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Preparation of solid-state micro- and nanocellular acrylonitrile-butadiene-styrene (ABS) foams using sub- and supercritical CO_2 as blowing agents

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ABSTRACT

In this work, micro- and nanocellular acrylonitrile-butadiene-styrene (ABS) foams were prepared by using sub- and supercritical CO_2 as blowing agents. The sorption kinetics at 10 MPa was first measured. The sorption amount depended on the saturation temperature Arrheniusly. The diffusivities did not follow the Arrhenius relation. This relation was interpreted by a retrograde behavior of ABS/CO_2 system. From the kinetics, ABS discs were saturated at 10 MPa at the temperatures from −20 °C to 40 °C, and foamed at the foaming temperature of 20 °C–80 °C. A network of closed cells with a diameter of 600–700 nm and nanopores with a diameter of 100 nm were observed in the foam obtained at low saturation temperatures and high foaming temperatures. The closed cell densities were in a range from $1.12 \times 10^{12} - 9.87 \times 10^{12}$ cells/cm^3 and an experimental correlation based on the CNT model was used to fit the data.

1. Introduction

Thermoplastic foams have many attractive features such as light weightiness, impact dampening and thermal/acoustic insulation. Thus, they provide great potential to be used for a wide range of usages such as a heat insulation material, packing materials, boards, upholstery, etc. [1] These characteristics depend on the cell structure as well as the polymeric material used. As the number of cells in a unit volume of polymeric materials increases, thermomechanical characteristics of the foams can be improved [2–4]. Therefore, a lot of studies were devoted for the sophisticated control of cell structures and the preparation of the solid-state nanocellular foams. A basic idea behind the preparation of nanocellular foams is to increase the cell nucleation rate. The more blowing agents dissolve in polymer, the faster the nucleation rate would be. A high amount of CO_2 could be dissolved in some kinds of polymeric materials such as poly (methyl methacrylate) at high pressure [5]. Therefore, many recent studies focused on the use of high pressure sub- and supercritical CO_2 as blowing agents. Several methods were proposed to increase the nucleation rate by using supercritical CO_2 as a blowing agent. First, an insertion of nanoparticles into a polymer was considered so that the nucleation rate can be increased by means of a heterogeneous nucleation. For instance, nanostructured materials such as polyurethane/montmorillonite, silica/poly (methyl methacrylate) and acrylonitrile-butadiene-styrene (ABS) terpolymer were used to prepare nanocellular foams [6–8]. Second, the synthesis of copolymers and/or the preparation of polymer blends were also used. Fluoropolymers and acrylate-based polymers and/or monomers were used to prepare polymer blends and copolymers because of their high CO_2 uptake. For instance, polystyrene/poly (methyl methacrylate) foams with a cell diameter of 40 nm were fabricated [9]. Poly[styrene-block-4-(perfluorooctylpropyloxy)styrene] and poly (styrene-block-perfluorooctylethyl methacrylate) were also fabricated as nanofoams with a cell diameter less than 40 nm [10]. Third, rapid depressurization (pressure quench) was also used to increase the nucleation rate [11]. When the pressure inside the vessel is released quickly, the nucleation rate could be greatly improved. Thus, many studies were devoted for the characterization of the influence of the depressurization on the cell structures [11–13].

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Table 1
Experimental conditions for the preparation of solid-state ABS foams.

Run	T_{sat}, °C	P, MPa	T_f, °C	t_{sat}, *hr*	d_{cell}, nm	N_{nuc}, 10^{12} cells/cm^3	ρ_b, g/cm^3
1	−20	10	*20*	16	594.90	2.00	0.79
2	−20	10	*40*	16	683.74	2.60	0.72
3	−20	10	60	16	724.07	3.69	0.47
4	−20	10	80	16	750.71	9.87	0.36
5	0	10	*20*	6	661.24	1.76	0.79
6	0	10	*40*	6	671.29	2.03	0.61
7	0	10	60	6	704.64	3.31	0.52
8	0	10	80	6	686.04	5.39	0.44
9	20	10	*20*	4	773.27	1.16	0.94
10	20	10	*40*	4	645.92	1.54	0.79
11	20	10	60	4	789.62	2.62	0.58
12	20	10	80	4	698.91	3.43	0.56
13	40	10	*20*	3	1016.1	1.12	0.78
14	40	10	*40*	3	1100.2	1.26	0.65
15	40	10	60	3	798.31	1.88	0.54
16	40	10	80	3	1270.3	2.40	0.36

More recently, CO_2 (l) was also studied for the preparation of nanocellular foams [14–16]. Nanocellular foams of polycarbonate, poly (methyl methacrylate) and polysulfone nanofoams were successfully fabricated at the saturation temperatures below 0 °C [15,17,18]. After the sorption stage, the polymeric material is given thermal contrast by immersing the sample in a heating medium to induce high supersaturation. This method is based on the retrograde behavior of polymer/CO_2 mixture [19]. The retrograde behavior of polymer/CO_2 mixture originates from the opposite dependence of the chain segmental motion and the amount of CO_2 absorbed in a polymer on the saturation temperature. At high saturation temperature, the segmental motions of polymer chains are active. Therefore, the glass transition temperature (T_g) of polymer/CO_2 mixture is depressed although a small amount of CO_2 is absorbed. As the saturation temperature decreases, the segmental motion becomes inactive. Thus, polymer/CO_2 mixture becomes glassy. However, as the saturation temperature decreases more significantly, the amount of CO_2 uptake can drastically increase. Therefore, the polymer swelling occurs, which makes the interchain interactions weak. This results in significant T_g depression.

Based on this idea, acrylonitrile-butadiene-styrene (ABS) micro- and nanocellular foams were prepared by using CO_2 (l) and CO_2 (sc) as blowing agents in this work. ABS nanocellular foam has been studied because of its good mechanical characteristics. Murray et al. fabricated ABS microcellular foams with a cell density of 10^{11} cells/cm^3 and an average cell size of 0.5 μm at the saturation temperature of 26.7 °C and at the pressures of 3 MPa and 6 MPa [20]. Nawaby et al. investigated on the retrograde behavior of ABS/CO_2 mixture and obtained the nanocellular foams with a cell density of 2.8×10^{12}cells/g and an average cell size of 0.47 μm at the saturation temperature of 0 °C and at the pressure of 3.4 MPa [19]. Forest et al. studied the influence of initial microstructures on the cellular morphologies of ABS foams at the saturation temperature of 0 °C and at the pressure of 3.4 MPa. They found that the cellular structure was largely dependent on the initial microstructure of butadiene nodules. In case of MAGNUM^{TM} ABS (d_{nodule} = 0.2–2 μm), a double structure which consists of open pores ($d_{pore} \sim 100$ nm) and large closed cells ($d_{cell} \sim 1$ μm) appeared. In case of SICOFLEX^{TM} ABS (d_{nodule} = 90 nm), no double structure appeared, but small closed cells with a diameter of 200 nm were observed. They argued that these structural features mainly originated from the nucleation inside the butadiene nodules [16].

All these studies mainly focused on the use of CO_2 (v) as a blowing agent at the saturation pressure below 6 MPa. In addition, the effects of saturation temperature on the cellular characteristics of ABS foams were not given yet. Therefore, the influences of the saturation temperatures (T_{sat}) and the foaming temperatures (T_f) on the cellular dimensions and the cell nucleation densities by using CO_2 (l) and CO_2 (sc) as blowing agents were studied in this work. First, the sorption kinetics was measured for the estimation of the equilibrium amount of CO_2 absorbed and the diffusivity of CO_2 in ABS terpolymer. Based on the thermodynamic and kinetic data, the foaming experiments were carried out. The characteristics of ABS foams were then investigated to examine the influence of the operating temperatures.

2. Material and methods

2.1. Materials

ABS HF 380 pellets, manufactured by LG Chem, Ltd. were used in this work. The physical properties of the ABS pellets given by the manufacturer were as follows. The melt flowrate was 43 g/min at the test condition of 220 °C/10 kg. The molecular weight was 110,000–130,000. The specific gravity was 1.04–1.06. ABS HF 380 consisted of 25 wt% acrylonitrile, 16 wt% butadiene, 59 wt% styrene. A small amount of ethylene bis-stearamide was used as a lubricant. These pellets were pressed by heat press machine (Ocean Science) at 210 °C to manufacture the disc-type samples (diameter: 50 mm, thickness: 1 mm) which were used for the sorption kinetics and the foaming experiments. Carbon dioxide (99.99%) was purchased from Hyupshin Gas Industry.

2.2. Characterization of the initial microstructure

Because the initial microstructure of the terpolymer could have a significant effect on the foaming behavior, the initial microstructure was observed by transmission electron microscope (TEM, JEM 110, JEOL, Japan) with an accelerating voltage of 80 kV. A cryomicrotome was used to prepare the thin film of the ABS terpolymer. Osmium tetroxide (OsO_4) vapor was used to enhance the contrast.

2.3. Measurement of sorption kinetics

Sorption kinetics was measured at the saturation temperature (T_{sat}) from −20 °C to 60 °C and at the pressure of 10 MPa. A gravimetric analysis was used to measure the amount of CO_2 uptake. The procedure was as follows. An ABS disc was weighed on the analytical scale (EPG 214, Ohaus) and moved into a high-pressure vessel. The vessel was in a thermostat to control the saturation temperature. A high-pressure plunger pump was used to deliver CO_2 into the pressure vessel until it reaches the sorption pressure. The sample was taken out from the vessel by releasing the pressure slowly. Then the disc was weighed to measure the weight change of