first depressurization (ΔP_1) on the formation and evolution of CCS were investigated.

2. Experimental

2.1. Materials

HDPE (5000S) with the melt flowing index of 1.02 g/10 min at 190 °C/2.16 kg and the density of 0.92 g/cm^3, was provided by PetroChina Co. Ltd. DCP was purchased from Sinopharm Chemical Reagent Co. Ltd. Multi-walled CNTs having a particle size of 7–11 nm and a more than 90% purity, were supplied by Beijing CNano Technology Co. Ltd. Xylene was provided by Tianjin Yongda Chemical Reagent Co. Ltd.

2.2. Preparation of various HDPE samples

HDPE, DCP, and CNTs were mixed in a Haake internal mixer at 190 °C, with a mixing time of 15 min and mixing speed of 60 rpm to prepare various HDPE samples, according to the formula shown in Table 1. The additives (DCP and CNTs) used the unit of "parts per hundred resin" (phr) for the formula. The resultant mixed HDPE samples were transferred to a mold, preheated at 160 °C and held for 5 min, then pressed at 10 MPa for 3 min, finally cooled to room temperature to obtain sheet samples of 2 mm in thickness for further characterization or foaming process.

2.3. Preparation of various HDPE foaming samples

Various HDPE foams were produced through two kinds of batch foaming methods: (i) one-step depressurization method and (ii) cooling and two-step depressurization method, using CO_2 as physical blowing agent. In a stainless-steel autoclave, the sheet HDPE sample and CO_2 were held at a temperature of 200 °C and a pressure of 20 MPa for 2 h to ensure the HDPE sample was fully dissolved and then the temperature was cooled to 135 °C at 1.5 °C/min. Subsequently, for method (i): quenched to atmosphere pressure within 3 s; or for method (ii): the pressure was reduced for a designed value (1.0, 1.5, 3.0, 4.0, 5.0 MPa), kept for 20 min and then quenched to atmospheric pressure within 3 s. The change of pressure in the autoclave with time was shown in Fig. 1.

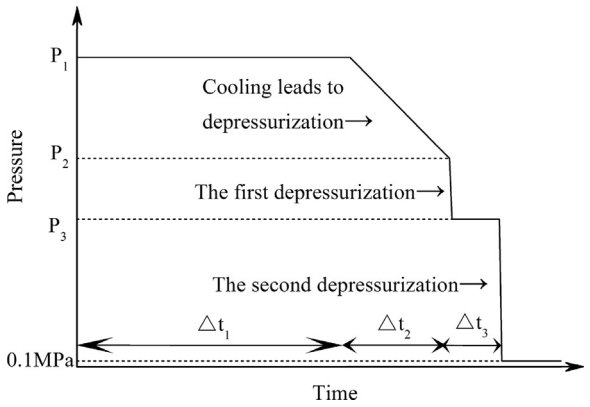

Fig. 1. Curve of pressure variation in the autoclave with time in cooling and two-step depressurization foaming process, P_1: 20 MPa; P_2: the pressure in the autoclave (about 15.0 MPa) when the temperature of the autoclave was cooled to 135 °C; P3: the remaining pressure in the autoclave after the first depressurization (1.0, 1.5, 3.0, 4.0, 5.0 MPa), Δt_1: the first holding time (2 h); Δt_2: cooling time: the temperature of the autoclave cooled from 200 °C to135 °C (about 45 min); Δt_3: the second holding time (20 min).

2.4. Characterizations

2.4.1. Measurement of gel content

Various HDPE samples were washed with xylene in a Soxhlet extractor until their weights were constant. The insoluble parts of various HDPE samples were dried in oven at 60 °C for 4 h to allow the xylene to evaporate completely. Every sample was tested three times, and the average value was taken. The gel contents of the HDPE samples (1# and 2#) and the HDPE sample of 3# were computed by the Eqs. (1) and (2), respectively:

$$\text{gel content}(\%)\frac{W_g}{W_0} \times 100\% \quad (1)$$

$$\text{gel content}(\%)\frac{W_g}{W_0 - W_c} \times 100\% \quad (2)$$

Where W_0, W_g, and W_c represented the weights of the initial polymer, dried insoluble part of samples, and carbon nanotubes, respectively.

2.4.2. Differential scanning calorimetry (DSC)

DSC instrument (Q100, TA, USA) was conducted to determine the crystallization and melting behaviors of various HDPE samples purged with nitrogen. Samples were equilibrated to 220 °C rapidly, held in the molten state for 5 min to erase prior thermal and stress histories, and then cooled down to 40 °C at a rate of 20 °C/min. Finally, samples were re-heated to 220 °C at the same rate. The crystallinity (χ) of various HDPE samples was calculated by the Eq. (3):

$$\chi(\%) = \frac{\Delta H_c}{\Delta H_c^0} \times 100\% \quad (3)$$

Where ΔH_c and ΔH_c^0 were the crystallization enthalpy of various HDPE samples and neat HDPE that 100% crystallized, respectively. ΔH_c^0 was considered to be 290.0 J/g [20].

2.4.3. Dynamic rheometer

The dynamic rheological properties of various HDPE samples were tested using a rotational rheometer (ARES Rheometer, TA, USA) at 220 °C with a pair of parallel plates (20 mm in diameter