

Preparation and Characterization of Biodegradable Foams from Calcium Carbonate Reinforced Poly(propylene carbonate) Composites

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ABSTRACT: Biodegradable foams were successfully prepared from calcium carbonate reinforced poly(propylene carbonate) (PPC/CaCO₃) composites using chemical foaming agents. The incorporation of inexpensive CaCO₃ into PPC provided a practical way to produce completely biodegradable and cost-competitive composite foams with densities ranging from 0.05 to 0.93 g/cm³. The effects of foaming temperature, foaming time and CaCO₃ content on the fraction void, cell structure and compression property of the composite foams were investigated. We found that the fraction void was strongly dependent on the foaming conditions. Morphological examination of PPC/CaCO₃ composite

foams revealed that the average cell size increased with increasing both the foaming temperature and the foaming time, whereas the cell density decreased with these increases. Nevertheless, the CaCO₃ content showed opposite changing tendency for the average cell size and the cell density because of the heterogeneous nucleation. Finally the introduction of CaCO₃ enhanced the compressive strength of the composite foams dramatically, which was associated with well-developed cell morphology. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5240–5247, 2006

Key words: polycarbonate; composite; foaming; morphology

INTRODUCTION

Loose-fill packaging materials offer effective protection for fragile products by absorbing or isolating impact energy during transportation and handling. Expanded polystyrene (EPS)-based loose-fill foam materials have enjoyed a steady growth in this application over the past three decades. However, they became recently targeted in the white pollution debate because of their undegradable nature. Therefore, the interest in environmentally friendly material has stimulated development of biodegradable materials as replacements for EPS in loose-fill packaging applications.^{1–4} For these applications, various synthetic polymers have been considered and used as the matrices for the foam materials. However, little information is available for biodegradable polymeric foams because of the very limited biodegradable

polymer.^{5,6} In recent years, poly(propylene carbonate) (PPC), copolymer of carbon dioxide (CO₂) and propylene oxide (PO), has attracted scientific and practice attention as a green environmental material because of the biodegradability and the fixation of CO₂.^{7–10}

In previous studies, we have successfully synthesized high-molecular-weight alternating PPC in an extremely high yield (126 g polymer per gram of catalyst) using zinc glutarate as catalyst under the optimized reaction conditions.^{11,12} Such a completely alternating PPC exhibited high transparency, superior mechanical strength, and good degradability in surroundings of both soil and buffer solutions.^{11–13} More recently, we have also prepared PPC foams with high blowing ratio using azodicarbonamide (AC) as the chemical blowing agent.¹⁴ However, compared to EPS-based loose-fill foams, the PPC foams have relatively poorer mechanical properties and higher production cost, which limited their practical applications in loose-fill packaging materials.

One possible way to overcome these drawbacks is to introduce inorganic filler such as talc, mica, clay, and calcium carbonate (CaCO₃) into PPC polymer. CaCO₃ is the most utilized filling material for polymer-based composites among the various mineral fillers.¹⁵ In a previous work, the biodegradable composites of PPC reinforced with CaCO₃ have been prepared and inves-

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tigated. Our research results indicate that incorporation of CaCO₃ into PPC can improve the mechanical and thermal properties of PPC considerably because of the good interfacial contact between CaCO₃ particles and PPC matrix.¹⁶ In this regard, addition of CaCO₃ into PPC foams can improve mechanical performance such as rigidity and dimensional stability as well, and also reduce the production cost.^{17,18} Owing to the heterogeneous nucleation, furthermore, CaCO₃ particles finely dispersed in the PPC matrix may contribute to cell nucleation during the foaming process and then form the uniform well-developed cellular morphology associated with improvement in mechanical properties.^{19,20} Another advantage of CaCO₃ is its hydrophilic characteristic that can increase the water adsorption of composite foams, thereby accelerate the biodegradation process of biodegradable foams.

Therefore, the biodegradable foams from CaCO₃ reinforced PPC composites are prepared using chemical blowing agents in this study. And the composites foams are investigated further to determine the effects of foaming conditions (foaming time and temperature) and blend composition on the void fraction and the cell morphology. The compressive properties of the foamed materials are also investigated and a relationship of the cell morphology to compressive strength is reported. It may be a good candidate for application in loose-fill packaging materials.

EXPERIMENTAL

Materials

The PPC used in this work was prepared in our laboratory with a number-average molecular weight (M_n) of 62,700 and a polydispersity of 4.27. CaCO₃ particles (Huaming, Shanghai, China) were used as the reinforcement fillers. The blowing agent used is azodicarbonamide (AC; Jianghao Chemical Industry, Guangzhou, China) whose decomposition temperature range is 190–240°C with a total gas yield of about 230–270 g/cm³. Zinc oxide (ZnO) in white powder form with 99.9% purity was used as a decomposition promoter for AC. All above-mentioned reagents were used as received without further purification.

Preparation of PPC/CaCO₃ composites

A Haake Rheomix_600 internal mixer with two roller rotors was used for the preparation of PPC/CaCO₃ composites containing AC-based blowing agent. The mixer was attached to a measuring drive unit (Haake Rheocord_9000). The compounding temperature was set at 140°C. The rotor rotating speed and mixing time were fixed at 30 rpm and 10 min, respectively. Five PPC/CaCO₃ composites containing 5–40 phr of CaCO₃ (phr = parts CaCO₃ per hundred parts of

PPC) along with the pure PPC sample were prepared in the presence of 6 phr of AC and 0.6 phr of ZnO. Before blending, PPC and CaCO₃ were dried in vacuum overnight. After mixing, the composites containing foaming agent were dumped out and compressed into sheets using hydrodynamic press (120°C, 2 min) for further foaming experiments.

Foaming of PPC/CaCO₃ composites

In the foaming experiments, PPC/CaCO₃ composites were placed into a hot forced convection oven at various foaming temperatures (150, 170, and 190°C) and timings of 10, 20, or 30 min, followed by immediately quenching in cold water. All the foamed samples were kept in vacuum for at least 1 day before characterization.

Characterization of PPC/CaCO₃ composite foams

Molecular weights and polydispersities of the PPC and PPC/CaCO₃ composite foams were determined using gel-permeation chromatography (GPC) consisting of a Waters Model 515 pump and a Waters Model 410 refractive index detector. Chloroform was used as solvent and the mobile phase was tetrahydrofuran (THF). Calibration was performed with polystyrene standards having molecular weights in the range of 2000–1,950,000 g/mol. Number-average (M_n), weight-average (M_w), and peak molecular weights (M_p) were calculated using the Waters Empower software. Because of the insolubility of CaCO₃ in chloroform, only the PPC component of the composites was determined in the chromatograms.

The apparent density of foams was determined by the ratio of the weight over the volume of each sample, according to ASTM D 1622-98. The dimensions were measured with a micrometer, and the weights were carefully measured. The average apparent density was obtained by determining three samples for each PPC/CaCO₃ composite foam. Void fraction (V_f) was calculated by²¹

$$V_f = (1 - \rho_f / \rho_m) \times 100\%$$

where ρ_m is the density of the unfoamed sample, and ρ_f is the density of the foamed sample.

The fractured surface morphologies were examined using a scanning electron microscope (Model JSM-6330F, JEOL, Japan) at 35× magnification. The samples were fractured in liquid nitrogen, followed by coating a thin layer of gold using a sputter coater. The average cell size, d , in micron was obtained by measuring the maximum diameter of each cell perpendicular to the skin from SEM micrographs. To determine the cell size distribution, the size of at

TABLE I
GPC Results of Pure PPC and the PPC/CaCO₃ Composite Foams

Specimen	M_n	M_w	M_p	Polydispersity
Original PPC	62,700	268,000	144,800	4.27
CaCO ₃ 20/PPC composite foamed at 150°C for 20 min	53,100	321,400	119,600	6.06
CaCO ₃ 20/PPC composite foamed at 170°C for 20 min	49,100	131,000	94,300	2.67
CaCO ₃ 20/PPC composite foamed at 190°C for 20 min	40,800	99,600	83,200	2.44
CaCO ₃ 30/PPC composite foamed at 170°C for 10 min	57,800	214,600	131,800	3.71
CaCO ₃ 30/PPC composite foamed at 170°C for 20 min	51,700	154,000	104,100	2.98
CaCO ₃ 30/PPC composite foamed at 170°C for 30 min	50,500	142,600	104,100	2.83

least 50 cells in an SEM micrograph was measured. The cell densities, N_c , in cells/cm³ are defined as:²²

$$N_c \approx 10[(1 - \rho_f/\rho_m)]/d^3$$

Compression test was performed according to ASTM D1621 standard. Rectangular foam specimens were prepared using a mold with 25 mm thick, 50 mm long, and 50 mm wide. The samples were foamed at 170°C for 20 min, and the obtained foams had approximately density of 0.24 g/cm³. The tests were performed using a SANS CMT mechanical tester with a crossheads speed of 2.5 mm/min. The load-dis-

placement curves were monitored till 30% deflection (30% initial thickness) was reached. The compressive moduli of elasticity were calculated as the slope of the linear portion of the compression loading curves.

RESULTS AND DISCUSSION

Factors affecting the preparation of PPC/CaCO₃ composite foams

PPC/CaCO₃ composite foams were prepared using AC and ZnO as a blowing agent mixture. AC is a blowing agent with higher gas evolution volume and better disparity. The resulting nitrogen gas gen-

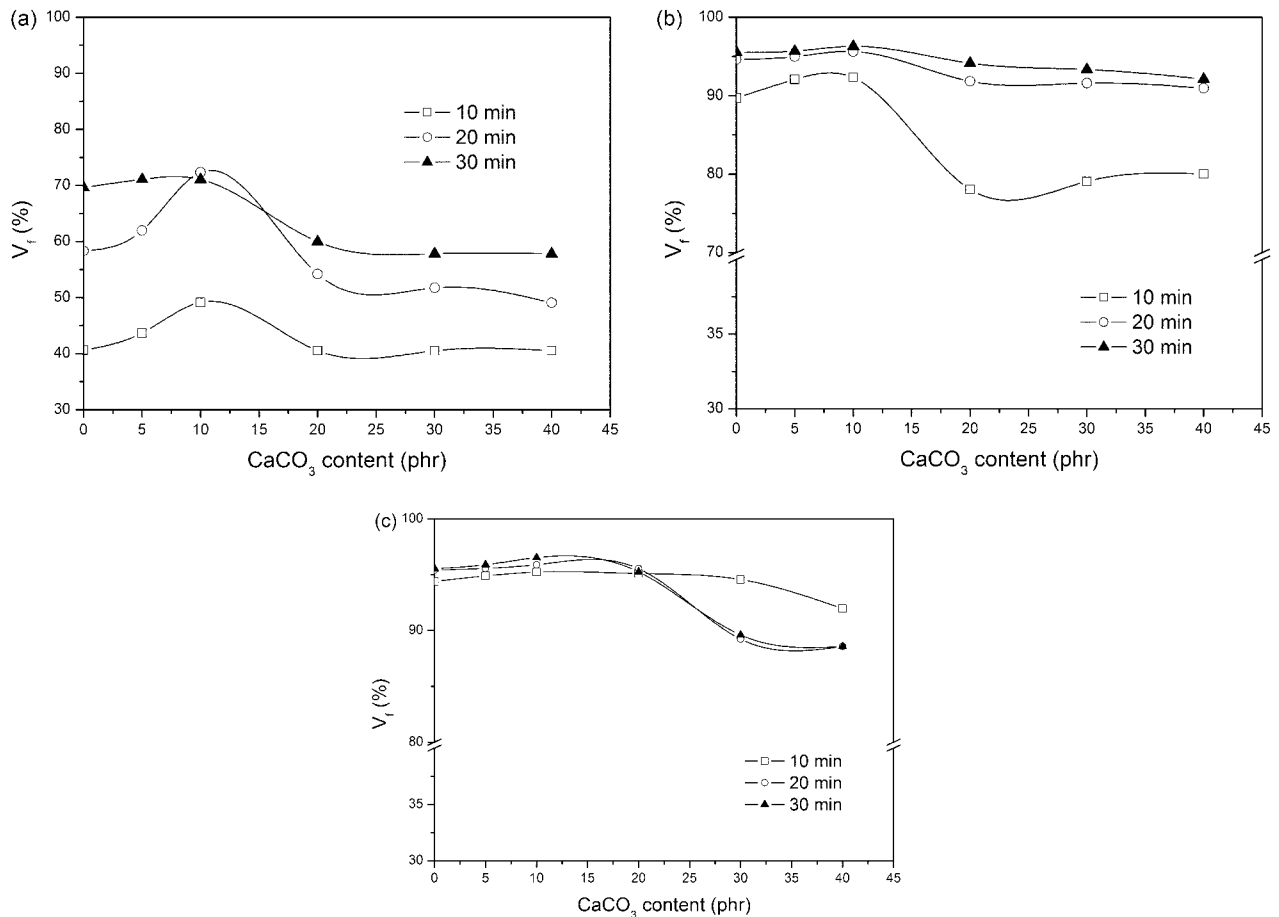


Figure 1 Effects of foaming time and CaCO₃ content on the void fractions of PPC/CaCO₃ composites foamed at (a) 150°C, (b) 170°C, and (c) 190°C.

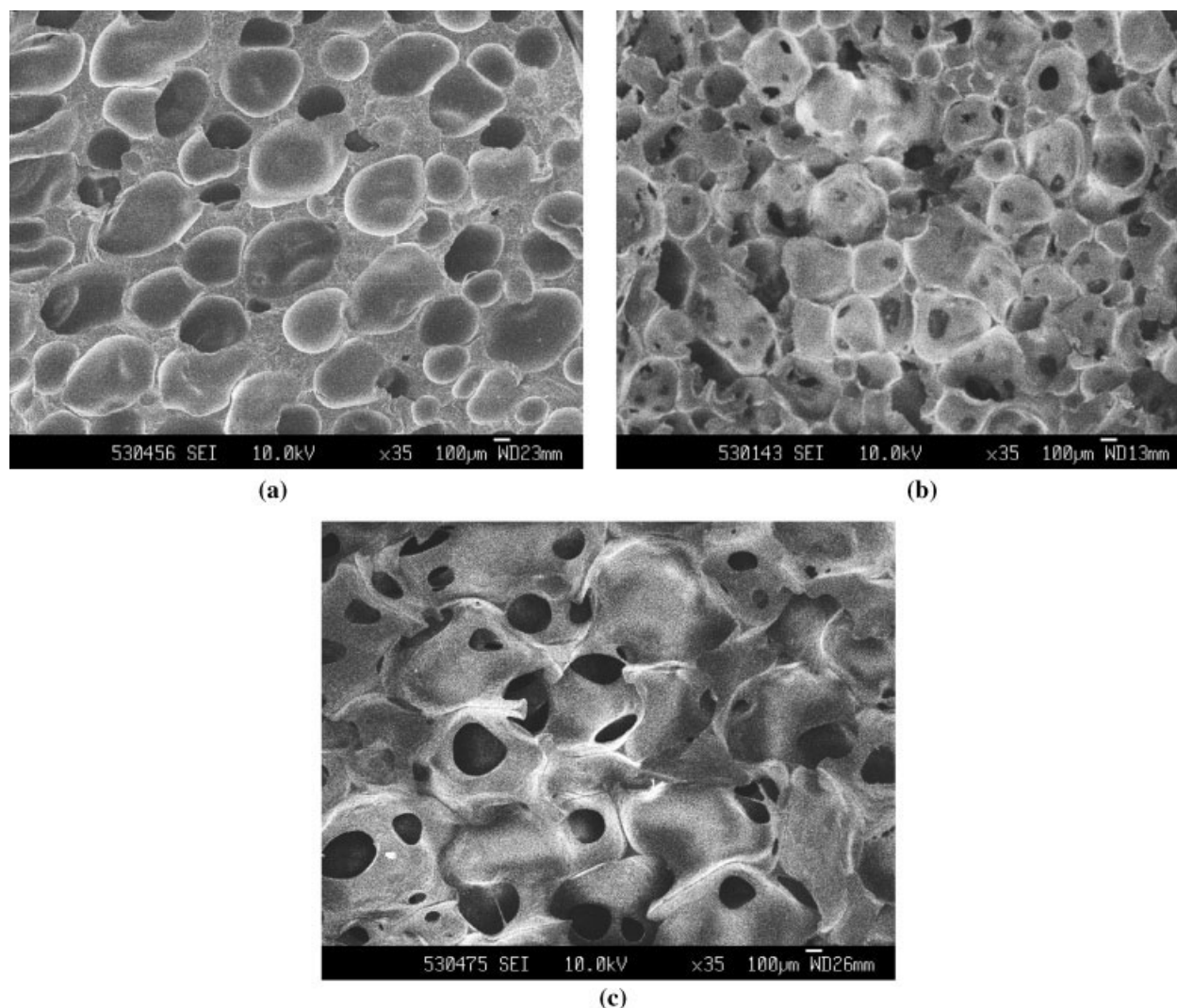


Figure 2 Scanning electron micrographs of PPC/10CaCO₃ composites foamed for 20 min at different foaming temperatures (a) 150°C, (b) 170°C, and (c) 190°C.

erally does not escape away from the foaming material. ZnO was chosen as an activator to decrease the decomposition temperature of AC. In a previous work, we had demonstrated the optimum ratio of ZnO to AC was 0.1 : 1 and the optimum AC content for the foaming PPC was 6 phr.¹⁴ In this work, PPC were blended with various amounts of CaCO₃ and foamed using the same AC/ZnO ratio as the previous work. The foamed PPC/CaCO₃ composite had densities ranging from 0.05 to 0.93 g/cm³ depending on the processing conditions. The processing parameters of interest here include foaming temperature and time, and CaCO₃ content.

According to a previous work,²³ high-molecular-weight PPC may suffer chain-unzipping decomposition or chain-scission decomposition at certain temperatures. Thus, the foaming parameters should be selected as carefully as possible. The changes in molecular weight and polydispersity of various PPC/

CaCO₃ composite foams were determined using GPC. As shown in Table I, the molecular weight decreased with the foaming temperature and foaming time. Therefore, it is limited to achieve low density by foaming at high temperature for long time due to the decrease of strength of the composites. It can also be seen that the addition of CaCO₃ resulted in obvious decomposition of PPC. This is owing to the presence of trace water absorbed in CaCO₃. Water can in turn cause the hydrolysis of PPC at high temperature.

Effect of foaming condition on the void fraction of PPC/CaCO₃ composite foams

The effects of foaming conditions such as foaming temperature and time, and CaCO₃ content on the void fractions of PPC/CaCO₃ composite foams are shown in Figure 1. It suggests that at the lowest foam-

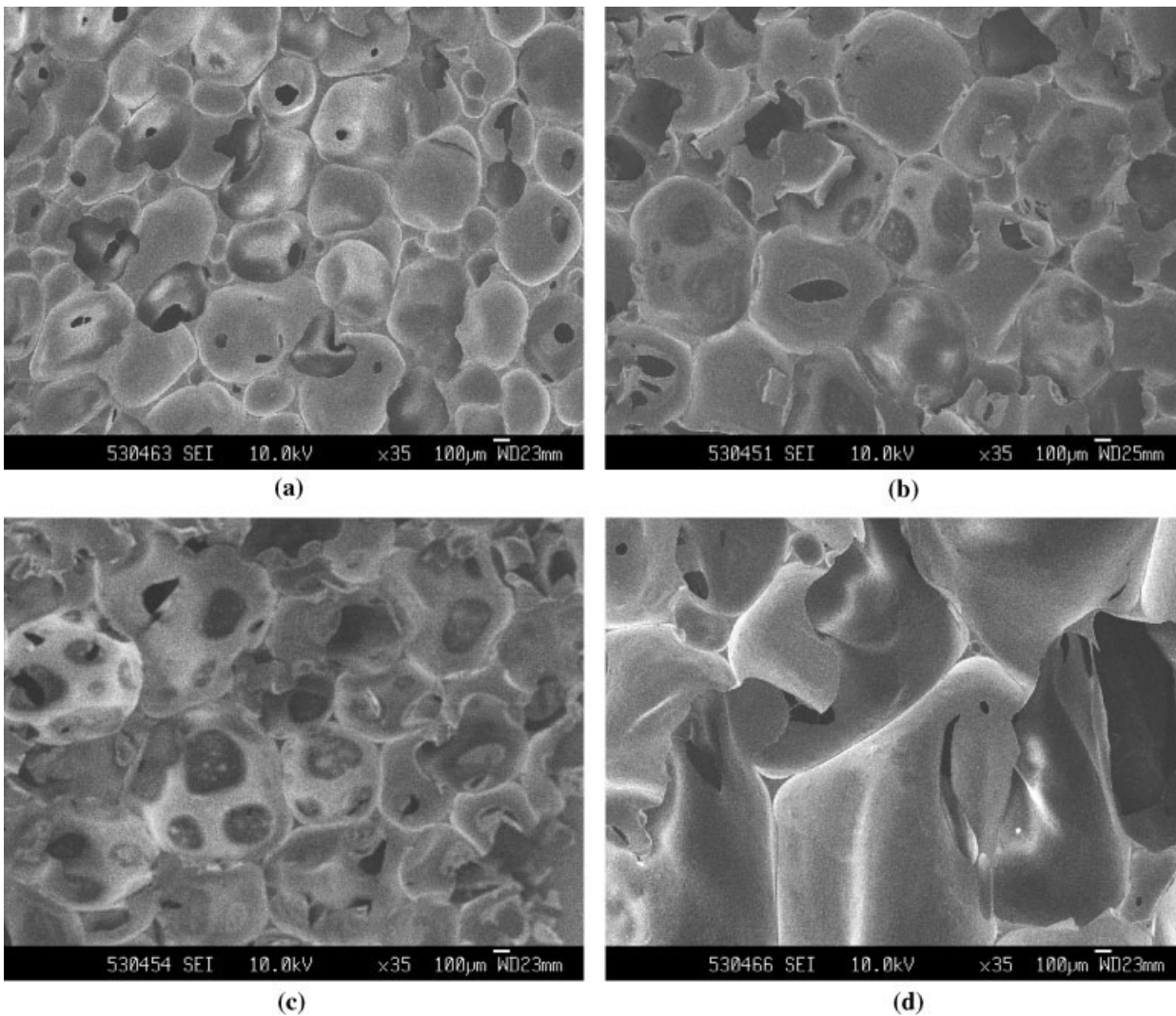


Figure 3 Scanning electron micrographs of PPC/20CaCO₃ composites foamed at 170°C for various foaming times (a) 10 min, (b) 20 min, and (c) 30 min.

ing temperature (150°C) regardless of foaming time and CaCO₃ content, a small void fraction ((70%) was obtained [Fig. 1(a)]. When foaming temperature was higher than the melting flowing temperature of PPC, the void fraction increased dramatically with increasing foaming temperature up to 170°C. However, the void fraction leveled off with further increasing foaming temperature. For instance, the void fractions of PPC/10CaCO₃ foamed for 20 min at 150, 170, and 190°C were 72.3, 95.6, and 95.8%, respectively. Figure 1 also shows that the void fraction increased obviously with foaming time up to 20 min, followed by slightly increasing with further increasing foaming time. At 190°C, however, the void fraction leveled off and then decreased significantly with the CaCO₃ content of higher than 30 phr [Fig. 1(c)]. Presumably, this behavior resulted from the decrease of the melt viscosity of polymer, and the produced gas diffused out of the cell. As a result, the cells coalesced and the foam structures col-

lapsed. Consequently, the void fraction decreased during the prolonged foaming time at higher temperature. Finally, the void fraction was strongly dependent on the CaCO₃ content. As shown in Figure 1, the void fraction increased with the CaCO₃ content up to 10 phr, and then decreased with the further increasing CaCO₃ content. It should be noted that the highest void fraction was afforded for PPC/10CaCO₃ composite foam under the same foaming condition.

Effect of foaming conditions on cell structure of PPC/CaCO₃ composite foams

As expected, the cell morphology, dimensions, and densities of the PPC/CaCO₃ composite foams were dependant upon the foaming temperature and time, and CaCO₃ content. The typical SEM micrographs of the foams under different foaming conditions are presented in Figures 2–4, respectively. The average cell

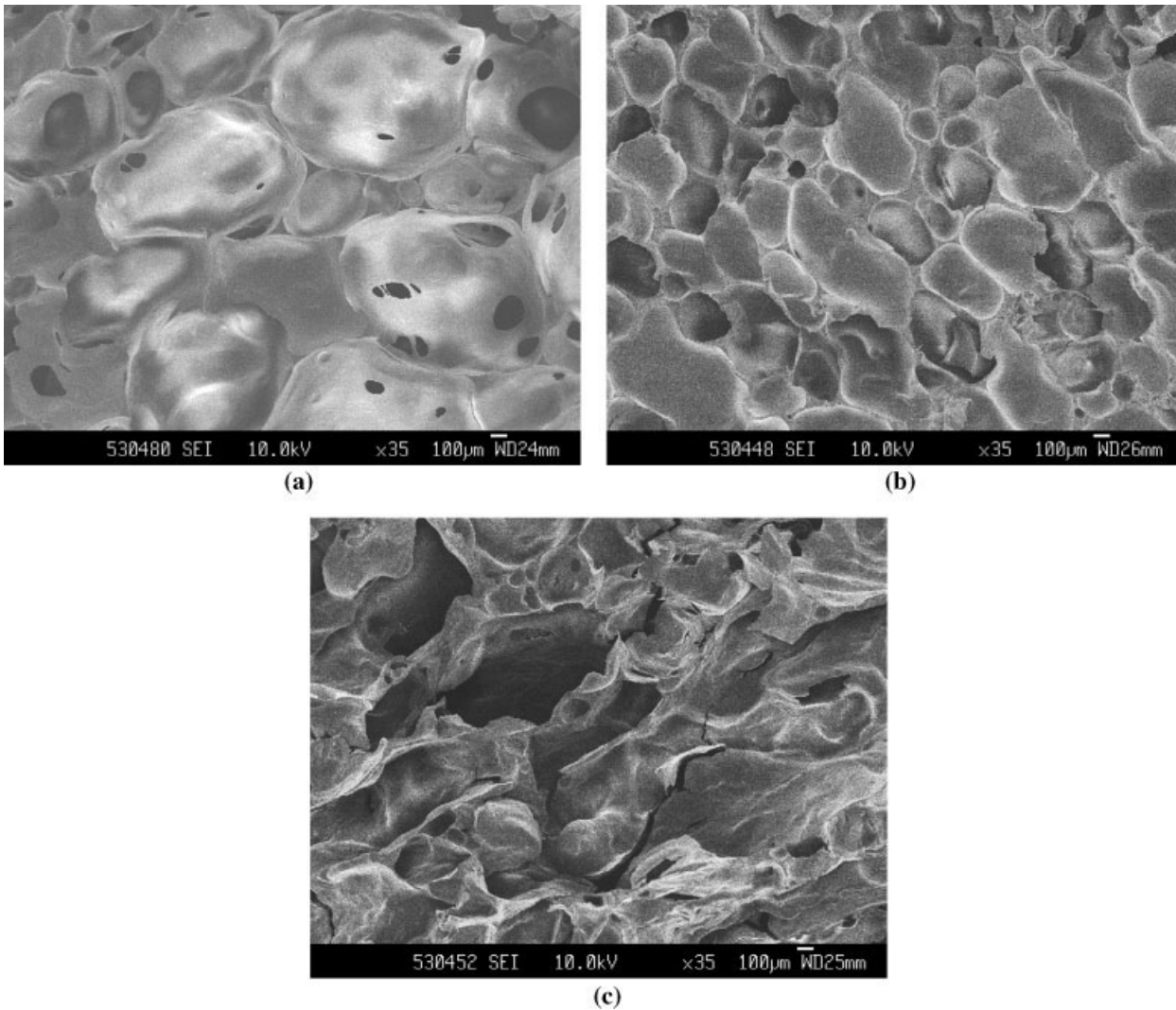


Figure 4 Scanning electron micrographs of PPC/CaCO₃ composites foamed at 190°C for 10 min with different CaCO₃ contents (a) PPC/0CaCO₃, (b) PPC/5CaCO₃, (c) PPC/20CaCO₃, and (d) PPC/40CaCO₃.

sizes and cell densities were also calculated from the SEM micrographs and are summarized in Table II.

As shown in Figure 2, the cell size and shape changed significantly with varying foaming temperature. At

lower temperature, well-separated spherical cells were formed, while the cells expanded and gradually connected with neighboring cells to give the polyhedral structures with increasing temperature. From Table II,

TABLE II
Effects of Foaming Conditions on Cell Size and Cell Density

Foaming temperature (°C)	Foaming time (min)	CaCO ₃ content (phr)	PPC/CaCO ₃ foam	
			Cell size (µm)	Cell density (cells/cm ³)
150	20	10	419.8	9.8 × 10 ⁴
170	20	10	567.9	5.2 × 10 ⁴
190	20	10	687.3	3.0 × 10 ⁴
170	10	20	359.7	1.7 × 10 ⁵
170	20	20	547.2	5.6 × 10 ⁴
170	30	20	666.3	3.1 × 10 ⁴
190	10	0	–	–
190	10	5	791.2	1.9 × 10 ⁴
190	10	20	437.0	1.1 × 10 ⁵
190	10	40	–	–

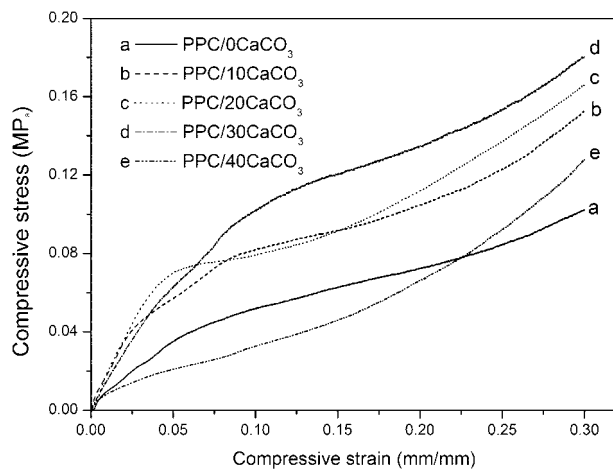


Figure 5 Compressive stress–strain curves for PPC/ CaCO_3 composite foams having different CaCO_3 content with the almost same normalized density of 0.24 g/cm^3 .

the average cell sizes of PPC/ 10CaCO_3 foam increased and the cell densities decreased with increasing foaming temperature. This behavior is obviously attributed to the decrease in the melt viscosity of the composites subjected to foaming process. On one hand, cell growth is governed by the diffusion rate of gas decomposed from blowing agents into the cells. The lower melt viscosity of the composite resulted in the higher diffusion rate of gas, leading to the increase in the average cell size. On the other hand, the energy minimization factor favors cell coalescence because a molten polymer with fewer and larger cells would be more stable than that with more and smaller cells. Moreover, the lower the melt viscosity of the polymer matrix was, the easier cell coalescence occurred,²⁴ resulting in the decrease in cell density.

From Figure 3, it can be seen that the cells structure grew up with increasing foaming time. Accordingly, the average cell size of PPC/ 20CaCO_3 composites increased from 359.7 to $666.3 \mu\text{m}$ (Table II), when the foaming time increased from 10 to 30 min. Relevant here is the fact that the more gas diffuses into the cell as the foaming time increases, the larger cells are produced until the cells are completely mature. However, the cell density decreased from 1.7×10^5 to $3.1 \times 10^4 \text{ cells/cm}^3$ (Table II). According to the results reported by Baldwin et al.,^{25,26} cell nucleation takes place over a finite time, i.e., a very short time compared with that for cell growth. Thus, as long as cell nucleation occurs, the cell density will remain constant. The primary method by which the cell density decreases is cell coalescence. Furthermore, longer foaming time causes more bubbles to coalesce.²⁷

Figure 4 shows that the cell size of PPC/ CaCO_3 composite foams decreased dramatically compared with that of pure PPC foam. This is due to that the introduction of CaCO_3 into PPC can increase the

melt viscosity of PPC/ CaCO_3 composites greatly. On the contrary, the cell density of PPC/ CaCO_3 composite foams increases with increasing CaCO_3 content, as presented in Table II. According to the classical nucleation theory,^{28–30} finely dispersed CaCO_3 particles induced heterogeneous nucleation in the PPC matrix, which contribute to cell nucleation during the foaming process by reducing the nucleation energy. The more CaCO_3 filled in the PPC matrix, the more cell nucleation sites are created, leading to increase in the cell density.

Compression property

The compressive strength of PPC/ CaCO_3 composite foams were tested to evaluate whether these foams could be used as a loose-fill packaging material, and to address the properties in terms of filler content and cell morphology. Figure 5 presents the compression stress–strain curves for PPC/ CaCO_3 composite foams having different CaCO_3 content with the almost same normalized density of 0.24 g/cm^3 . These curves behave as a typical curve for “elastic–plastic” foams.³¹ They show linear elasticity at low stresses followed by a long collapse plateau, truncated by a regime of densification over which the stress rises steeply. At the elastic stage, compressive moduli of PPC/ CaCO_3 composite foams as function of CaCO_3 content are shown in Figure 6. With the CaCO_3 content increased from 0 to 30 phr, the compressive strength and moduli of the PPC/ CaCO_3 composite foams increased from 0.05 to 0.10 MPa and from 0.40 to 0.88 MPa, respectively. When the foams were compressed, CaCO_3 particles dispersed in PPC greatly confine the deformation of the composite foams, leading to the significant increase in strength and modulus of the composite foams. The cell structure

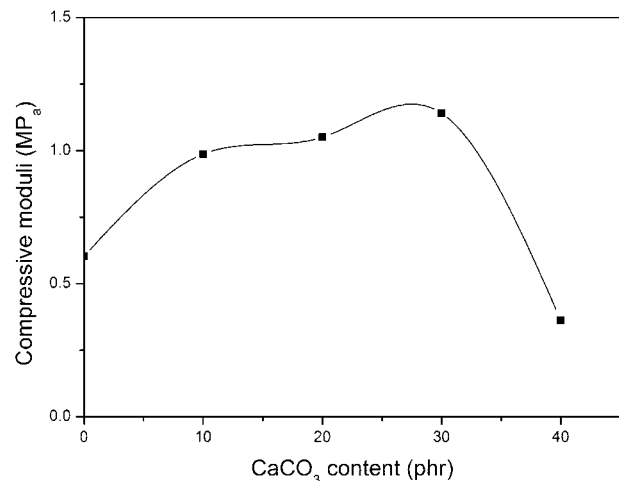


Figure 6 Compressive moduli for PPC/ CaCO_3 composite foams as versus of CaCO_3 content.

of the foams is another reason to account for the increase in the compression strength.^{32,33} According to the previous section, the cell size became smaller and the cell density became bigger with more CaCO₃ particles, resulting in a well-shaped morphology. Thus, the PPC/CaCO₃ composite foams had the uniform well-developed cellular morphology. However, with further increasing the CaCO₃ content up to 40 phr, the compressive stress and moduli began to decrease because of the agglomeration of CaCO₃ particles and cell coalescence.

CONCLUSIONS

Using chemical foaming agents, calcium carbonate reinforced poly(propylene carbonate) (PPC/CaCO₃) composites were foamed to produce completely biodegradable and cost-competitive composite foams. The obtained foams had low densities ranging from 0.05 to 0.93 g/cm³. Foaming conditions such as temperature, time, and content strongly affected the void fraction. To achieve high void fraction, the foaming temperature should be higher than the melting temperature of the composites. Introduction of CaCO₃ into the PPC limited the foaming of PPC/CaCO₃ composites. SEM examinations revealed that the average cell size increased with increasing both the foaming temperature and the foaming time, whereas the cell density decreased with these increases. It is also found that the average cell size decreased but the cell density increased with increasing in CaCO₃ content, due to the melt viscosity of composites and their heterogeneous nucleation behavior. Finally, the introduction of CaCO₃ particles was responsible for the great enhancement of compression property of the composite foams. The addition of CaCO₃ into PPC can result in a well-developed and uniform cellular foam structure with small cell size and high cell density, and consequently improve the compressive strength.

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