

Study of Different Effects on Foaming Process of Biodegradable PLA/Starch Composites in Supercritical/Compressed Carbon Dioxide

Ayou Hao,¹ Yuanyuan Geng,² Qun Xu,² Zhanyong Lu,² Long Yu³

¹College of Textile Engineering, Donghua University, Shanghai 200051, China

²College of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450052, China

³CSIRO, CMIT, Melbourne 3169, Australia

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ABSTRACT: Microcellular foaming of biodegradable and biocompatible PLA/starch composites in supercritical/compressed CO₂ has been studied. The purpose of this study is to explore the potential application of this kind of materials in medical materials or drug containers. The rate of CO₂ uptake and CO₂ equilibrium concentration in PLA/starch composites were studied by performing sorption and desorption experiments. The effects of a series of variable factors, such as saturation time and saturation temperature on the foaming morphology were studied through SEM observation and density measurement. The experimental results

show that, while keeping other variables unchanged, longer saturation time leads to reduced bulk foam densities and different saturation pressures result in different bulk foam densities. The crystallinity of PLA-starch sample was characterized by differential scanning calorimetry. It indicates that the foaming treatment with supercritical CO₂ increased the crystallinity of PLA/starch composites. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2679–2686, 2008

Key words: supercritical/compressed CO₂; biodegradable; PLA/starch composites; microcellular

INTRODUCTION

Microcellular polymeric materials are found to have more and more applications in the biomedical field, such as guided tissue regeneration and cell transplantation. As far as guided tissue regeneration is concerned, porous implants are used as size-selective membranes to promote the growth of tissue in a healing site. Ideally, the implant should be inherently biocompatible, have well-defined cell size, and be absorbed with appropriate biodegradation rates.¹ Polylactic acid (PLA) is the material that meets the above demands well. PLA is biocompatible and biodegradable aliphatic polyester, that is, bioresorbable and nontoxic for living organisms. Because of its unique combination of biocompatibility, permeability, and biodegradability, PLA and some of its copolymers with cornstarch have been widely applied in medicine as artificial skin, artificial bone, and containers for

sustained drug release.^{2–8} And pure PLA foaming materials can be used as scaffolds.^{9–11}

There has been a growing interest in the development of starch-based products in recent years, because of limited petroleum resources and environmental issues. Starch-based foams have been seen as a potential alternative to expandable polystyrene. PLA has potential use in disposable and biodegradable plastics. Blending starch with PLA would increase biodegradability and reduce costs.¹² In addition, the composites are not carcinogenic.¹³

Supercritical fluids (SCF), especially supercritical carbon dioxide (SC CO₂), possess many advantageous properties including adjustable solvent strength, plasticization of glassy polymers, and enhanced diffusion rates, etc. CO₂ is a gas at ambient condition and this avoids creation of vapor-liquid coexistence upon release of pressure, so damage to the cellular structure by capillary forces can be evaded.^{14–17} In addition, it is the most potential and feasible alternative in foam industries. Much work has been done using this method on foaming amorphous and semicrystalline glassy polymers such as PS, PMMA, PET, and PC^{18–21} with cell densities up to 10¹⁰/cm³ and average cell size varying from 10 to 50 μm depending on their specific experimental condition.

As biodegradable plastics have been receiving a great deal of attention from industrial and ecological

Correspondence to: Q. Xu. (qunxu@zzu.edu.cn).

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point of view, a number of plastics with biodegradability have been developed over the years. PLA/starch, because of its low-cost for manufacture and less independent on petroleum, is considered to be one of the most prospected materials. It is expected to become as an alternative to ordinary plastics in the future. In this work, SC CO₂ was used in foaming PLA/starch composites. And the effects of different processing conditions on the foaming process were studied.

EXPERIMENTAL

Materials

PLA/starch composites was provided by CSIRO, CMIT of Australia in the form of ivory-white granules and used as received. The PLA and cornstarch were blended at a 60 : 40 weight ratio. After being dried in vacuum at 80°C for 48 h, PLA/starch pellets were placed in a desiccator prior to use. CO₂ (99.95% purity) was supplied by Zhengzhou Shuangyang Gas (China). All reagents were used without any further purification.

Apparatus

Reactions were run in an 80.0-mL high-pressure variable volume stainless steel reactor with two glass view windows. A high-pressure syringe pump (Beijing Satellite Manufacturing Factory, DB-80) was used to charge CO₂ into the reaction vessel and attached to the reactor via a coupling and high-pressure tubing. A pressure gauge consisting of a transducer (IC Sensors, Model 93) and an indicator (Beijing Tianchen Automatic Instrument Factory, XS/A-1) with the accuracy of ±0.01 MPa were also connected to the reactor to observe the *in situ* pressure change of the system. The setup is shown in Figure 1. In the experiments, the reactor was placed in a constant temperature circulator, which consists of a temperature control module (Thermo Haake, C10) and a bath vessel (Thermo Haake, P5). The fluctuation of temperature in the bath was less than ±0.1°C.

Generation of foaming materials

Foams were prepared in a glass tube (φ 15 mm × 50 mm) inside the view reactor to facilitate removal of the foamed samples. PLA/starch pellets were placed into the tube, and then they were put into the reactor together. The closed reactor was preheated in the bath to a certain temperature, which was manipulated by the heating system. Then the cell was filled up to the saturation pressure. The sample was exposed in SC CO₂ for prescribed saturation time. In the end, the

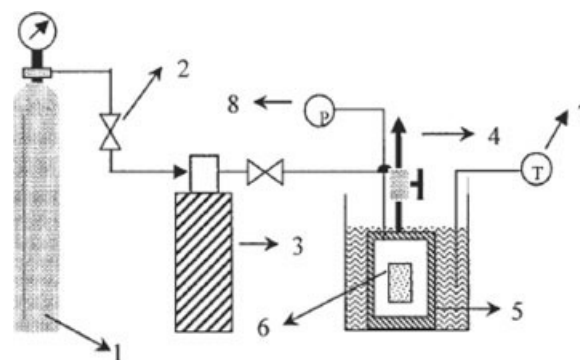


Figure 1 Apparatus description diagram: 1, gas cylinder; 2, valve; 3, syringe pump; 4, vent; 5, variable-volume reaction with view windows; 6, sample; 7, temperature circulator; 8, pressure gauge.

valve of the reactor was opened and the pressure was quenched rapidly to atmospheric conditions and the rapid depressurization is less than 5 s.

Characterization of foaming materials

The foaming materials were characterized to determine their densities. Density was measured using a gravity bottle with a capillary tube in its lid. The weight of the bottle filled with distilled water was measured with an electronic balance (with the accuracy of 10⁻⁵ g) at a preset temperature. The sample was put into the bottle. The same volume of water as the sample, overflowed into the capillary tube. The bottle containing both water and sample was weighed and its density was calculated using the following equation:

$$\rho = \omega_1 \rho_0 / (\omega_1 + \omega_2 - \omega_3)$$

where ρ is the density of sample; ρ_0 is the density of water; ω_1 is the weight of the sample; ω_2 is the weight of the bottle filled with water; and ω_3 is the weight of the bottle containing both water and the sample.

Foamed samples were also observed with a FEI-QUANTA 2000 scanning electron microscope (SEM). The samples were prepared by freezing in liquid nitrogen, fracturing the surface, mounting the fracture on stubs with carbon paint, and sputter coating with an approximately 100 Å layer of gold.

DSC measurements were conducted to examine the crystallinity of the foamed materials, on a Netzsch 204 differential scanning calorimeter under a N₂ atmosphere at a heating rate of 10°C/min in a temperature range of 30–240°C.

Sorption and desorption experiments

Sorption experiments were carried out to study the rate of uptake and the equilibrium concentration of

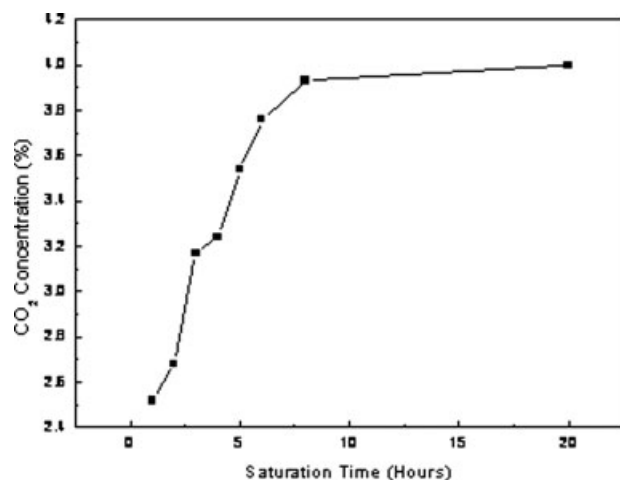


Figure 2 CO₂ uptake weight percent of PLA/starch samples as a function of saturation time at temperature of 70°C, pressure of 5 MPa.

CO₂ gas in PLA/starch composites. Sorption experiments were performed at 70°C at pressures of 5 MPa. The samples were placed in the pressure vessel and saturated at the prescribed pressure and temperature. Then periodically, the samples were removed for weighing. The difference in weight of the sample is equal to the amount of CO₂ absorbed by the polymer. Sorption experiments were carried out until the CO₂ uptake stopped changing, indicating that CO₂ concentration had reached equilibrium.

Following the sorption study at 5 MPa, a desorption study was conducted at 5 MPa for 3 h by retrieving a sample from the pressure vessel and measuring its weight periodically in the atmospheric environment. Desorption time was defined as the time elapse between when the samples were retrieved from the pressure vessel and when they were foamed.

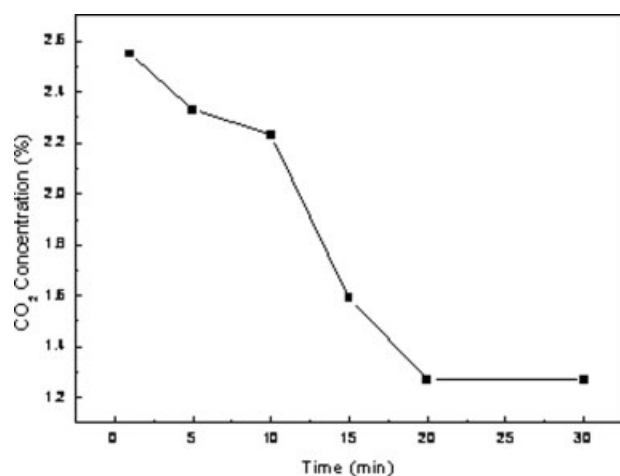


Figure 3 Desorption study at 70°C with a saturation pressure of 5 MPa and saturation time of 3 h.

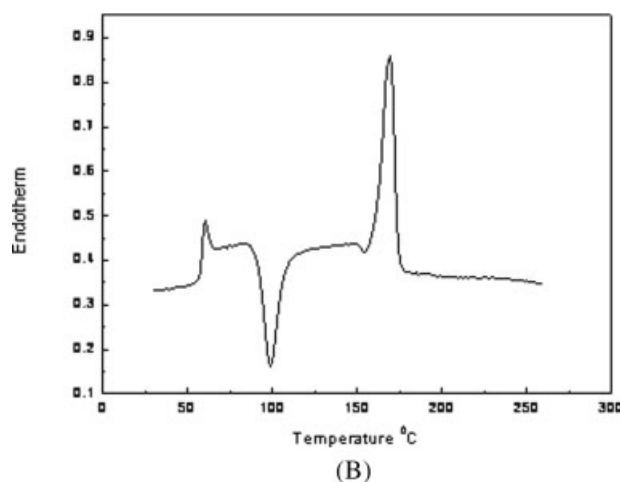
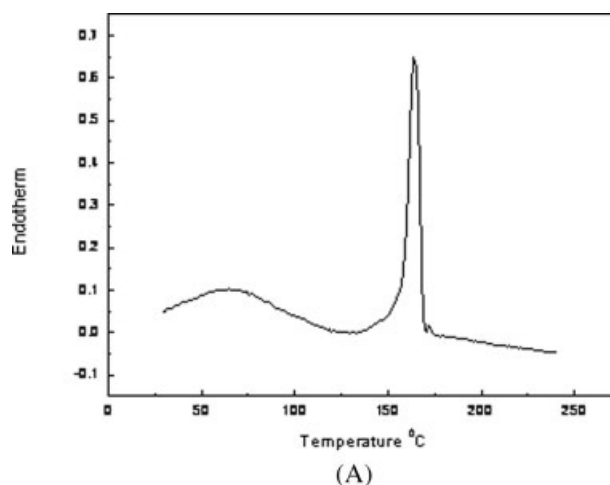


Figure 4 DSC thermographs for the (A) virgin PLA/starch composites; (B) foamed PLA/starch composites saturated at 150°C, 12 MPa for 30 min.

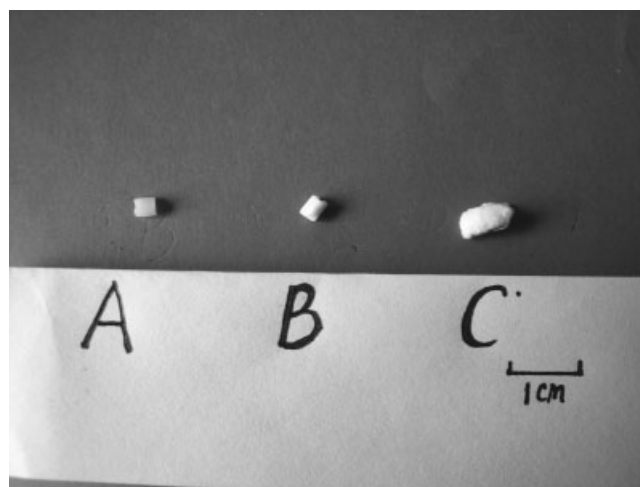


Figure 5 Photographs of the PLA/starch composites samples foamed at different saturated pressure (saturation time = 1 h, temperature 150°C) (A) untreated, (B) 10 MPa and (C) 12 MPa.

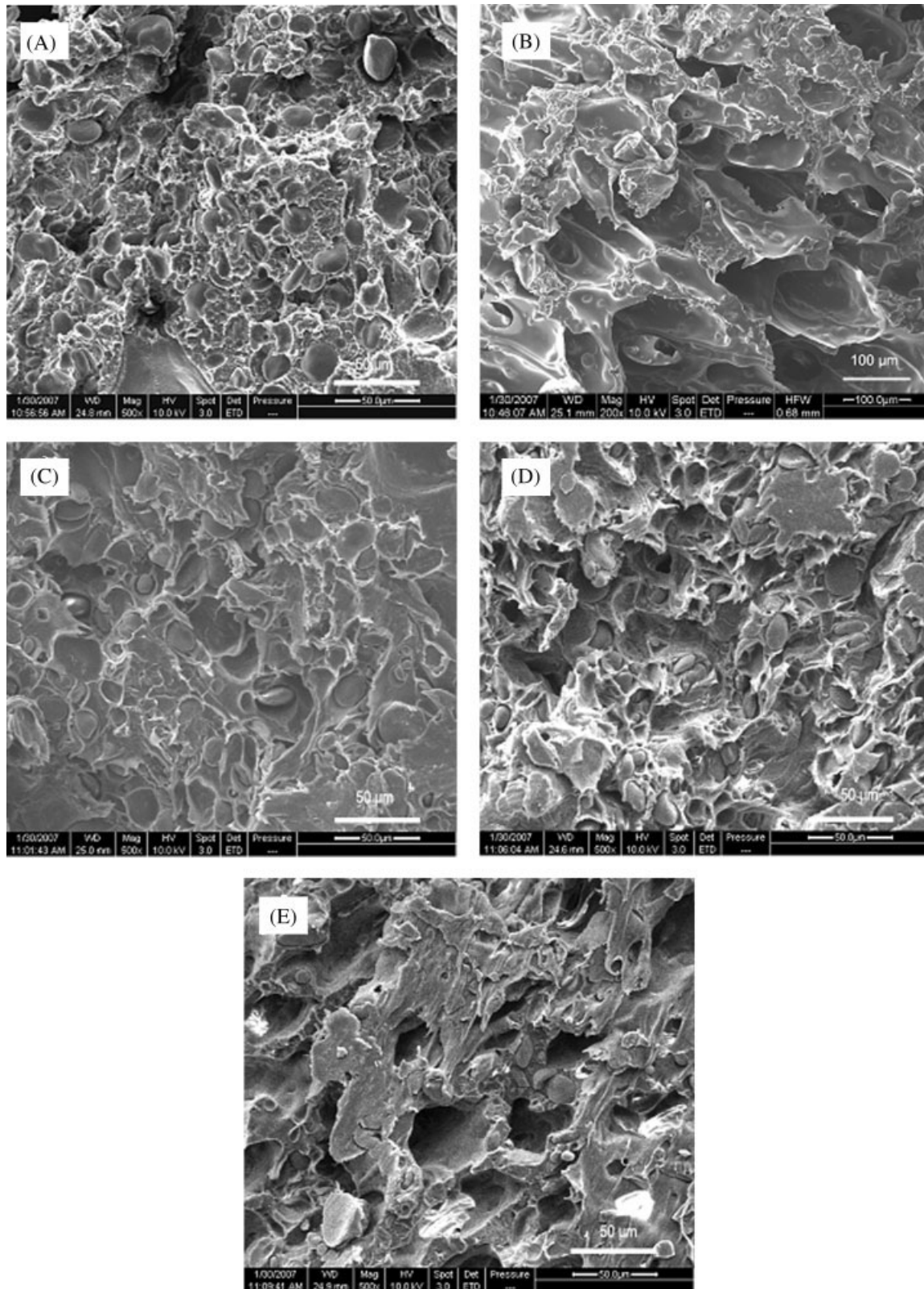


Figure 6 SEM photographs of PLA/starch composites foams foamed at different saturated pressures (saturation time = 1 h, temperature = 150°C) (A) 10 MPa (magnification = $\times 500/50$); (B) 12 MPa (magnification = $\times 200/100$); (C) 14 MPa (magnification = $\times 500/50$); (D) 16 MPa (magnification = $\times 500/50$); (E) 18 MPa (magnification = $\times 500/50$).

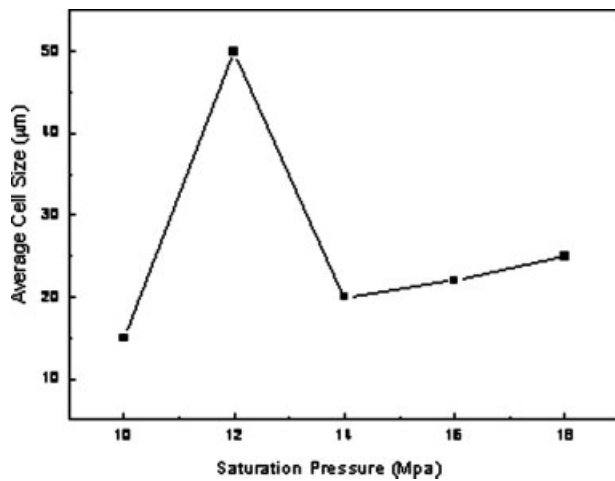


Figure 7 Average cell size as a function of saturation pressure (temperature = 150°C, saturation time = 1 h).

RESULTS AND DISCUSSION

CO₂ sorption results

The compressed CO₂ saturation sorption on PLA/starch composites sample is shown in Figure 2. The equilibrium concentration of CO₂ in the polymer sample was 4%. Compared to Wang's study,²² the equilibrium concentration of CO₂ in pure PLA sample was 21% at room temperature at 5 MPa. The decrease of CO₂ uptake is due to the increase of sorption temperature from room temperature to 70°C. Meanwhile, the existence of starch particles in the PLA/starch composites maybe contribute to this reduction because of the crystallization increase, which will be indicated in the following part.

CO₂ desorption results

Figure 3 shows the experimental result of the compressed CO₂ desorption studies with a sample saturated at 5 MPa for 3 h. It is observed that the gas concentration started to decrease at a slower rate, and then sharply decrease from 10–20 min. Within 20 min, the gas concentration of PLA/starch composite decreased from 2.55% to about 1.27%. This indicates that the desorption time could be a significant factor affecting the foaming process. Samples foamed at different desorption times could have different relative density, since the gas concentration of the saturated samples could be dramatically different. Therefore, desorption time should be carefully controlled to obtain consistent foaming results.

Crystallinity of the foaming materials

It is well-known that the absorption of CO₂ in polymer matrix can plasticize the polymer material and

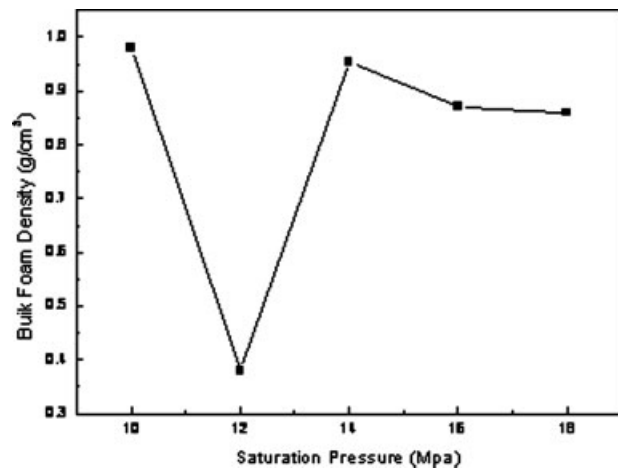


Figure 8 Effect of saturation pressure on the bulk density of foamed PLA/starch composites saturated at 150°C, 1 h.

in turn decrease the glass transition temperature (T_g). Further, it can induce crystallization of the matrix and cause an increase in the melting temperature and melting enthalpy.^{23–26} Here, differential scanning calorimetry measurement was performed to study the crystallinity of virgin and foamed PLA/starch composites. The experimental results are shown in Figure 4. From Figure 4(B), it can be seen that the thermal stability of virgin PLA/starch improved remarkably by the plasticization effect of supercritical CO₂ as shown by the disappearance of the original exothermic peak from foamed sample. This means that the SC CO₂ which assisted the foaming process could notably improve the service performance of this kind of biodegradable material. Usually after treated in SC CO₂, the degree of crystallinity was found to increase. At higher pressure

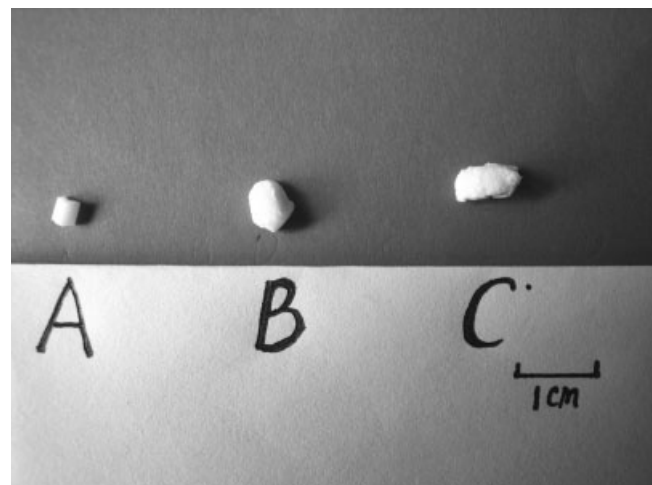


Figure 9 Photographs of the PLA/starch composites samples foamed at different saturated time (saturation pressure = 12 MPa, temperature 150°C) (A) untreated, (B) 30 min, and (C) 60 min.

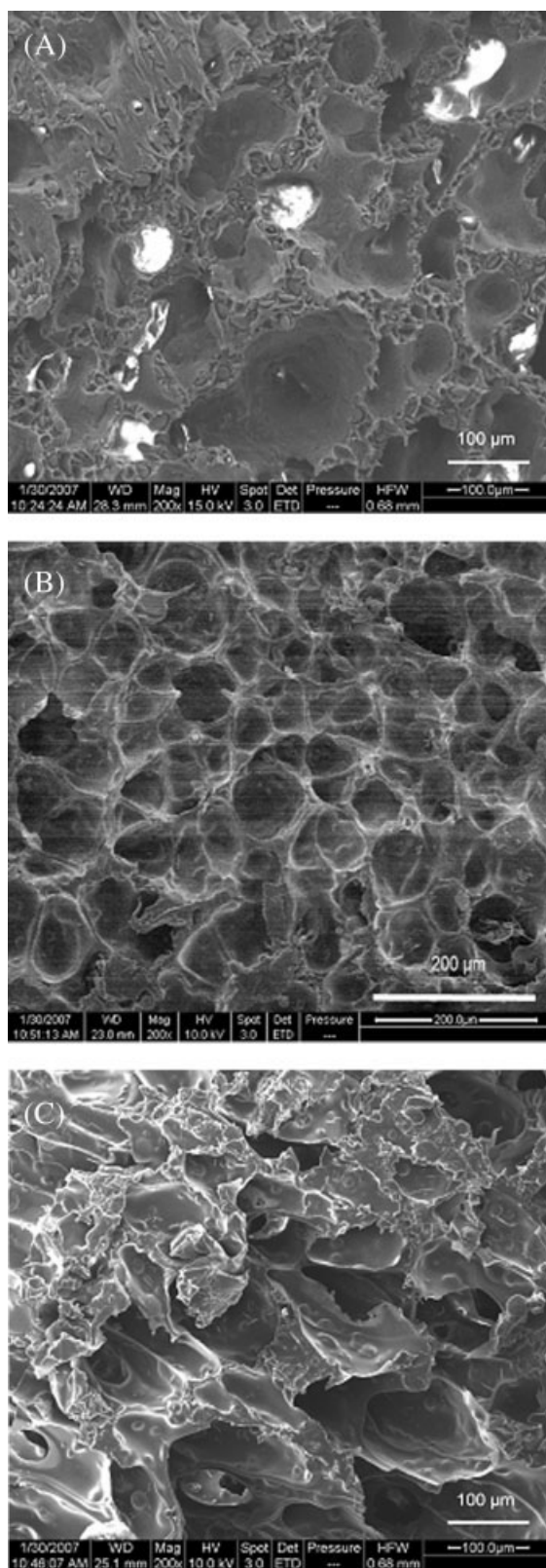


Figure 10 SEM photographs of cross sections of PLA/starch composites foams foamed at different saturated time (saturation pressure = 12 MPa, temperature 150°C) (A) 15 min (magnification = $\times 200/100$); (B) 30 min (magnification = $\times 200/200$); (C) 60 min (magnification = $\times 200/100$).

under isothermal condition, the absorption of more CO_2 results in substantial swelling of polymer and profound plasticization effect to polymer which favors polymer chains rearrange themselves into a lower free energy.^{27–29} Similarly, the higher temperature under isobaric conditions contributes to increasing mobility of polymer chain segments and a longer period for crystalline growth, so the crystallinity of polymer ascends markedly too.^{27–31} In this study for the PLA/starch composites, from Figure 4, the areas of the fusion peak of virgin and foamed composite are 22.81 and 30.98 J/g, respectively. According to the equation $X_C = \Delta H_f / \Delta H_{F0}$, (where X_C is the crystallinity, ΔH_f is the fusion heat of foamed sample, ΔH_{F0} is the fusion heat of virgin sample), the heat of fusion is proportional to the crystallinity of polymers. Therefore, the larger the area of the fusion peak is, the higher is the crystallinity of the polymer. It can be concluded that after treated in SC CO_2 , the degree of crystallinity increased after foaming.

Effect of saturation pressure on foaming materials

The effect of saturation pressure on the foaming materials was studied at fixed time (1 h) and temperature (150°C). Figure 5 is the digital photograph of PLA/starch composites at different saturation pressure. It shows a macroscopic view of the foaming result. Apparently the sample saturated at 12 MPa is foamed amply. At 10 MPa, the sample is also plasticized and this can be observed from its color becoming white when compared with the yellow virgin sample. In addition, the experimental results in Figure 6 show that sample saturated at 12 MPa has the largest cell size. Figure 7 shows that the cell size first sharply increases with saturation pressure until 12 MPa and then sharply decreases

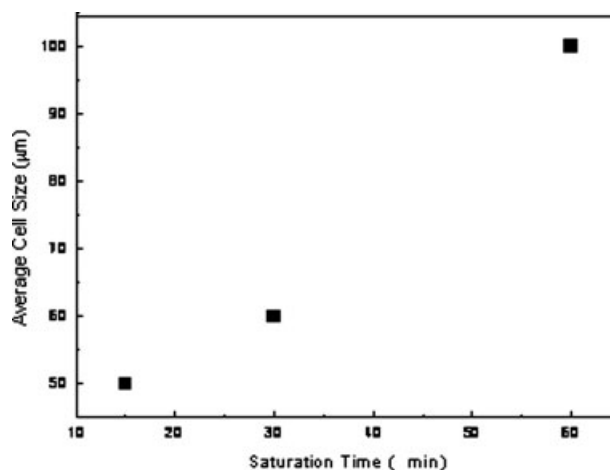


Figure 11 Average cell size as a function of saturation time (temperature = 150°C, saturation pressure = 12 MPa).

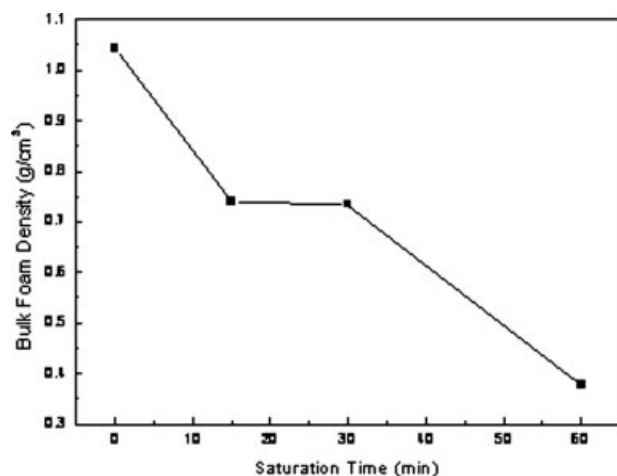


Figure 12 Influence of saturation time on the bulk density of foamed PLA/starch composites saturated at 12 MPa and 150°C.

from 12 to 14 MPa. Finally keep almost the same of 20 μm between 14 and 18 MPa. The V-shape chart in Figure 8 indicates that there is an optimal saturation pressure for foaming PLA/starch composites, neither lower nor higher is better. In this study, it is 12 MPa, which has the largest cells and lowest bulk foam density (see Fig. 8). In the lower pressure range, not enough CO_2 was absorbed since it did not reach the necessary saturation pressure. As a result, samples at lower pressure cannot foam well. And the detail foaming mechanism needs to be further explored by the heterogeneous nucleation mechanisms, considering the existence of inhomogeneous starch particles in the foaming sample and supercritical fluid conditions.

Effect of saturation time on foaming materials

Saturation time was defined as the time elapse between when the samples reached the desired supercritical condition in the reactor and when SC CO_2 begin to release. The effect of saturation time of PLA/starch composites with SC CO_2 has been studied at fixed pressure (12 MPa) and temperature (150°C). Figure 9 is the digital photograph of PLA/starch composites at different saturation time, which shows a macroscopic view of the foaming result. Both of the samples are foamed. Here, the SEM micrographs were taken in the central region of the samples (Fig. 10) and the average cell sizes were calculated (Fig. 11), i.e., the influence of concentration gradient across the sample thickness was excluded. According to the SEM observation and cell size calculation, the longer the time, the larger the cell produced. In addition, it can be seen from the experimental results shown in Figure 12 that the bulk

foam density decreases sharply at the beginning, from 0 to 15 min. It then changes subtly from 15 to 30 min and decreases from 30 to 60 min, finally reaches the lowest density of 0.35 g/cm^3 at 60 min. Although saturation pressure is a decisive factor on the foaming materials, our study as well as Goel and Beckman's indicates that saturation time also has contributed to the foaming materials. As explained by Goel and Beckman,^{19,20} the longer the polymer is exposed to the high-pressure CO_2 , the greater is the amount of CO_2 absorbed by the polymer. Therefore the larger cells were obtained.

CONCLUSION

Foaming of biodegradable PLA/starch composites in SC/compressed CO_2 and the various factors affecting the microcellular structure has been studied. Different saturation pressures results in different bulk foam density, therefore there is an optimal saturation pressure for foaming PLA/starch composites. Besides, longer the saturation time, the larger is the cell produced and the lower is the bulk foam density. It is another decisive factor governing the structure of the product. DSC experimental results indicate that the plasticization and crystallization effect of supercritical CO_2 improved the thermal stability of the PLA/starch composite as well as its service performance, and this is a valuable result to further explore the application of this biodegradable composite sample.

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