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Probing structure–heterogeneous nucleation efficiency relationship of mesoporous particles in polylactic acid microcellular foaming by supercritical carbon dioxide

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ABSTRACT

Heterogeneous nucleating agents that can improve cell morphology of polymer foams have been studied extensively, however, the exact relationship among particle structure, surface modification and nucleating efficiency still remain elusive. Previously, we demonstrated that mesoporous structure benefited nucleating efficiency by comparing solid silica particles and mesoporous particles (MCM-41). Herein, the feasibility of using another type of mesoporous particles, namely, SBA-15 as a nucleating agent for polymer foaming was investigated, but surface modification issue was emphasized. Results reveal that SBA-15 particles show excellent nucleation performance on polylactic acid foaming, and such nucleating effect are dependent on the surface modification. The surface modification using fluorinated silane significantly decreases nucleation energy barrier, and thus shows the highest nucleation efficiency. This work provides a comprehensive insight into structure–nucleating efficiency relationship for mesoporous particles, and highlights the importance of surface modification as a structural factor to optimize the design of effective nucleating agents for polymer foaming.

1. Introduction

Microcellular foaming of polymer has shown its importance for polymer application since it can generate lightweight structure, and confer improved energy absorption and fatigue life, elevated toughness and high thermal stability, as well as low thermal conductivity and dielectric constant [1,2]. However, the realization of microcellular structure is not easy, which relies on optimization for polymer properties [3], blowing agent choices, as well as foaming conditions [4]. For blowing agent, $scCO_2$ has proven to be the most promising candidate as next generation blowing agent due to its non-toxicity, environmental affinity and low cost [5,6]. However, its low solubility and high diffusivity in polymer matrix limits the application in preparing polymeric foams, especially in preparing microcellular foams. The properties and applications of polymer foams are highly dependent on their morphology, such as cell size, cell density, open cell and/or close cell, toward which tuning foam morphology becomes crucial for this area [7]. In case of microcellular foams, small cell size, high cell density and narrow distribution are the aims of cell morphology optimization for many efforts to prepare high-performance microcellular foams. Among the approaches which can effectively tune the cell morphology, adding inorganic particles [8] has demonstrated its cost-effectiveness as compared to other methods such as enhancing foaming pressure and increasing pressure drop rate [9]. It has been demonstrated that inorganic particles may serve as preferential nucleation site with lower energy barrier [10], which can facilitate the formation of embryo and increase the cell density. To date, many inorganic particles ranging from microscale to nanoscale [11], as well as with various surface properties have been investigated. Although a lot of studies discussed how the structure and surface modification of these particles affect their nucleation performance [12], and some literatures even predicted the optimized structure to achieve high nucleating efficiency, this field

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still suffers from the lack of comprehensive understanding on the structure–nucleating performance relationship and on the mechanism underlying this relationship.

Recently, we have proposed a novel structure, i.e. mesoporous structure, capable of dramatically reducing nucleation energy barrier and demonstrated this idea by comparing solid silica particles [13] with ordered mesoporous silica particles [14] served as nucleating agents in PMMA microcellular foaming. To get convincing comparison, spherical MCM-41 particles were synthesized by a delicate reaction condition control [15]. SBA-15 is another kind of commercial particle with mesoporous structure. Differing from MCM-41 mesoporous particles, these particles possess larger pores [16] which may further facilitate the formation of embryo during polymer foaming due to the higher possibility to form gas-cave structure for larger pores. Therefore, this study investigated the nucleating effect of SBA-15 particles in polymer foaming process, although they are in microscale. Polylactic acid (PLA) was chosen as polymer matrix for this investigation due to its semi-crystalline structure, biocompatible and environmental friendliness [17]. The results showed that SBA-15 particles were able to dramatically improve the cell morphology of PLA foam, which are more significant than that of other inorganic particles in microscale. Among factors affecting the nucleation efficiency of SBA-15 particles, such as surface modification, dispersion state in polymer matrix, rheology properties etc, it is found that surface modification plays the dominant role. This work offers a systematical study on heterogeneous nucleating effect of SBA-15 particles on PLA foaming and highlights how the surface modification can potentially influence the nucleation efficiency of these particles, which in turn will benefit the design of effective nucleating agents for polymer foaming.

2. Experimental

2.1. Materials

SBA-15 (XF013) was purchased from Nanjing Pioneer Nanomaterials Technology Co. Ltd., Jiangsu, China. Ionic liquids, [C_{12}MIM][PF_6] was purchased from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. Fluorinated silane, (heptadecafluoro-1,1,2,2-tetradecyl) trimethoxysilane (F1060) was purchased from Sicong Chemical Co., Ltd., Fujian, China. Aminopropyltriethoxysilane (KH550), toluene, ethanol, methanol, were commercial products with chemical purity and used as received. PLA (2003D) was purchased from NatureWorks Limited Liability Company.

2.2. SBA-15 particles modification

SBA-15 particles modified by ionic liquids were prepared by a typical impregnation–vaporization method [18]. Typically, 0.5 g of dried SBA-15 particles were added into the solution of 0.125 g of [C_{12}MIM][PF_6] in 25 ml of anhydrous ethanol. After overnight stirring, the ethanol was evaporated under vacuum, and the product was dried at 50 °C under vacuum.

To modify SBA-15 particles with KH550, SBA-15 particles were dried at 100 °C under vacuum for 2 h, and then placed into 1 mM anhydrous toluene solution of KH550 at room temperature for 24 h. The product was collected by filtration, washed by methanol and dried in vacuum. SBA-15 particles modified with fluorinated silane were prepared in the similar manner.

2.3. Preparation of PLA/SBA-15 composites

PLA/SBA-15 compounds were prepared by mixing SBA-15 particles with PLA polymer via a HAAKE Minilab microcompounder. The modified SBA-15 particles and PLA granules were dried at 80 °C under vacuum for more than 10 h. Then, 0.5 g of the dried particles, 0.01 g of antioxidants and 4.49 g of PLA granules were added into the machine, and the extrusion was set at 170 °C for 5 min with rotation speed of 60 r/min. Neat PLA was also prepared in the same manner for comparison.

2.4. PLA and its composites foaming

Foaming of PLA and composites was conducted by rapid pressure releasing method using $scCO_2$ as blowing agent. The PLA and composites were first saturated by $scCO_2$ at prespecified condition, and the pressure was then quickly released. When the pressure was completely released, the chamber was immediately moved into an ice-water bath to fix the morphology of the samples.

2.5. Characterization

Transmission electron microscopy (TEM) observations were performed using a Philips-FEI microscope (Tecnai G2 F30 S-Twin, FEI Company, Netherlands) with an acceleration voltage of 300 kV to characterize the morphology change of SBA-15 particles before and after modification Nitrogen adsorption/desorption isotherms were measured at −196 °C using a Micromeritics ASAP 2020 analyzer. The pore size and specific surface area distributions were derived from the Barrett–Joyner–Halenda (BJH) method. Thermo gravimetric analysis (TGA) was carried out on an SDT Q600 (thermal analysis instruments) with a heating rate of 20 °C/min from 40 °C to 800 °C under nitrogen atmosphere. The morphology of PLA and composites, the morphology of foams were observed with a scanning electron microscope (SEM, Hitachi S-4700, Japan). The cell size and cell density were calculated via image analysis. The cell density (N_c), is calculated by Eq. (1):

$$N_c = \frac{6V_f}{\pi D^3} \quad (1)$$

in which D is the average cell diameter and V_f the void fraction of the foamed sample. The void fraction is defined as

$$V_f = 1 - \frac{\rho_f}{\rho_c} \quad (2)$$

where ρ_f expresses the bulk foam density measured according to ASTM-D792, ρ_c is the density of the unfoamed material.

3. Results and discussion

3.1. Morphology and property of modified SBA-15 particles

The SBA-15 particles used in this study are commercialized product, and various surface modifications are applied to increase the dispersability of these particles in polymer matrix and their CO_2 affinity. We will first discuss the morphology and properties of these particles before and after modification. Specific area and pore structure are first characterized by nitrogen adsorption and desorption method, as shown in Fig. 1. Fig. 1a shows typical nitrogen adsorption and desorption isotherms of the original and modified particles. For all the samples, the isotherm exhibits a type IV isotherm cycle with a typical H1 hysteresis loop at approximately P/P_0 = 0.6–0.8. The pore size distribution calculated from desorption branch of the isotherms based on Barret–Joyner–Halenda (BJH) model is shown in Fig. 1b, which shows that the SBA-15 particles used here has an average pore size of around 7.4 nm. All the modifications decrease the specific area and average pore size due to presence of modifiers in the pores through chemical and/or physical manners. Among these modifications, the modification with fluorinated silane remains the highest specific area. Fig. 2a shows