



Fabrication and mechanism of poly(butylene succinate) urethane ionomer microcellular foams with high thermal insulation and compressive feature

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ABSTRACT

To fabricate biodegradable microcellular foams with high thermal insulation and compressive feature, poly (butylene succinate) urethane ionomer (PBSUIs) were synthesized and foamed by supercritical CO₂ via batch foaming method. The intrinsic viscosities, rheological and crystallization properties of PBSUI were characterized by Ubbelohde viscometer, rotational rheometer and X-ray diffraction test, respectively. The results revealed that the complex viscosity of PBSUIs vastly increased with the rise of urethane ionic groups (UIG) content, while its intrinsic viscosity and crystallinity slightly decreased due to the physical network upon UIG aggregation. The morphology, mechanical and thermal insulation properties of PBSUIs foams were evaluated. The results demonstrated that foams morphologies were sensitive to UIG content and dominated their mechanical and thermal insulation properties. PBSUI-3 (3 wt% UIG content) and PBSUI-5 (5 wt% UIG content) microcellular foams exhibited elliptical shape and stretched in the foam-mold height direction, their cells size and opening ratio are smaller than 7.0 μm and 13%, while their cell densities are higher than 4.7 × 10⁹ cells/cm³. Meanwhile, PBSUI-3 microcellular foam achieved 1.6 MPa compressive strength and 76 mW/m·k thermal conduction. Meanwhile, the foamed, mechanical and thermal insulation properties of PBSUIs microcellular foams were proposed. The study promoted a promising solution for biodegradable thermal insulation material applications.

1. Introduction

Microcellular polymeric foams have been engaging increasing interests as lightweight, low price, high impact resistance and heat insulation materials [1,2]. These superior properties are appropriate for a versatile of applications ranging from automotive industry, food packaging, insulation to absorbers for acoustic and electromagnetic wave [3–7]. Physical foaming and chemical foaming are the traditional methods to fabricate microcellular polymeric foams [8–10]. Compared with chemical foaming process, physical foaming method provides many advantages, such as less materials usage, no residues and lower cost [10–12]. Particularly, foaming by supercritical carbon dioxide (sc-CO₂) is attracting considerable attention because of its environmental friendly performance and relatively mild critical conditions [13].

For foamed materials, the morphology and cell structure are general defined as open cells and closed cells, and act as the crucial effect on the foams' properties [14,15]. For example, the energy absorption performance of the microcellular polymeric foams strongly depends on the cell structure and size simultaneously [16]. For the rigid polyurethane foam, its compressive strength is depended on the cell walls

morphology [17]. While the foams with open cells are great favorite for thermal insulation application. Microcellular polymers offer better thermal insulation performances, easier handling and lower cost than other foams fabricated by mineral wools, fiberglass and cellulose [18–22]. Nano-fibrillar/Polypropylene (PP) foams with 36.5 mW·m⁻¹·K⁻¹ thermal conductivity had been successfully fabricated by Park group via high-pressure foam injection molding followed by mold-opening with CO₂ as a blowing agent [23]. It demonstrated that the unique cell wall structures with micro-holes could promote the thermal insulation performance based on the phonon scattering factor. M. A. Rodriguez-Perez et al. have proposed the conduction mechanism of low density PP foams that the thermal conduction was dominated by the gaseous phase [24].

Poly (butylene succinate) (PBS), a typical biodegradable aliphatic polyester, has attracted considerable attention due to its excellent physical properties and totally renewable sources [25–29]. Notably, PBS foam exhibits prominent compressive strength, flexural strength and impact strength with optimized cell structure [30]. From this perspective, PBS is a promising substitution for fabricating biodegradable foams with high compressive property and thermal insulation. This

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environmental friendly foam is alternative type of petroleum-based polymer and expected to eliminate the “white pollution”, mainly caused by the disposable food packages, thermal insulation materials and cushioning packaging material. Unfortunately, the drastically defects in low-melt strength of PBS because of linear molecules structure restricts it to be foamed by sc-CO₂ [31,32]. To the best of our knowledge, it had no reports on fabricating the PBS microcellular foam with high mechanical properties. Theoretically, the increase in molecular chain entanglements will improve the polymer melt strength and foamability [33]. Based on the principle, several chemical or physical approaches have been employed to promote the viscoelasticity and foamability increase of PBS [34–37]. Though the melt viscosity of PBS increased by the incorporating with MWCNTs, CNF, halloysite nanotube and organ clay [37–39], the diameter cells of PBS composites foams in these researches are too large size to achieve PBS microcellular foams. Consequently, there are few studies involving in evaluating the effects of cell size and morphology on the mechanical and thermal properties of PBS microcellular foams. Compared with traditional approaches, ionization modification is a novel and effective method to improve polymer melt strength [40–43]. The introduction of ionic groups into PBS promotes to form the ion electrostatically force, then hindered molecular chain mobility, just like a physical cross-linking sites. As a result, melt strength and complex viscosity of PBS increase [44,45]. Furthermore, Due to aggregation of ionic groups, the clusters consisting of numerous multiplets could be formed. The cluster is in nano scale and has two opposing roles in PBSIs crystallization. One is serves as heterogeneous nucleation and improves the crystallization rate, the other is interferes the lamellar growth [45,46]. However, to the best of our knowledge, there is no study on the fabrication of PBSIs microcellular foams by supercritical CO₂ and their performances investigation.

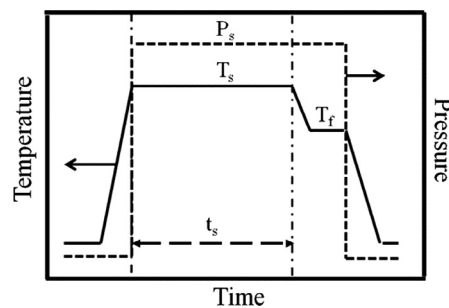
In this manuscript, poly (butylene succinate) urethane ionomer (PBSUIs) were synthesized and foamed by supercritical CO₂ via batch foaming method. The intrinsic viscosities, rheological and crystallization performance of PBSUI were characterized by Ubbelohde viscometer, rotational rheometer and X-ray diffraction test, respectively. The effects of urethane ionic group (UIG) content on the melt strength and viscosity, crystallization behavior of PBSUIs were clarified. Moreover, surface contract angle, thermal conductivity and compressive strength were measured to evaluate the performances of PBSUIs foams. The mechanisms of cellular structure's effect on thermal conductivity and compressive strength were discussed. The prepared PBSUI-3 and PBSUI-5 foams exhibited excellent compressive strength as well as high thermal insulation performance.

2. Experimental

2.1. Materials and sample preparation

Succinic acid (SA) (AR grade), 1,4-butanediol (BD) (AR grade) and Tetrabutyl titanate (TBT) were purchased from Macklin Biochemical Corporation (Shanghai, China) and used without further purification. Diethanolamine hydrochloride (DEAH) and Hexamethylene diisocyanate (HDI) were supplied by Sigma-Aldrich. Commercial purity grade CO₂ (purity 99%, Air Liquide) was used as physical blowing agent. All the reagents were used without any further purification.

PBSUI containing urethane ionic groups was synthesized by chain extension reaction of dihydroxyl terminated poly(butylene succinate) (HO-PBS-OH) and DEAH in the presence of HDI with a temperature of 150 °C [45,47–49]. Prior to that, dihydroxyl terminated poly(butylene succinate) was prepared via condensation polymerization of SA and BD with molar ratio of 1/1.2 at 220 °C for 4 h. The number average molecular weight of HO-PBS-OH was obtained by NMR (Nuclear Magnetic Resonance) analysis (Bruker Avance DRX 400). Then the predetermined amounts of HO-PBS-OH and DEAH were reacted with HDI as a chain extender to synthesize the PBSUI. The molar ratio of –NCO group to –OH group of HO-PBS-OH and DEAH was kept at 1:1 for the synthesis



Scheme 1. Schematic diagram of the pressure and temperature evolution versus the time in the foaming strategy via one-step depressurization.

of all samples. A series of PBSUI samples with DEAH contents of 1, 3 and 5 wt% (based on the weight of HO-PBS-OH) named as PBSUI-1, PBSUI-3 and PBSUI-5, respectively [45]. For reference, PBS without any DEAH was synthesized by the same method as discussed above and designated as PBSU.

Both the PBSU and PBSUI samples were foamed in an autoclave foaming chamber by supercritical carbon dioxide in a batch process via rapid depressurization [50]. Samples were molded and cut into small sheet specimens with dimensions of 5 mm × 1 mm × 0.5 mm and then placed inside the high-pressure vessel. As shown in Scheme 1, the pressure vessel was first heated to a saturation temperature (T_s , 130 °C) and kept for 5 min. Subsequently, supercritical CO₂ was fed into the pressure vessel using a Teledyne ISCO high-pressure syringe pump. The saturation time was 2 h with a saturation pressure (P_s) of 200 bar. The vessel temperature was then cooled to foaming temperature (T_f) of 85 °C with the pressure unchanged and followed by equilibrium for additional 10 min. Ultimately, the pressure was rapidly released by opening a ball-valve connected to the vessel and the chamber vessel was cooled in a water bath.

2.2. Intrinsic viscosity measurement

The Intrinsic viscosity of PBSU and PBSUI samples was measured using an Ubbelohde viscometer (25 ± 0.05 °C) at a concentration of 0.075% (w/v) in chloroform via one point method and calculated by Equation (1).

$$[\eta] = \frac{\sqrt{2(\eta_{sp} - \ln \eta_r)}}{C} \quad (1)$$

2.3. Dynamic rheological measurement

The dynamic rheological measurement was carried out on a rotational rheometer (Bohlin Gemini 200 instrument) using a heat stream of nitrogen gas for temperature control. Under the nitrogen atmosphere, samples loaded between the 25 mm parallel plates were compressed 1 mm thick after melted at temperature of 165 °C for 3 min. Then frequency sweep was performed at 165 °C using parallel plates in the range of 0.01–100 Hz. The relaxation times of PBSU and PBSUI could be calculated using Eq. (2) and the values to ω at 0.0628, 10 and 628 rad/s were exhibited in Table 1.

Table 1
Intrinsic viscosity and Relaxation time (λ) of PBSU and PBSUIs.

Samples	PBSU	PBSUI-1	PBSUI-3	PBSUI-5
$[\eta]/\text{dLg}^{-1}$	0.75	0.89	0.84	0.88
$\lambda_{0.0628}(\text{s})$	2.66	1.33	2.38	5.63
$\lambda_{10.00}(\text{s})$	0.79×10^{-2}	1.26×10^{-2}	3.42×10^{-2}	4.94×10^{-2}
$\lambda_{628.00}(\text{s})$	1.30×10^{-3}	1.04×10^{-3}	1.45×10^{-3}	1.59×10^{-3}

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