

**Special Issue: Manufacturing of Advanced
Biodegradable Polymeric Components**

Guest Editors: Prof. Roberto Pantani (University of Salerno) and
Prof. Lih-Sheng Turng (University of Wisconsin-Madison)

EDITORIAL

Manufacturing of advanced biodegradable polymeric components

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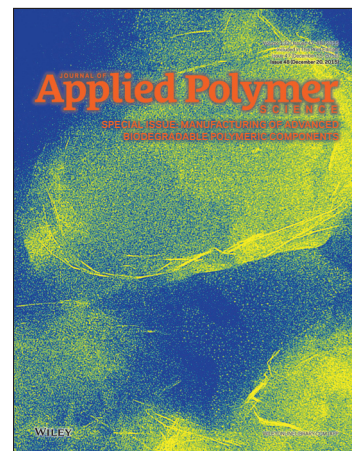
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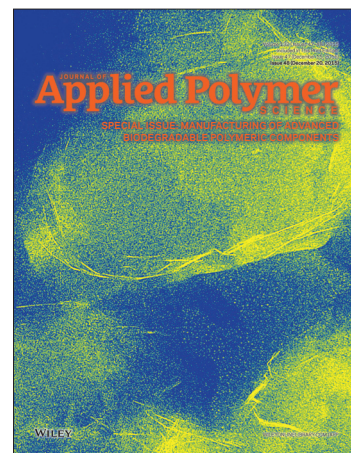
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Batch foaming poly(vinyl alcohol)/microfibrillated cellulose composites with CO₂ and water as co-blowing agents

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ABSTRACT: We studied the foaming behavior of poly(vinyl alcohol) (PVOH) and microfibrillated cellulose (MFC) composites in a batch process using supercritical carbon dioxide (scCO₂) and water as co-blowing agents. In PVOH/MFC composites, water is an economical plasticizer. It not only suppresses the potential thermal degradation of PVOH but also extends the processing window. A uniform cell structure and a high cell density were achieved in the PVOH/MFC foams. The results showed that cell density was increased by increased water content. Further, the MFC contained both micro- and nano-sized fibers. These created numerous heterogeneous nucleation sites and caused local pressure variations. However, cell density decreased when the MFC was overdosed. Due to the high crystallinity that then developed around the MFC, the gas content was too low, and the stiffness was too high. The experimental results also showed that the cell morphology and density could both be controlled by the water and the MFC content. The effects of the foaming temperature and pressure on the cellular morphology of the PVOH/MFC composite foams were examined systematically. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42551.

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INTRODUCTION

Poly(vinyl alcohol) (PVOH) is a commercially available water soluble polymer. In addition to being compatible with numerous organic and inorganic materials, its ion exchange, physical adsorption, and polarity are good.¹ Also, when it is dissolved in water, it becomes biodegradable, and its applications in surgical absorptions, drug delivery, packaging, heavy metal ions adsorption, and in acoustic noise reduction are all excellent.² Thus, PVOH foam has been attracting research attention. However, PVOH's melting temperature is very close to its thermal degradation temperature, and this means that it may easily degrade during thermal processing.^{2–6} To solve this problem, water can be used to decrease the melting temperature and to minimize thermal degradation during thermal processes. Water is an ecologically friendly blowing agent, and it has already been used in thermoplastic foams.^{2,7–10} While many thermoplastic polymers are hydrophobic, which limits the dispersion of water throughout the matrix, PVOH is hydrophilic. Thus, water can easily be dispersed in its matrix. Additionally, to increase water dispersion, hydrophilic natural cellulose additives such as wood

fibers,^{8,9} nanofibrillated cellulose,⁵ and microfibrillated cellulose (MFC)^{11,12} can be used as “water carrying agents.”¹³ Water can be easily released during processing. Therefore, water content absolutely must be increased at that time. If water is prematurely released, the cell distribution becomes non-uniform and cells become large.^{8,14,15} Thus, it was critical for us to control the content and dispersion of the water and the MFC during foaming. MFC is composed of microsized and nanosized fibrils obtained from cellulose fibers. MFC, which is biodegradable, has excellent mechanical properties and a high aspect ratio.^{16–19} It has also been investigated as a reinforcing material. Good mechanical properties for MFC reinforced polymers have been reported.^{13,20–24} It was also found that a hydrophilic MFC can form a stable aqueous suspension, and a homogenous dispersion of MFC in PVOH was achieved.^{20,25}

Recently, PVOH foam composites with natural fibers were reported. Avella *et al.*^{11,12} used additional plasticizers, such as glycerol, to improve PVOH foam's processability. Adding multi-layer cartons (MC) to PVOH improved its swelling behavior, its mechanical properties as well as its thermal stability. This was

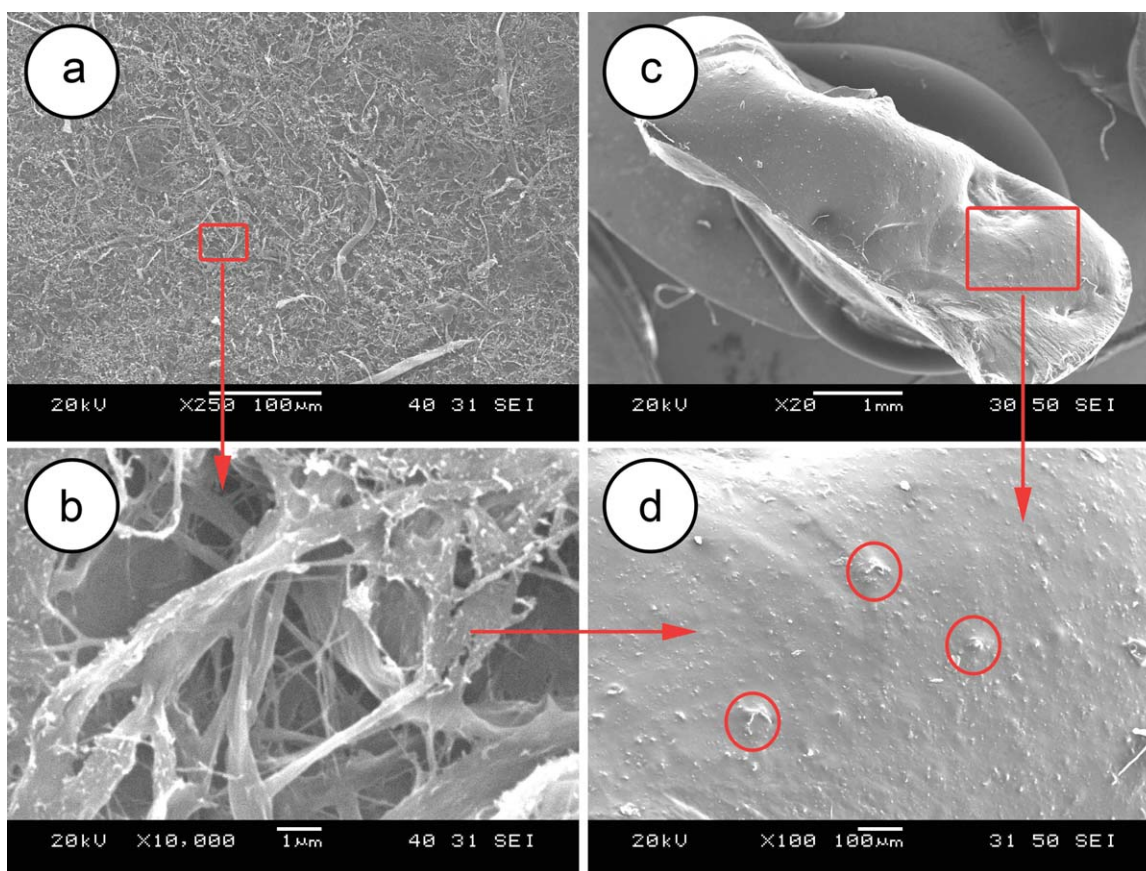


Figure 1. (a,b) SEM micrographs of MFC, (c,d) SEM micrographs of PVOH/MFC composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the result of a good interaction between the fibers and the polymer. At the same time, cell size decreased with increased MC content, which resulted in improved mechanical properties. Srithep *et al.*⁵ investigated the foaming behavior of PVOH/nanofibrillated cellulose (NFC) using CO₂ both with and without water as the blowing agent. Foams were observed when high moisture samples were foamed with CO₂. No bubbles were found in the neat PVOH or in the PVOH/NFC composites. Wang *et al.*^{2,26–28} studied PVOH foaming using water as a blowing agent. The PVOH water states or phases strongly affected cell nucleation, cell growth, and cell stability. Calcium carbonate and talc were used as nucleating agents. They also improved cell density and decreased the cell size. Because of the low thermodynamic instability generated by the pressure drop of when only water was used, it was hard to achieve a high cell density and an uniform cell morphology in the PVOH foams. There has been no research done to show how PVOH and/or PVOH/MFC composites' foaming behavior affects the water contents needed scCO₂ to produce microcellular foams. Our earlier work demonstrated the effect of scCO₂ and water on the foaming behavior of PVOH and/or PVOH/MFC composites in extrusion.¹⁰ But water can be easily lost in the extrusion barrel, and lost water is not easily quantifiable. This is because the screw shape, the melt temperature, and the RPM all affect it. Therefore, it is impossible to know how much water is left in PVOH extrusion foaming. The water-induced foaming mechanism, and

the cell nucleation mechanisms of both the water and the scCO₂ in PVOH/cellulose fiber composite foams are not yet clearly understood.

The foaming behavior of PVOH/MFC composites with various water contents was investigated using a batch process wherein the water content was more easily measured at each stage. Therefore, it was more easily controlled. Since both PVOH and MFC have a strong moisture-carrying ability, water was used as a plasticizer and as a co-blowing agent along with the scCO₂. We investigated the effects of water concentration, the MFC content, the saturation temperature, and scCO₂ pressure on cell morphology, cell density, and the expansion ratio.

EXPERIMENTAL

Materials

The MFC used in this study was commercial grade KY100G, supplied by Daicel FineChem. The MFC was obtained as an aqueous suspension. The MFC fibers are 10 nm to 15 µm thick and 0.1 to several µm long. Poly (vinyl alcohol) (Mowiol 23-88), supplied by Kuraray Company, was used as the polymer matrix. It was a partially hydrolyzed grade (86.7–88.7 mol %) with a weight-average molecular weight of 150,000 g·mol⁻¹ and had a density of 1.3 g·cm⁻³ at 20°C. Carbon dioxide (99.98% of purity), supplied by Linde Gas, was used as a physical blowing agent. Potassium sulfate (K₂SO₄) (P304-3), supplied by Fisher

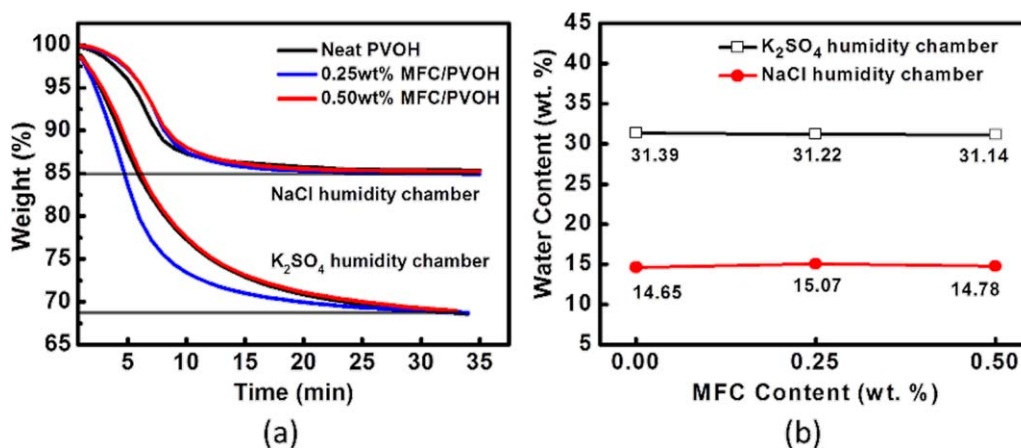


Figure 2. (a) TGA curves and (b) the water contents of PVOH/MFC composites in NaCl and K₂SO₄ saturated salt solutions chambers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Scientific, and sodium chloride (NaCl), supplied by Sifto Canada Corporation, were used to control the water content of the PVOH/MFC sample, which is described below in detail.

Sample Preparation

MFC fibers were compounded into PVOH using a co-rotating twin-screw extruder and were pelletized for the batch foaming experiments. Figure 1 shows the scanning electron microscopy (SEM) micrographs of MFC fibers and the MFC dispersion in the PVOH/MFC composites. A relatively uniform MFC dispersion was achieved and only some very small MFC agglomerates could be seen. Because the water content of PVOH/MFC composite is extremely sensitive to ambient humidity, it is necessary to condition the samples to reach a consistent water content. Therefore, salt baths were used to control the relative humidity within a small conditioning chamber. PVOH/MFC samples were sealed in the chamber until they reached an equilibrium state. Sodium chloride (NaCl) and potassium sulfate (K₂SO₄) were used to achieve different humidity levels within the conditioning chamber. In the PVOH/MFC samples, changing the ambient humidity produced various water contents. The water content was verified by thermo gravimetric analysis (TGA). It took approximately two weeks for the samples to reach an equilibrium state at a room temperature of 25°C. During the TGA measurements, the samples were heated to 150°C at a rate of 20°C·min⁻¹, and held up for 30 min to remove the residual water.

Figure 2 depicts the TGA curves and the water content of the PVOH and PVOH/MFC composite pellets in the NaCl and K₂SO₄ saturated salt solution chambers. Figure 2(b) shows that the water content of the PVOH/MFC composites conditioned with NaCl and K₂SO₄ was around 15 and 31 wt %, respectively. We note that pellets can maintain a constant water content by being conditioned in a sealed humidity chamber for over 2 weeks.²⁹ Further, due to a small amount of fibers, the water content was very close with or without MFC in the PVOH.

The thermal behaviors of the equilibrated PVOH pellets with various water contents were investigated by differential scanning calorimetry (DSC) (Model Q2000, TA Instruments). Samples

were ramped from 30°C to 230°C with a heating rate of 10 °C·min⁻¹. Figure 3 shows the second heating curves of the PVOH pellets affected by water. The glass transition temperature (T_g), melting temperature (T_m), and crystallinity (X_c) all decreased as the water content increased. It indicated that water as a plasticizer invaded into the amorphous regions and into the imperfect crystal region of PVOH. Thus, the free volume increased and overall crystallinity decreased which increased the solubility of sCO₂ in PVOH.

Batch Foaming Process

As shown in Figure 4, we carried out a batch foaming process as follows: (1) Samples were put in a batch foaming chamber. (2) They were saturated with the sCO₂ at the desired foaming pressure and temperature for 30 min. (3) To foam the samples, a quick pressure drop was effected inside the chamber using a quick pressure release valve. (4) After the pressure drop, the batch foaming chamber was quenched in cold water to stabilize the foam structure. Foaming experiments were conducted three

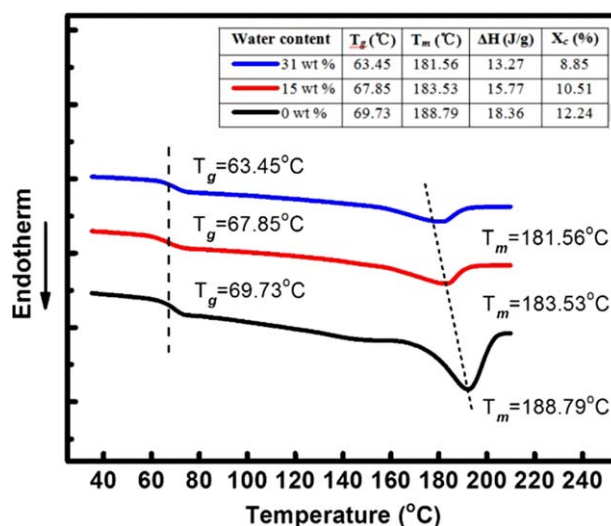


Figure 3. DSC thermograms of PVOH with various water contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

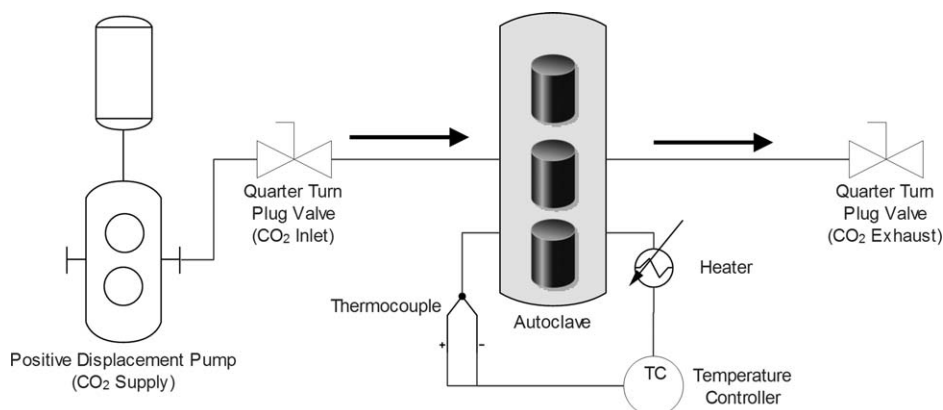


Figure 4. A batch foaming schematic.

times for each composition to examine the repeatability of the results. Table I summarizes the formulations for the batch foaming parameters.

Foam Characterization

To analyze the cellular morphology, we cut the foamed samples with a razor blade. A cryo-fracture using liquid nitrogen was not used. This was because it causes condensed water droplets to appear on a sample (and on tools) when exposed to ambient air. The condensed water could then dissolve the foam samples and the fractured surfaces. Next, the foam's cross-section was coated with a thin layer of platinum using a sputter coater. The microstructure was examined using a scanning electron microscope (SEM) (JSM-6060, JEOL). The expansion ratio (Φ) was evaluated using a water-displacement technique based on the ASTM Standard D792-00. By analyzing the SEM micrographs, cell sizes were measured and cell densities were calculated by eq. (1) as follows:

$$\text{Cell Density} = \left(\frac{nM^2}{A} \right)^{\frac{3}{2}} \times \Phi \quad (1)$$

where n is the number of cells in the micrograph; A and M are the area and magnification factor of the micrograph, respectively.

RESULTS AND DISCUSSION

We wanted to better understand the process–structure relationships and to control the cell morphology of the microcellular foamed PVOH/MFC composites. To this end, we investigated how water and MFC content and processing conditions affect the structures and properties of foamed PVOH and PVOH/MFC composites.

Table I. Batch Foaming Parameters of PVOH/MFC Composites

Saturation temperature (°C)	Saturation time (min)	Saturation pressure (MPa)	Blowing agent	Water content (wt %)	MFC content (wt %)
70–190	30	6.90	scCO ₂	0	0
		10.34	water	15	0.25
		13.79		31	0.50

Effect of Water as a Co-Blowing Agent on Foaming Behavior

In previous studies, water had a strong effect on the melting temperature and crystallinity of PVOH. It also facilitated CO₂ processing and improved the extrusion foaming process.¹⁰ Siró and Plackett claim that water molecules can increase the free volume and reduce its overall crystallinity. This can then increase the solubility of scCO₂ in PVOH.¹⁹ The result is higher nucleation rates and higher cell densities. In this section, we discuss how a batch foaming process generated a higher cell density and a smaller cell size than was the case for extrusion-foamed samples with the same blowing agent content (BA) in the same PVOH composites. In addition, the processing window for batch foaming was extended due to the decreased melt viscosity that occurred with increased water content. As the PVOH melting temperature is decreased, it moves further away from its degradation temperature, and this is the case in continuous extrusion foaming.¹⁰

Figure 5(a) shows the expansion ratio and Figure 5(b) the cell density of neat PVOH with respect to the water content. It is obvious that in PVOH with increased water content the expansion ratios increase and a visible mountain shape³⁰ develops across the range of foaming temperatures. For 0 and 15 wt % water/PVOH foams, the highest expansion ratio was seen at 185°C when the expansion ratios were 7.7 and 9.4, respectively. With 31 wt % water, a peak expansion ratio of 11.9 occurred at a lower temperature of 175°C. These results indicate that the foaming window had shifted to a lower temperature range. This was caused by the water's plastization. Further, Figure 5(b) shows that the cell density of PVOH foams ranged from 10¹⁰ to 10¹¹ cells cm⁻³. Figure 6 shows the SEM micrographs of the neat PVOH foams and the PVOH conditioned with water at a foaming temperature of 175°C. The cell size increased and the

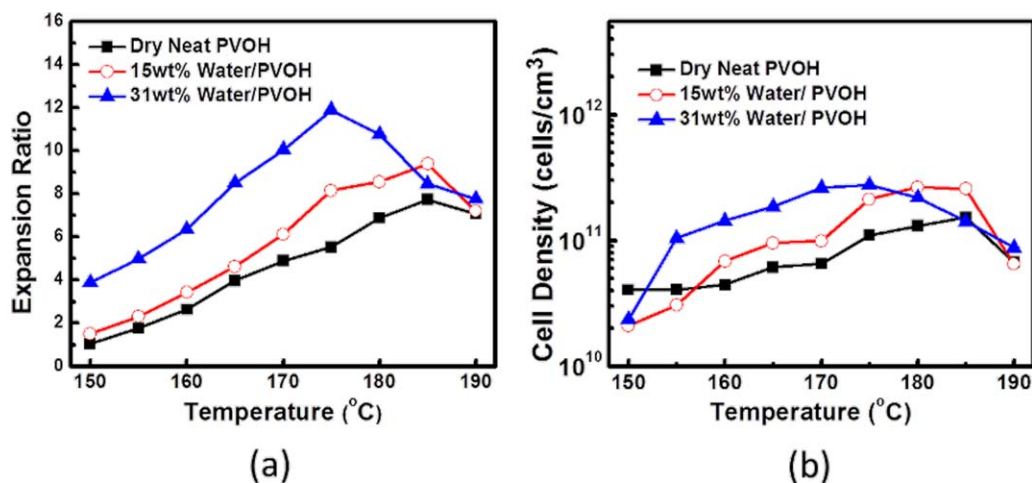


Figure 5. (a) Expansion ratio, (b) cell density of water/PVOH foams as a function of the water content with a saturation pressure of 13.79 MPa. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cell wall thickness decreased. Undoubtedly, these changes in the neat PVOH's cell morphology were caused by the water molecules. The molecules had diffused into the amorphous PVOH region and changed the viscosities and elasticity by disrupting the inter- and intra-hydrogen bonding. Since cell nucleation is governed by pressure (or stress) variations within the polymer matrix,^{31–35} the parameters affecting the shear viscosity, the extensional viscosity, and the elasticity significantly influence cell nucleation behaviors.

As the PVOH pellets become completely saturated with water in the salt solution conditioning chambers, water molecules will adhere to hydrogen groups in the PVOH and destroy the crystal structure by forcing the polymer chain configuration from a crystalline planar zig-zag into an amorphous configuration.^{29,36} Therefore, a good permeation of the PVOH by the scCO₂ is possible. This can dramatically increase the amount of blowing agent for cell nucleation and cell growth. In addition to the PVOH's decreased crystalline region which increases the scCO₂'s solubility, the swelling of the amorphous region with water is also believed to increase the scCO₂'s solubility in PVOH. The solubility of the blend blowing agents and the effect of one dissolved blowing agent on the solubility of the other blowing agent are still under investigation. Only a few combinations of the polymer and gases have been studied.^{37–40} Measurements of the solubility of water and scCO₂ in PVOH would require a

proper setup. This would provide a controlled water content from a conditioning chamber. A controlled amount of scCO₂ would also be added to our existing magnetic suspension balance^{41,42} and to the swelling measuring device.^{43,44} This will be the subject of future research.

We also note in Figure 5(a) how the expansion behavior was governed by the PVOH matrix's stiffness. At a temperature of over 190°C, degradation was severe, so the processing temperature was limited to 190°C. But below this temperature, the stiffness of the matrix was high enough to govern the expansion behaviors, despite the addition of water. For example, when the water content was 15 wt %, the PVOH foam's maximum expansion was obtained at 195°C. As we increased the water content to 31 wt %, the maximum expansion occurred at 175°C. Therefore, at a temperature higher than this optimal one, the expansion ratio decreased because the blowing agent was increased.³⁰ But in the most effective processing temperature range, the expansion ratio was governed by the PVOH's high stiffness. In other words, as its stiffness was decreased by increasing the temperature or by adding water, the PVOH's expansion was facilitated. We also note that the high water content increased the PVOH foam's expansion ratio. Since water was a co-blowing agent,^{2,10} the water itself must have contributed to the expansion. But it seems that the plasticizing effect of the water decreased the stiffness of the PVOH matrix to make it more

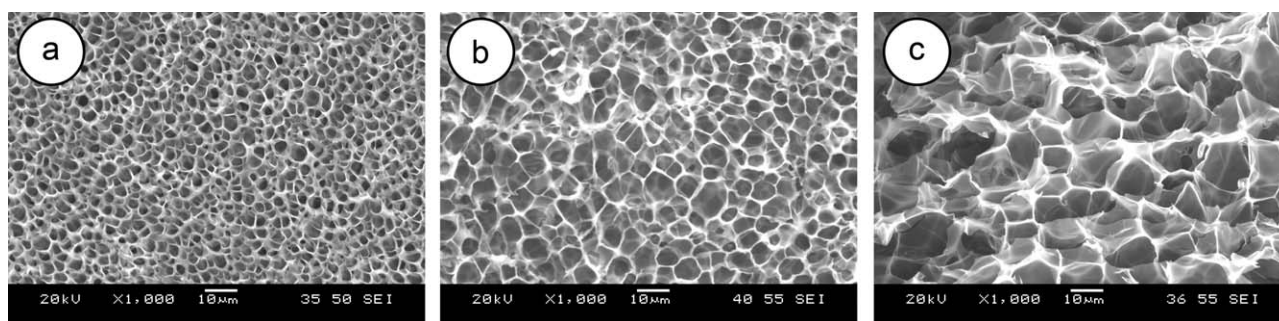


Figure 6. SEM micrographs of neat PVOH foamed at 175°C with: (a) 0 wt % water, (b) 15 wt % water, (c) 31 wt % water.

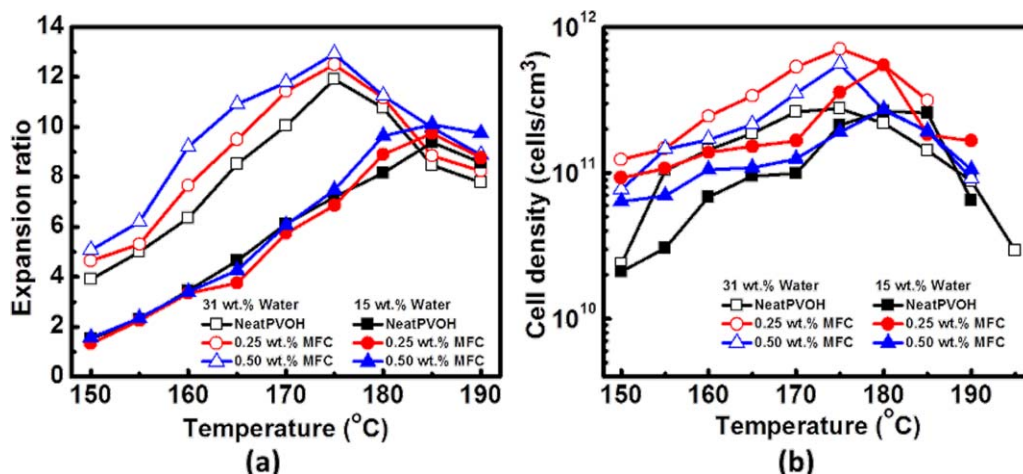


Figure 7. (a) Expansion ratio, (b) cell densities of PVOH/MFC composite foams at different foaming temperatures with 15 and 31 wt % water, 0.25 and 0.50 wt % MFC, and 13.79 MPa saturation pressure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

expandable. This means that the increased expansion ratio stemmed not only from the increased blowing agent content but also from the decreased stiffness of the matrix. Most thermoplastic materials foam processing has a narrow temperature range wherein the stiffness governs, especially when scCO_2 is used as a blowing agent. This is because of its high diffusivity and, therefore, its high rate of escape from the polymer.^{45–48} One is supposed to decrease the processing temperature to increase the expansion ratio for most thermoplastic materials. But a unique characteristic of the PVOH foam is that one needs to increase the temperature to achieve a high expansion ratio because of the PVOH material's high stiffness.

Effect of MFC Content on Foaming Behavior

Figure 7 shows the expansion ratio and cell density of the PVOH/MFC composite foams as a function of the saturation temperature with varying water content of 15 and 31 wt % and MFC content of 0.25 and 0.50 wt %. The PVOH/MFC composite foam with 0.25 wt % MFC had the highest average cell density of 7.07×10^{11} cells·cm⁻³. MFC has a wide range of dimensions and is composed of nanofibrils, fiber fragments, and fibers.¹⁸ Because of this a large number of interfaces between fibers and the polymer matrix created heterogeneous nucleation sites^{49–52} and caused local pressure variations.^{33,35} All of these factors increased the nucleation rate, which improved the cell density in the PVOH/MFC composite foams. Nevertheless, it does not mean that the cell density will continue to increase when more MFC is added to the PVOH matrix. Figure 7(b) shows that when the MFC content exceeded 0.25 wt %, the cell density decreased. These results indicate that the melt stiffness may have been too high when the MFC was overloaded. In other words, the MFC and MFC-induced PVOH crystals may have formed a network which adversely affected the nucleation behavior.^{30,53} In addition, neither solid natural fibers⁵⁴ nor crystallites in PVOH/MFC composites can dissolve scCO_2 .^{55,56} This led to decreased scCO_2 solubility in the PVOH/MFC composites.¹⁹ But we note that the expansion ratio increased with increased MFC content, despite the lower

solubility of the scCO_2 . The water in the MFC must have contributed to the expansion ratio.

On the other hand, the water released from the moisture in the MFC did not produce a non-uniform cell structure or large bubbles in the PVOH/MFC composite foams, as had been reported in other studies.^{7–9,51,57} It seems that the cell nucleation mechanisms were governed by the scCO_2 , and that the large number of cells nucleated by the scCO_2 prevented the formation of a non-uniform cell morphology.

It is worthy to note that the water content in each sample was measurable in the batch foaming. Therefore, we could measure the amount of water lost. By contrast, it would be very difficult to measure the amount of water lost during extrusion foaming because there is no reference sample with a known water content. But in batch foaming, we can even control the water content that dissolves in the sample, and we can accurately investigate the water's effect on foaming behavior. As Figure 8 shows, the loss of moisture during the batch process still occurs

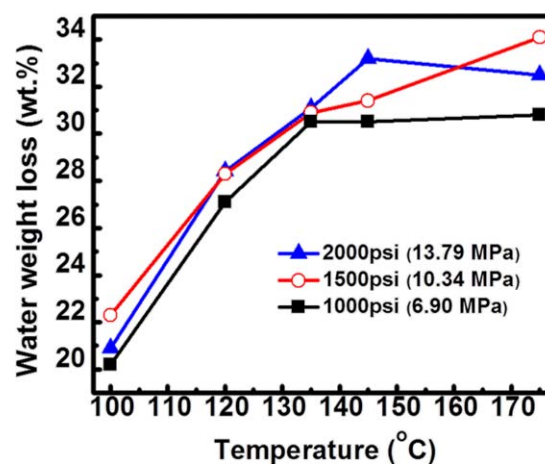


Figure 8. The water weight loss at different temperatures under various saturation pressures of pure PVOH with 31 wt % water. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

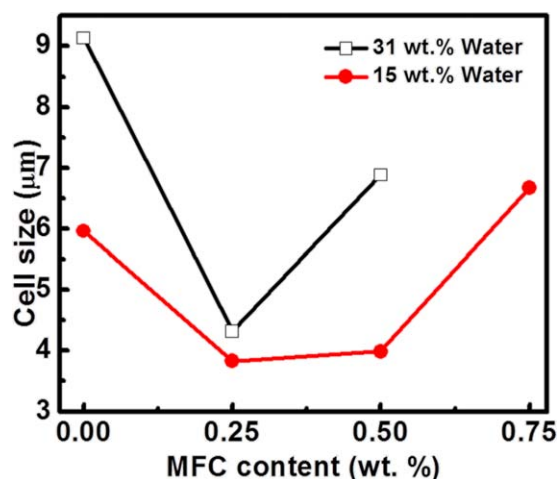


Figure 9. Cell size of PVOH/MFC composite foams as a function of MFC content with 15 and 31 wt % water at a foaming temperature of 175°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

because the water evaporates during the gas saturation stage at a high temperature. Figure 8 also shows that about 20–35 wt % water was lost from the PVOH sample with 31 wt % water during the batch foaming process. Figure 6 shows that with a high water content, the PVOH/MFC composite samples' expansion ratio and cell density increased.

Figure 9 illustrates the effect of the MFC content on the cell size of PVOH/MFC composite foams with 15 and 31 wt % water content. The cell size of the PVOH/MFC composite foam samples with a 31 wt % water content was larger than in those with a 15 wt % water content. The cell size first decreased and then increased with the added MFC content. This may have

been responsible for the increased stiffness with a higher MFC content. The excessive content of MFC may have created channels for the gas to escape between the MFC and the PVOH, as shown in Figure 1(b).^{18,50} Figure 10 shows the SEM micrographs for PVOH/MFC foams at a foaming temperature of 175°C.

Effect of the Saturation Temperature and Pressure on Foaming Behavior

Temperature is one of the most important parameters for foaming, especially for expansion control.³⁰ Figure 7 shows that the foaming temperature affected cell density and the expansion ratio. The peak cell density of the PVOH/MFC composite foams with 15 and 31 wt % water content was in most cases at 180°C and 175°C, respectively. Coincidentally, these are the same temperatures at which the maximum expansion ratio was obtained. This indicates that the PVOH matrix's high stiffness at a low temperature prevented the pressure change from propagating uniformly in the polymer matrix when the pressure drop was triggered during the foaming stage. As PVOH is a semi-crystalline polymer, small crystals and unperfected crystals are melted with increased temperature. Also, with increased temperature, the PVOH chains had sufficient energy to move and the free volume increased. This decreased the PVOH/MFC composite's stiffness. At low foaming temperatures, the PVOH/MFC composite's stiffness is too high and prevents cell nucleation and growth. On the other hand, at high foaming temperatures, the viscosity of PVOH/MFC composites decreases, and the chains' mobility increases. At too high a temperature, there may be cell coalescence because the melt strength is lower, and thermal degradation may occur.⁵⁸

Figure 11 shows the expansion ratio and cell density of neat PVOH foams with 15 wt % water at various saturation

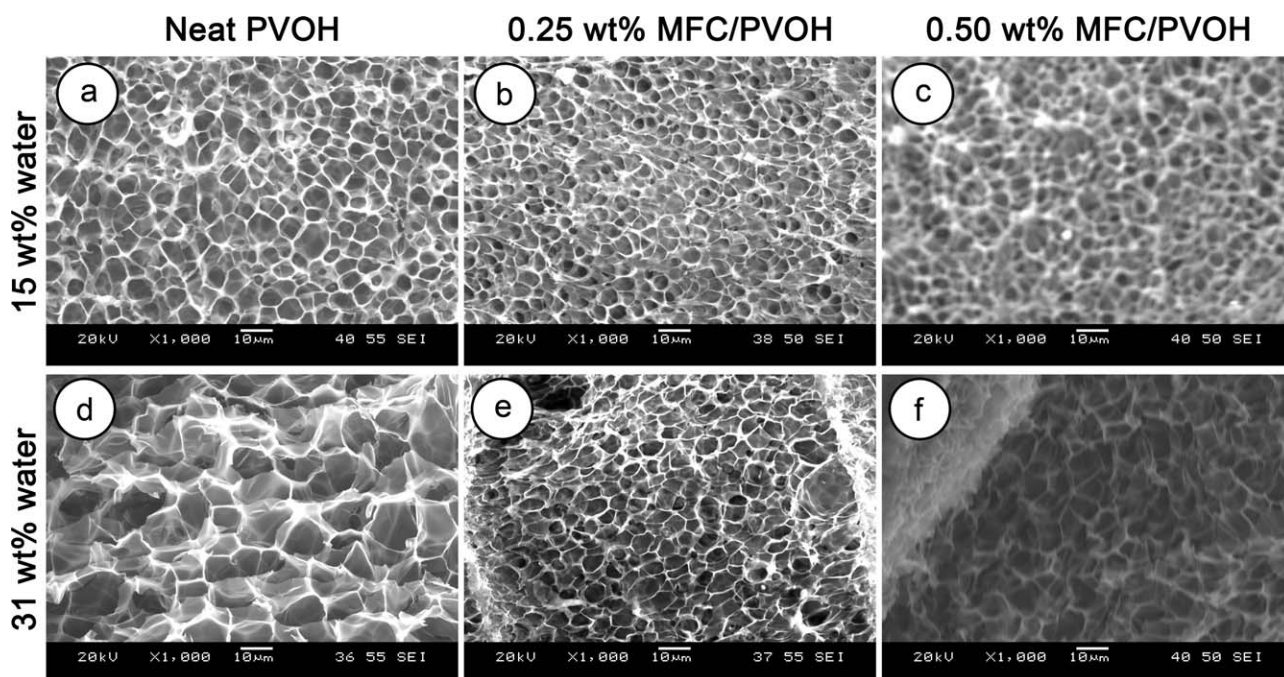


Figure 10. SEM micrographs of PVOH/MFC foams at a foaming temperature of 175°C: (a–c) 15 wt % water; (d–f) 31 wt % water.

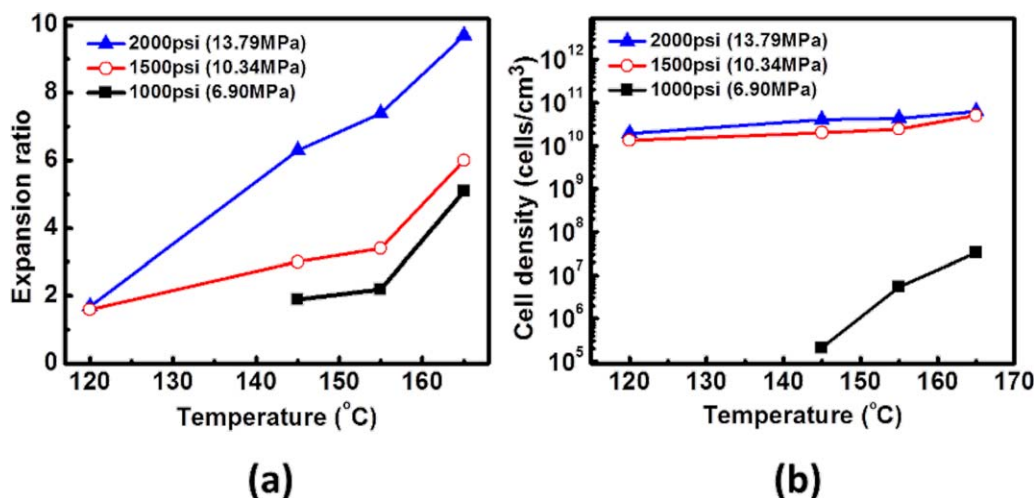


Figure 11. (a) The expansion ratio and (b) the cell density of neat PVOH foams with 15 wt % water content as a function of the saturation temperature at a few constant pressures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

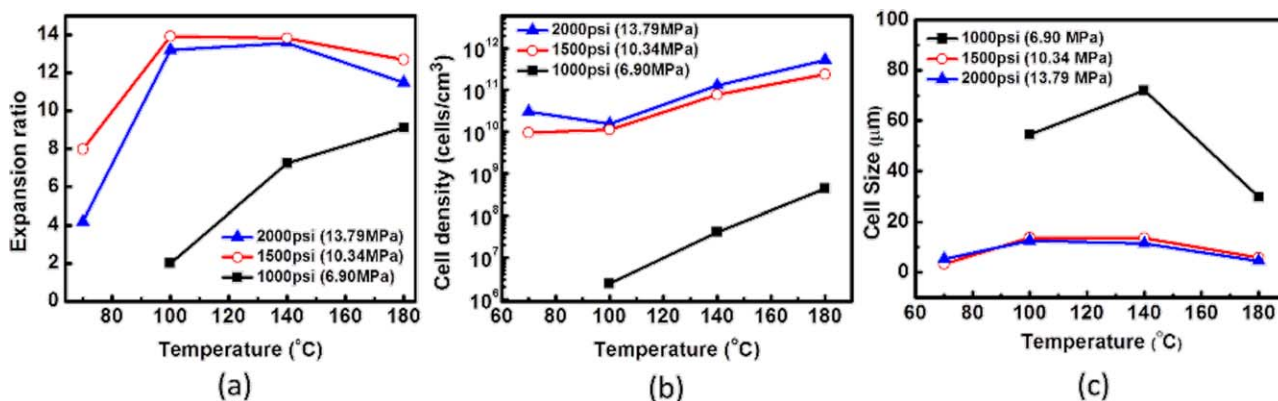


Figure 12. (a) The expansion ratio, (b) the cell density, and (c) the cell size of PVOH/0.25 wt % MFC composite foams with 31 wt % water content as a function of the saturation temperature at a few constant pressures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

pressures. With a higher scCO₂ saturation pressure, a higher expansion ratio and a higher cell density were observed. For example, the expansion ratio of neat PVOH at 165°C under 13.79 MPa scCO₂ was around 10. Compared with the 6.90 MPa scCO₂ foam sample, the 10.34 MPa and 13.79 MPa foam

samples of neat PVOH had a higher cell density. Figure 12(a) shows the expansion ratio, Figure 12(b) the cell density, and Figure 12(c) the cell size of PVOH/MFC foams with 0.25 wt % MFC and 31 wt % water under various scCO₂ saturation pressures. When the scCO₂ saturation pressure increases, the cell

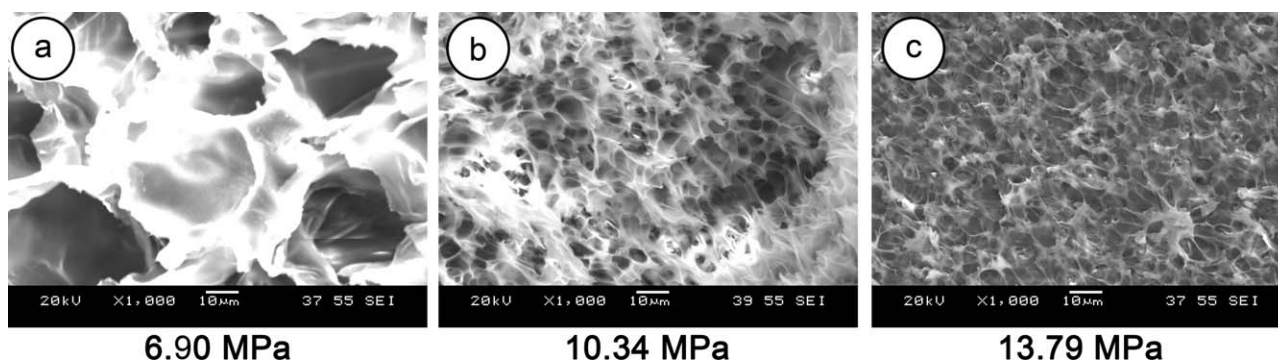


Figure 13. SEM micrographs of PVOH/0.25 wt % MFC foams with 31 wt % water content at a saturation temperature of 180°C: (a) 6.90 MPa, (b) 10.34 MPa, and (c) 13.79 MPa.

density increases and cell size decreases as more gas is available for cell nucleation. As the cell density increases, the cell sizes consequently decrease, resulting in more refined cell morphologies.^{58,59} Figure 13 shows the SEM micrographs of PVOH/0.25 wt % MFC foams with 31 wt % water at a foaming temperature of 180°C. The cell structure is uniform and the cell size decreased with increased saturation pressure.

CONCLUSIONS

High cell density microcellular PVOH/MFC composite foams with uniform cell morphology were achieved via a batch foaming system by using scCO₂ and water as co-blowing agents. The effects of water and MFC on foaming behavior and cell morphology were investigated. As a plasticizer, water improved cell growth and helped to maintain a stable cell structure. MFC used as a nucleation agent in PVOH affected the composites' cell nucleation behavior. The cell density increased by increasing both the water content and the saturation scCO₂ pressure in the examined range.

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