

Processing and Properties of Supercritical CO₂ Foamed Poly (Vinyl Alcohol)

HORNG-JER TAI¹, MING-YUAN CHENG²

^{1,2}*Institute of Biotechnology and Chemical engineering, I-Shou University*

Abstract- *In this study, polyvinyl alcohol was acetalized with formaldehyde under acidic conditions and foamed with supercritical CO₂ to obtain foam products. We then studied the effects of temperature, CO₂ pressure and formaldehyde concentration on properties such as foam density, swelling ratio and open cell ratio. It was found that the density decreased with increasing temperature, increasing CO₂ pressure, but increased with increasing formaldehyde concentration. The swelling ratio decreased as the formaldehyde concentration increased, which meant that an increase in formaldehyde concentration could effectively increase the degree of crosslinking. However, CO₂ pressure and processing temperature have no effect on the swelling ratio. The foam products obtained were mostly closed-cell type. The resulting open cell ratios were very low regardless of foaming temperature, CO₂ pressure or formaldehyde concentration.*

Indexed Terms- *Crosslink, Foam, Polyvinyl Alcohol, Supercritical Carbon Dioxide*

I. INTRODUCTION

Polyvinyl alcohol, PVA, is a biodegradable polymer that is completely soluble in water. PVA begins to rapidly decompose at 200°C, so PVA can not be used in traditional plastic processing technologies such as extrusion or injection molding. PVA foams have good biocompatibility, excellent water absorption capacity, sufficient durability, resistance to bacterial growth, high toughness and is easy to process. They are widely used in various fields, such as cleaning products such as mops or cleaning equipment for various surfaces, surgical foams, various tampons and wound drainage dressings, construction materials such as imitation wood building materials or lightweight foam building materials, and packaging materials such as biodegradable mulch films, etc.

The traditional method for producing PVA foams uses PVA aqueous solution with the addition of formaldehyde, acetaldehyde, butyraldehyde, glutaraldehyde or other aldehydes, the addition of hydrochloric acid, sulfuric acid or organic sulfonic acid as a catalyst, and the addition a foaming agent. The entire solution forms a stable froth under strong stirring and undergoes acetalization at 20-60°C. Finally, the temperature is raised in the mold to 80°C for additional 2-4 hours, and an open cell foam with a density of about 0.05 g/cm³ and high-water absorption capacity can be obtained [1]. There are three major foaming processes for producing cellular polymers [2,3]: bubbles within the polymer matrix can be generated by adding chemical or physical foaming agents or by mechanical stirring with the addition of surfactants. Physical foaming uses high-pressure gases such as nitrogen or highly volatile liquids (such as hexane) to be directly injected into the polymer melt during processing. During the pressure release process, the melt expands to achieve foaming. Chemical foaming uses chemical blowing agents which mix with the polymer melt and will decompose at high temperature to generate gases that dissolve into the melt. During the pressure release process, the melt expands to achieve foaming. Chemical foaming agents are substances that can be decomposed by heat to release gases such as carbon dioxide, nitrogen, etc. Mechanical foaming uses intensive mechanical agitation to evenly mix gas into the material in a high-viscosity liquid phase polymer/surfactant solution to form bubbles. In this study, a physical foaming method was adopted using supercritical carbon dioxide as the blowing agent. The clean characteristics of supercritical carbon dioxide foaming method are very ideal for producing foams used in biomedical products or semiconductor manufacturing processes [4,5]. The PVA acetalization reaction was carried out using hydrochloric acid as the catalyst. Acetalization helps to create crosslinks that hinder the segmental motion

of polymer chains and maintain bubble growth to a stable size. We then explored the variations in density, swelling ratio and open cell ratio after foaming under different temperatures, foaming pressures and formaldehyde dosages.

II. EXPERIMENTALS

A. Materials

Polyvinyl alcohol (PVA, BF-26, 98.5 – 99.2 % hydrolysed, Chang Chun Petrochemical Co.), formaldehyde (CH₂O, reagent grade, Shimakyu), hydrochloric acid (reagent grade, Shimakyu) were purchased and used as received.

B. Sample Preparation

In an Erlenmeyer flask, PVA/water/hydrochloric acid with a weight ratio of 10/89/1 was mixed completely and evenly in an oscillating shaker at 90°C and a shaking rate of 125 rpm for 6 h. The solution was left to stand to room temperature, then poured into a beaker. Different amounts of formaldehyde were added (1 g of CH₂O was added to 100 g of PVA mixture for each phr), stirred with a high-speed mixer for 1 h. Finally, the solutions were poured into a rectangular mold and placed in an oven at a reaction temperature of 60°C for 4 h. The reacted specimens were dried, then rinsed with clean water for 6 h, and then dried again. Each specimen was placed in a foaming mold fixed in a hot press for 30 min at the preset temperature. The high pressure supercritical CO₂ was injected into the mold at a specified foaming pressure. The specimen was kept inside the mold under constant temperature and pressure for 30 min. The mold was then open promptly to release the pressure. After the cell structure of the specimen reached a stable state, different tests and characterizations were performed

C. Characterization and Testing

The crosslinked samples were immersed in room temperature water for 24 h to swell. The swollen samples were removed from water, gently blotted with tissue paper to remove excess moisture from the surface, and weighed (W_s). The wet samples were dried in an oven at 60°C for 24 h and weighed (W_d). The swelling ratio was calculated as $(W_s - W_d)/W_d$. To measure the open cell ratio, the foam samples were soaked thoroughly in water and weighed to obtain

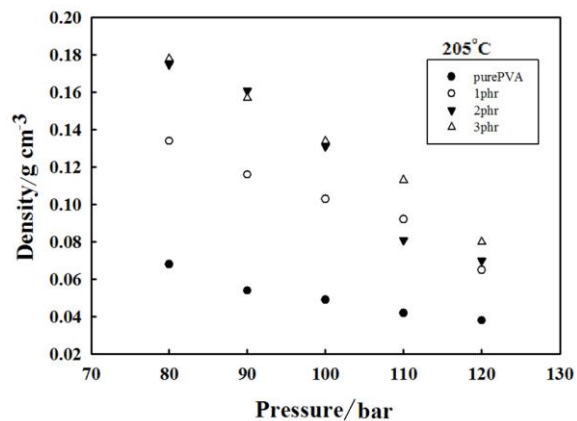


Figure 1. Foam density vs. pressure at different formaldehyde concentrations at 205°C.

the volume of the open pores. The open cell ratio was the ratio of the open pore volume to total pore volume. The total volume could be evaluated from the foam density values.

III. RESULTS AND DISCUSSION

A. Foam Density

Foam products with different densities have different properties and therefore have different applications. We want to know how different processing conditions and different formaldehyde concentrations will affect the density of the foamed product. When the foaming temperature is 205°C, as shown in Figure 1, the foam density decreases with increasing CO₂ pressure. This is to be expected as higher pressure means more CO₂ can be dissolved into the polymer matrix and therefore more gas can expand the foam. It can be seen that PVA foams without the addition of formaldehyde have larger foaming ratios and foam products with low foaming density are obtained. As the formaldehyde dosage increases, the density increases. This may be because as the degree of crosslinking increases, the mobility of the polymer chain decreases. The increase in extensional modulus restricts the expansion of the gas, resulting in the lower extent of bubble growth. The effect of foaming temperature on the foam density at a pressure of 110 bar is shown in Figure 2. The density clearly decreases with increasing temperature. At high temperatures, the mobility of molecular chains is higher and the resistance to gas expansion is lower, and the density of the obtained foams is lower. It

should be noted that the foam density does not seem to change with the

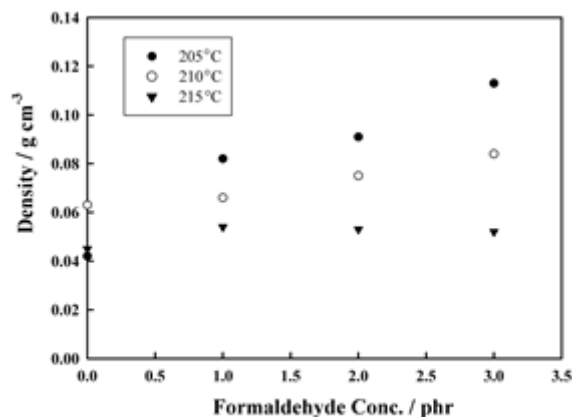


Figure 2. Foam density vs. formaldehyde concentration at different temperatures.

concentration of formaldehyde at high temperatures (215°C). Perhaps this processing system has reached the limit of its foaming ratio under this processing condition, and at higher temperatures, we would not be able to successfully obtain a good foamed product. In general, at low formaldehyde dosage, the structure was too soft due to insufficient acetalization, unable to support the foamed cells and shrank quickly, so the density would increase. However, if the formaldehyde dosage was too high, the polymer matrix would be too rigid and difficult to foam. We also found that adding different additives would destroy the crystallinity of PVA, plasticized the polymer, and effectively reduced the foaming temperature. For example, adding methacrylic acid could effectively reduce the foaming temperature to 180°C and the pressure range was 40 to 80 bar. When the foaming pressure was higher than 90 bar, the foam cells would not be able withstand the blowing gas and qualified foamed products could not be obtained. Adding urea could even reduce the foaming temperature to 160°C, and the pressure range was also 40 to 80 bar. When the foaming pressure was higher than 90 bar, the polymer matrix was too soft to withstand the blowing gas and the structure would break and was unable to support the foaming cells.

B. Swelling Ratio

When a polymer network is immersed in a good solvent, the solvent will diffuse into the network,

causing it to expand. The higher the degree of crosslinking, the lower the degree of network expansion, and the lower the amount of solvent that can be absorbed. Figure 3 shows the swelling ratio of crosslinked PVA under different processing

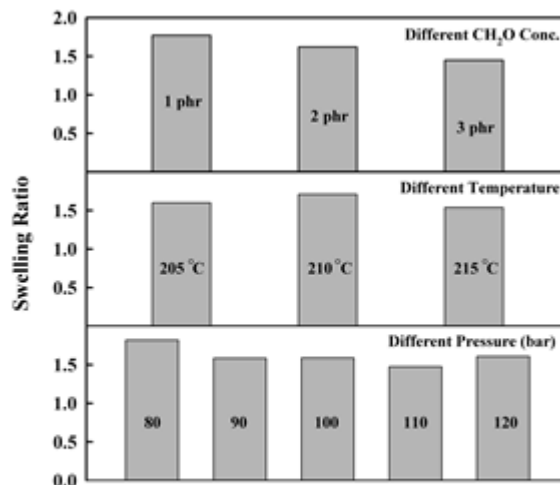


Figure 3. Swelling ratio vs. formaldehyde concentration, temperature and pressure.

conditions. Since the experimental data varied widely, we averaged a large amount of data to generalize the effects of individual processing conditions. It can be seen that the concentration of formaldehyde is the most influencing condition. The swelling ratio decreases with increasing formaldehyde concentration. This is expected because a higher amount of formaldehyde will result in higher levels of crosslinking. In contrast, processing temperature and foaming pressure have less effect on the degree of crosslinking. The reason why the effect of temperature is not so prominent may be that these reaction temperatures are already high enough to complete the crosslinking reaction. Generally speaking, these swelling ratio values are

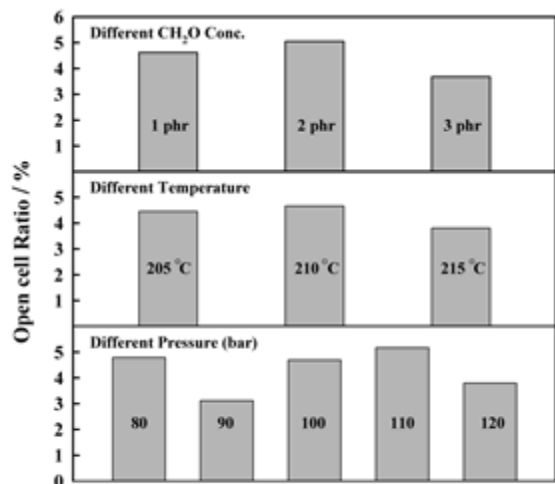


Figure 4. Open cell ratio vs. formaldehyde concentration, temperature and pressure.

quite low, indicating that the degree of crosslinking of these PVA compounds is very high.

C. Open cell Ratio

Open cell foam has excellent sound-absorbing acoustic properties, while closed cell foam has better cushioning properties. Figure 4 shows the open cell ratio of PVA foams under different processing conditions. All the foam open cell ratio values are lower than 10%, that is, they are closed cell foams. These values did not change in a specific trend with foaming temperature, CO₂ pressure or formaldehyde concentration. A possible reason is that the open cell values were so low that the changes caused by these conditions were below the errors of the experimental measurements and therefore did not present an observable trend.

REFERENCES

- [1] B. Xue, R. Li, J. Deng, J. Zhang, —Sound Absorption Properties of Microporous Poly (vinyl formal) Foams Prepared by a Two-Step Acetalization Method, *Ind. Eng. Chem. Res.*, vol. 55, no. 14, pp. 3982-3989, 2016.
- [2] I. Tsivintzelis, A. G. Angelopoulou, C. Panayiotou, —Foaming of polymers with supercritical CO₂: An experimental and theoretical study, *Polymer*, vol. 48, no. 20, pp. 5928-5939, 2007.
- [3] D. L. Tomasko, A. Burley, L. Feng, S. K. Yeh, K. Miyazono, S. Nirmal-Kumar, I. Kusaka, K. Koelling, —Development of CO₂ for polymer foam applications, *J Supercrit. Fluid*, vol. 47, no. 3, pp. 493-499, 2009.
- [4] J. A. Sarver, E. Kiran, —Fabrication Foaming of polymers with carbon dioxide – The year-in-review – 2019, *J Supercrit. Fluid*, vol. 173, article 105166, 2017.
- [5] J. J. A. Barry, H. S. Gidda, C. A. Scotchford, S. M. Howdle, —Porous methacrylate scaffolds: supercritical fluid fabrication and in vitro chondrocyte responses of Novel Synthetic Cryoprotectants, *Biomaterials*, vol. 25, no. 17, pp. 3559-3568, 2004.