Effect of Processing Conditions on Poly(butylene succinate) Foam Materials

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Received 18 July 2011; accepted 24 January 2012
DOI 10.1002/app.36867

ABSTRACT: Polymeric foams have many advantages such as light weight, high specific strength, strong energy absorption, as well as good sound and thermal insulation. Unfortunately, most polymeric foams such as polyvinyl chloride foams do not undergo natural degradation and thus giving rise to white pollution to the environment. Here, we report the preparation and properties of poly (butylene succinate) (PBS) foam which is a biodegradable plastic. Ammonium bicarbonate is used as the foaming agent during the formation of the PBS foam by the molding method, and under the optimal conditions of 5 wt % ammonium bicarbonate, 10 MPa pressure, and 5 min pressing time, the pristine PBS foam with the smallest bulk density can be obtained, whereas under the conditions of 5 wt % ammonium bicarbonate, 7.5 MPa pressure, and 7 min pressing time, the toughening PBS foam has the smallest bulk density. Adding talc as a nucleating agent can reduce the bulk density of the foam and in this case, an NH_4HCO_3 content of 3 wt % yields the best result. Moreover, addition of plasticizers can effectively improve the mechanical properties of the products. J Appl Polym Sci 126: 756–761, 2012

Key words: poly(butylene succinate); biodegradable; foam; environment friendly; condition

INTRODUCTION

Foams with internal air cells, a type of microporous plastic materials, can also be regarded as composite materials consisting of gas fillers. The majority of thermoplastics and thermosetting plastics such as polyurethane,[1] polystyrene,[2] polyolefin,[3] polyvinyl chloride,[4] and phenolic[5] can be converted into foams. Compared to pure plastics, polymeric foams have advantages such as light density, high specific strength, strong energy absorption capability, as well as good sound and thermal insulation. In spite of the advantages, most foam materials cannot degrade naturally and constitute "white pollution" to the environment. With growing concerns about our environment and awareness of environmental protection, the development of degradable foams has become a top research topic. As it is easier to control the degradation conditions and degradation time of biodegradable plastics, they can better meet environmental requirements.[6]

Poly(butylene succinate) (PBS) is a type of fully biodegradable polymer materials having a repeating unit of  $\left[O\text{-}(CH_2)_4\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}(CH_2)_2\text{-}\underset{\underset{O}{\|}}{C} \right]_n$[7] which can be decomposed into carbon dioxide and water by enzymes produced from various micro-organisms, plants, and animals in nature. The materials, which can be synthesized by polycondensation of 1,4-butanediol with succinic acid, are milky white, odorless, and tasteless. The general properties of PBS are summarized in Table I. PBS has many advantages such as excellent mechanical properties approaching those of polyolefins, polyethylene, and polypropylene, good heat resistance with a softening temperature close to 100°C, and easy to process. Hence, many general-purpose plastic processing machines can be readily modified to produce PBS foams. PBS degrades only under attack by micro-organisms but during normal

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Contract grant sponsor: The Key Project of Chinese Ministry of Education; contract grant number: 107023.

Contract grant sponsor: Doctoral Program Foundation of Institution of higher education of China; contract grant number: 2-2-08-07.

Contract grant sponsor: City University of Hong Kong Strategic Research Grant (SRG); contract grant number: 7008009.

Contract grant sponsor: The Fundamental Research Funds for the Central Universities; contract grant number: 2010ZD08.

Journal of Applied Polymer Science, Vol. 126, 756–761 (2012)

TABLE I
Properties of PBS Compared to Those of Other General-Purpose Resins

Properties	PBS	PP	HDPE	LDPE
Density (g/mL)	1.25	0.90	0.95	0.92
Melting (°C)	115	170	135	110
Glass transition temperature (°C)	−30	15	−60	−60
Softening temperature (°C)	96	110	85	83
Degree of crystallinity (%)	35–40	55	75	50
Tensile strength (MPa)	36	31	27	15
Elongation (%)	430	500	650	800
Bending strength (MPa)	37	–	–	16
Bending modulus (MPa)	530	1370	1070	600

storage and usage, its performance is very stable. Recent research on PBS has been focusing on the role inorganic minerals play in the properties[8–21] and blending modification with other polymers.[22] Lim et al.[23] investigated the effect of the foaming conditions such as temperature and time, and the amount of the crosslinking agent on the structure of the expanded PBS foams. Bahari et al.[24] studied the crosslinking behavior of Bionolle blended with blowing agents after electron beam irradiation at various doses. In this article, we report the preparation of PBS foam materials and examine the roles of foaming agents and additives for both the pristine PBS foam and the toughening PBS foam.

EXPERIMENTAL DETAILS

Materials

The pristine PBS and the toughening PBS used in this study was a commercial product purchased from HKH National Engineering Research Center of Plastics, Beijing, China. The PBS was dried at 60°C for 24 h before use. Ammonium bicarbonate used as the foaming agent was supplied by Xilong Chemical Works in Shantou. Chloroform serving as the solvent was purchased from Beijing Chemical Works. Dibutyl phthalate (DBP) was the plasticizer and obtained from Sinopharm Chemical Reagent, Shanghai, China. All the chemicals used in this study were of reagent grade and used without additional purification.

Preparation of the PBS foam

A molding method was utilized in the synthesis. The materials were first mixed to a prescribed proportion and put into the mold. The processing temperature was controlled between 110 and 150°C. The foaming agent content was from 1 to 10% and the molding pressure is tested between 1.5 and 12.5 MPa. The holding pressure time was controlled in 1–20 min and the content of nucleating agent was from 1 to 10%. DBP, which was used as plasticizer content, was controlled between 0 and 30%. After foaming, insulation, annealing, and cooling, the products were obtained. To enhance the uniformity of the mixture, chloroform was used as the solvent. We made use of the high volatility of chloroform to get evenly mixed materials as the chloroform vaporized at room temperature.

Characterization and measurement

Scanning electron microscopy

The PBS foams were examined by scanning electron microscopy (Hitachi Limited S-4300) after a thin Au layer was sputter coated onto the specimen.

Bulk density of PBS foam

The bulk density of the product was calculated by eq. (1) according to the standard protocol of GB/T6343-1995:

$$\rho = \frac{m}{V} \times 10^5 \tag{1}$$

where ρ is the bulk density in kg/m^3, m is the quantity of the sample, and V is the sample volume in mm^3. The final result was the mean value with a precision of 0.1 kg/m^3.

Bending strength of PBS foam

The bending strength of the PBS foam was measured by a three-point bending method on a DXLL-1000 machine according to GB/8812-88. The specimen dimensions were 120 mm × 25 mm × 5 mm. A crosshead speed of 10 mm/min was used and the average bending strength values were calculated by averaging five PBS foam specimens.

RESULTS AND DISCUSSION

Structure and morphology

The structures of the cells of the crosslinked PBS foams were examined by scanning electron microscope. The cells of PBS foams are shown in Figures 1 and 2. Figure 1 shows the SEM image of the PBS foams whose density was 0.2 g/cm^3 and without nucleating agent. Figure 2 shows the one whose density was 0.15 g/cm^3 and with 3 wt % nucleating agent. As it can be seen from the micrographs, the majority of the cells were oval shaped. With the addition of nucleating agent, the cells became small, which guaranteed the strength of this kind of material when the foaming agent achieved the certain amount. The cells were not ruptured, that is closed cells were formed. It means that the growing cells were effectively stabilized.

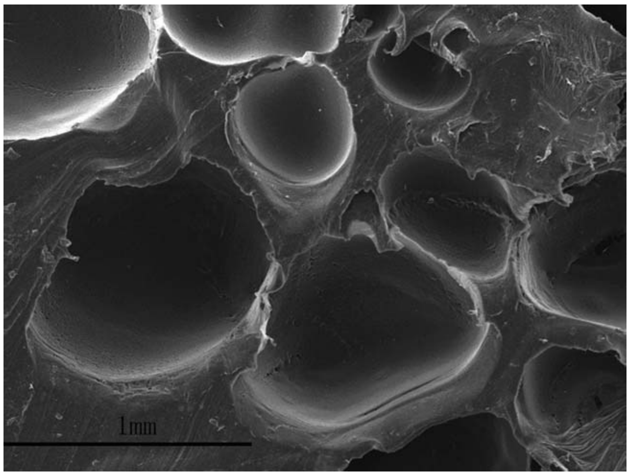

Figure 1 SEM images of the PBS foams prepared with 0.2 g/cm^3 and without nucleating agent.

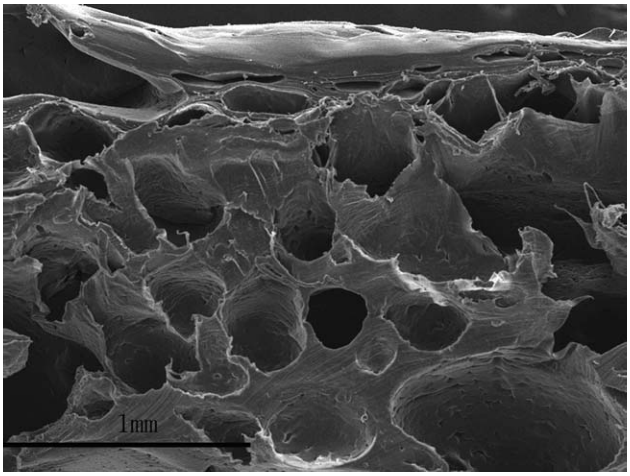

Figure 2 SEM images of the PBS foams prepared with 0.15 g/cm^3 and 3 wt % nucleating agent.

Effects of foaming agent contents on the bulk density and bending strength

The foams were prepared using 1, 3, 5, and 10 wt % of ammonium bicarbonate as the foaming agent. We set the processing temperature as 130°C, the pressing time as 3 min, and the pressure as 2.5 MPa. Figure 3 shows that the bulk density and bending strength values vary with different foaming agent contents irrespective of the pristine PBS or the toughening PBS. The bending strength for toughening PBS was the logarithm (base 10) of the value. The bulk density of the product diminishes gradually with increasing foaming agent content. For the neat PBS foam, the bulk density reached 0.36 g/cm^3 when the foaming agent concentration was 5 wt % which was the smallest. The bulk density of toughening PBS foam achieves 0.3 g/cm^3 at the same amount of foaming agent as neat PBS. In this case, a higher content led to integration of different small holes. However, the product melt strength cannot maintain these large holes and hence the cells collapsed and it was very difficult to achieve a smaller bulk density.

The bending strength of the product increases with decreasing foaming agent content because a higher foaming agent content increases the number of cells in the matrix. However, because of the limited surface tension on the cell wall, the bending strength of the matrix continues to decline.

Effect of processing temperature on the bulk density and bending strength of PBS foams

Figure 4 compares the bulk density and bending strength of the PBS foams prepared at 110, 120, 130, 140, and 150°C under the conditions of 5 wt % ammonium bicarbonate, 3 min pressing time, and 2.5 MPa pressure. The bending strength for toughening PBS was the logarithm (base 10) of the value. The bulk density of the pristine PBS and reached the minimum (0.36 g/cm^3) when the temperature was 130°C and it reached the minimum (0.26 g/cm^3) when the temperature was 140°C for the toughening PBS. If the temperature was too high or too low, the bulk density was adversely affected. When the temperature was low, we observe that the viscosity of the melt was not very high, and the increase of bulk density results from the incompletely decomposition of the foaming agent. The matrix cannot achieve a molten state and hence the foaming effect was not optimal. On the other hand, if the temperature was too high, the foaming agent decomposes completely and the solubilization of the foaming agent decreases. These two factors led to the decline in the melt strength of the matrix and increases in the melt flow, which caused the gas to escape and cells to collapse. As a result, the bulk density increased.

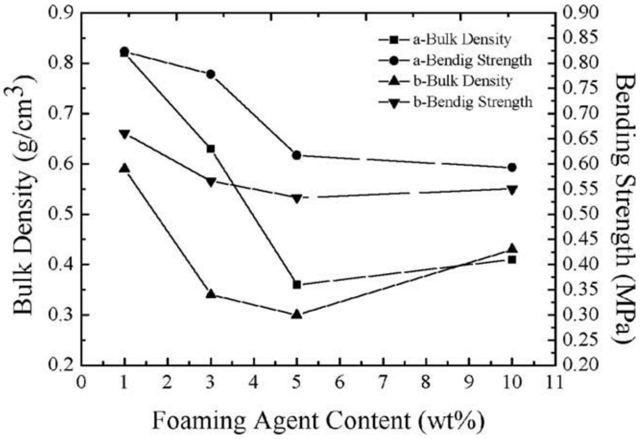

Figure 3 Effects of different foaming agent contents on the bulk density and bending strength of (a) pristine PBS foams and (b) toughening PBS foams.

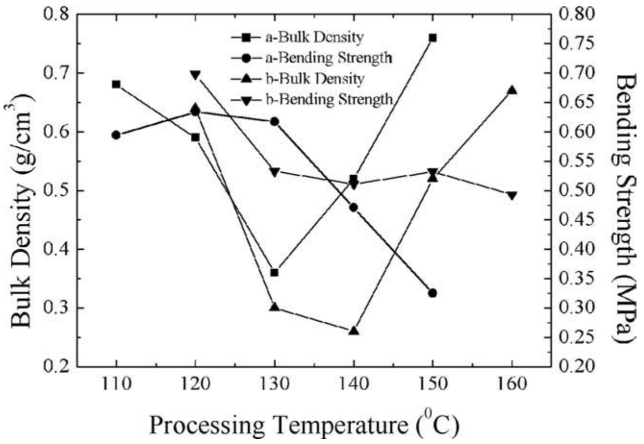

Figure 4 Effects of different processing temperatures on the bulk density and bending strength of (a) pristine PBS foams and (b) toughening PBS foams.

The bending strength of the product was relatively stable until the processing temperature reached 130°C. At a temperature higher than 130°C, a significant decline in the bending strength was observed. This is because single very large cells were formed, which caused by cell coagulation, acting as defects.

Effect of molding pressure on the bulk density and bending strength of PBS foams

The effects of different molding pressures of 1.5, 2.5, 5.0, 7.5, 10.0, and 12.5 MPa (Owing to the previous experimental data, we set the ammonium bicarbonate content as 5 wt %, the processing temperature as 130°C for pristine PBS, whereas as 140°C for toughening PBS, and the pressing time as 3 min for pristine PBS, whereas as 5 min for toughening PBS.) are shown in Figure 5. The bending strength for toughening PBS was the logarithm (base 10) of the value. The bulk density and bending strength values of samples prepared under different pressures vary. For the pristine PBS, with increasing pressure, the bulk density of the product decreased. It reached 0.22 g/cm^3 when the pressure was 10 MPa, which was the smallest. For the toughening PBS, the bulk density was the smallest when the pressure was 7.5 MPa. This was because a higher pressure facilitates the production of nuclei from which the cells start to grow. Additionally, the solubility of the foaming gas was much better and therefore the number of nuclei was higher. The bending strength also decreased with higher pressure generally. For the pristine PBS, the bending strength actually increased slowly and gradually becomes stable when the process pressure exceeded 5 MPa, compared to the toughening PBS, which became stable at 2.5 MPa. This indicated that the pressure little influences on the bending strength of the product.

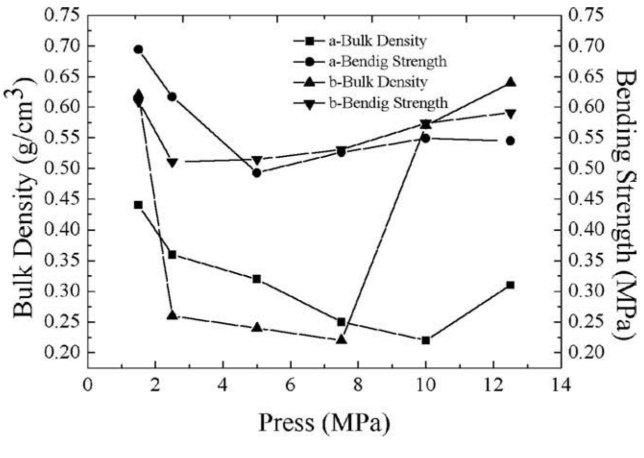

Figure 5 Effects of different pressures on the bulk density and bending strength of (a) pristine PBS foams and (b) toughening PBS foams.

Effect of holding pressing time on the bulk density and bending strength of PBS foams

The effects of different pressing time (ammonium bicarbonate content of 5 wt %, processing temperature of 130°C for pristine PBS, whereas 140°C for toughening PBS, and pressure of 10 MPa for pristine PBS, whereas 7.5 MPa for toughening PBS) are shown in Figure 6. The bending strength for toughening PBS was the logarithm (base 10) of the value. The pressing times of pristine PBS were 1, 3, 5, 10, 15, and 20 min and the toughening PBS were 3, 5, 7, 10, 15, and 20 min. The bulk density and bending strength were observed to vary with pressing time. The bulk density of pristine PBS reached the smallest (0.2 g/cm^3) when the time was 5 min, whereas the time for the bulk density of toughening PBS reaching the smallest (0.19 g/cm^3) was 7 min. This was because

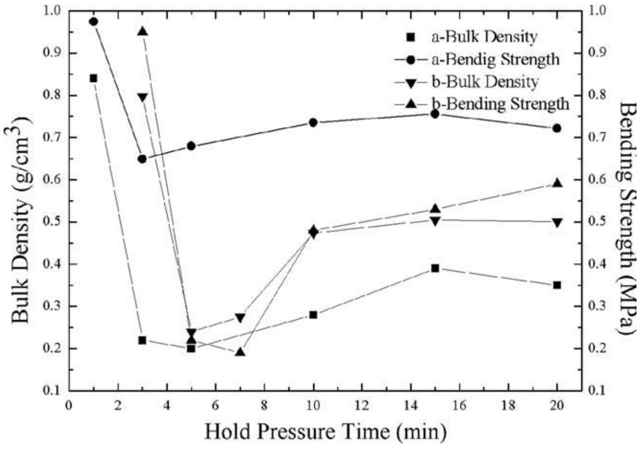

Figure 6 Effects of different pressing times on the bulk density and bending strength of (a) pristine PBS foams and (b) toughening PBS foams.

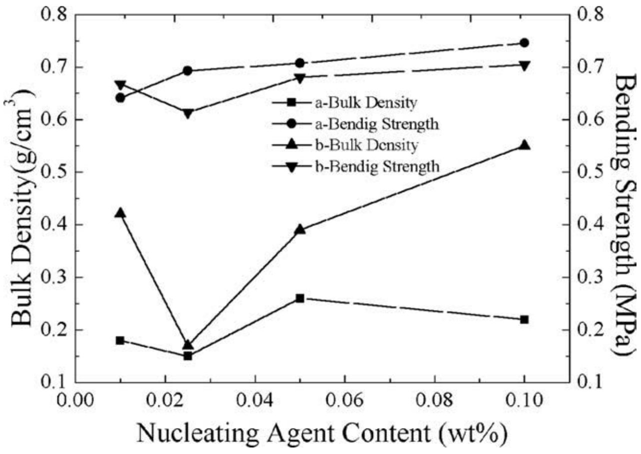

Figure 7 Effects of different nucleating agent contents on the bulk density and bending strength of (a) pristine PBS foams and (b) toughening PBS foams.

as the pressing time increases, the amounts of dissolved gases in the melt and cells increased gradually. This reduced the bulk density. But when the holding pressing time was longer than 5 min, the bulk density would increase with pressing time because the melt absorbed more heat and the strength of the melt decreases which result in the collapse of cells. The bending strength exhibited a similar trend as the bulk density. When the pressing time was longer than 15 min, a downward trend was observed owing to partial degradation of the PBS and consequently worse mechanical properties.

The above data showed that for the pure PBS, when a foaming agent content of 5 wt %, temperature of 130°C, pressure at 10 MPa, and pressing time of 5 min, the bulk density of the product reached a minimum value of 0.2 g/cm^3. The bending strength was associated with the structure of the product. A large quantity of cells and more holes in the matrix reduced the bending strength. At the same time, it could be seen that the processing parameters had little influence on the bending strength of the product.

Effect of nucleating agent concentration on the bulk density and bending strength of PBS foams

The effects of different talc nucleating agent contents of 0, 1, 3, 5, and 10 wt % (ammonium bicarbonate concentration of 5 wt %, temperature of 130°C, pressure of 10 MPa, and pressing time of 5 min for pristine PBS; temperature of 140°C, pressure of 7.5 MPa, and pressing time of 7 min for toughening PBS) are shown in Figure 7. The bending strength for toughening PBS was the logarithm (base 10) of the value. The bulk density and bending strength values were observed to change with different nucleating agent contents. Adding the nucleation agent reduced the bulk density of the product. In particular, when the nucleating agent concentration was 3 wt %, the bulk density of the pristine PBS had a minimum value of 0.15 g/cm^3 and that of the toughening PBS was 0.17g/cm^3. This was because of addition of a nucleating agent that promoted the crystal nucleation and reduced the bulk density. As the talc was insoluble solid particle, there were both homogeneous nucleation and heterogeneous nucleation, which seemed that the more nucleating agent adds, the more cells were formed. However, the bulk density increased when the nucleating agent concentration was higher than 3 wt %. It was because crystal areas had a much higher density than the amorphous phase, and hence the foaming grade decreased and therefore the density increased. The bending strength increased as the nucleating agent content increased because the solid particles in the nucleating agent played the role of the reinforcing filler.

Effect of plasticizer content on the bulk density and bending strength of PBS foams

Figure 8 shows that the bulk density and bending strength were different in PBS foams with different contents of DBP, which played a role of plasticizer. Here, the PBS foams were prepared using an ammonium bicarbonate concentration of 5 wt %, different contents of DBP of 0, 10, 20, and 30% as plasticizers, temperature of 130°C, pressure of 10 MPa, and pressing time of 5 min. Addition of the plasticizer improved the mechanical properties of the product. As the DBP content increased, the bending strength of the product becomes larger. The bending strength achieved 1.62 MPa when the amount of plasticizer reached 30 wt %. This was an obvious increase compared with the other PBS foams which was out of plasticizer. It was because DBP could reduce the Van der Waals forces between the polymer molecule which led to the mobility of the polymer chains and decreased the crystallinity of polymer chains. DBP

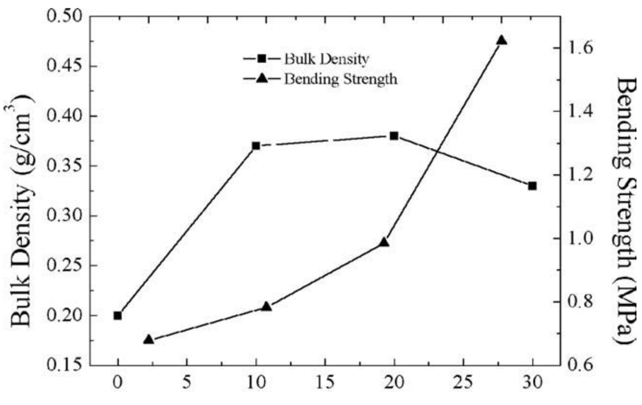

Figure 8 Effects of different plasticizer contents on the bulk density and bending strength of the PBS foams.

together with the polymer forms created swelling at an elevated temperature and altered the plastic characteristics of the polymer.

CONCLUSIONS

A series of PBS foam samples with different bulk densities and bending strength had been prepared using ammonium bicarbonate as the foaming agent. The smallest bulk density for pristine PBS was attained under the following conditions: ammonium bicarbonate concentration of 5 wt %, pressure of 10 MPa, and pressing time of 5 min. The bulk density for toughening PBS reached the smallest when the ammonium bicarbonate concentration was 5 wt %, the pressure was 7.5 MPa, and the pressing time was 7 min. Addition of talc as a nucleating agent reduced the bulk density of the foam and a concentration of 3 wt % yields the best results. Incorporation of a plasticizer could improve the mechanical properties of the products. Larger quantities of cells and hollow space led to a smaller bending strength, but changes in the pressure, time, and other processing parameters had little effects on the bending strength of the products.

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