

Production of Water-base polyurethane Microfoaming Matrix by Using Supercritical Carbon Dioxide

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ABSTRACT

The study was carried out by using supercritical carbon dioxide to prepare water-base polyurethane foaming matrix and to discuss the influence of foaming conditions such as temperature, pressure, depressurization rate and soaking time. Furthermore, the change of thermal conductivity was discussed in this study.

According to the experimental result, the temperature to make a water-base polyurethane foamed should be controlled above 40°C, and it shows the lower the temperature the foaming result was more obvious. In a further study, it found out that with an increasing depressurization rate, the foaming result more better. The comparison of cell density and cell size at different temperature and soaking time, it can be found that both characteristics increased with soaking time, but that decreased with temperature. In this study, the minimum cell size of foam material is 2.7 μm , and the maximum cell density is around 10^{11} cell/cm³. Under the temperature of 40°C, pressure of 4000psi, and the soaking time of 3hrs, the foamed matrix with thermal conductivity around 0.19W/mK can be obtained.

Keywords : Supercritical CO₂, Microfoaming, Water-base polyurethanes

1. INTRODUCTION

Microcellular forms are typically defined as having sizes on the order of 10 μm or less. It was developed by Martini et al.[1] at the Massachusetts Institute of Technology in early 1980s to reduce the materials consumption and increase the toughness of materials. Polymeric forms have been widely used because of their excellent properties such as light weight, high strength/weight ratio, superior insulating abilities, and energy-absorbing performance. Traditionally, polymers are formed by a variety of ways. In general, the common forming techniques are divided to chemical and physical forming. According to cheap and easy to operation, the forming technique developed an interested in physical forming. For long, the polymeric foams were blown mostly with chlorofluorocarbons (CFCs) that were phased out following concerns about the ozone depletion potential. Furthermore, CFCs were replaced by HCFCs of HFCs as blowing agents. Despite their improved ozone depletion, tighter restrictions were imposed on HCFCs of HFCs, due to concern the global warming effect, leading to a phase out schedule. Recently, two main types of alternative blowing agents has been developed: hydrocarbons (HCs) and nature gas such as CO₂ and N₂. For example, supercritical carbon dioxide (scCO₂) which is the most widely used in industry, due to cheap, nontoxic, and nonflammable and under ambient conditions makes its removal from the product every easily. The supercritical fluids (SCFs) have many desirable properties as both solvents and foaming agents including the tenability of the solvent power and the gaslike diffusivity; other unique properties of SCFs can be found in book by McHugh and Krukonis[2]. The environmental advantage of using scCO₂ for polymer forming stems from the fact that they may as a substitute blowing agent. The theory and method to generate microcellular polymeric foam has been reported by several reports during last tow decades (such as Colton and Suh[3-4], Kumar and Suh[5], Baldwin et al.[6-7], Goel and Beckman[8-10] etc.).

The purpose of this study is to present the forming of the water-base polyurethane with supercritical CO₂. Polyurethane products have many uses. Over three quarters of the global consumption of polyurethane products is in the form of foams. water-basaed polyurethane that use water as the primary solvent. It can be regarded as a environment friendly polyurethane product and rare article to study about foaming by supercritical fluid. The influence of foaming pressure, foaming temperature and soaking time on the foamed matrix morphology and properties is reported. Furthermore, the change of thermal conductivity with cell density are discussed in this study.

2. EXPERIMENTAL

2.1 Material

The anion type water-base polyurethane was provided from Sun-East Co., the form of solution. The glass transition temperature $T_g = -49.16^\circ\text{C}$ for hard segment and $T_g = 46.3^\circ\text{C}$ for soft segment were determined by differential scanning calorimeter. The molecular weight was analyzed by gel permeation chromatography GPC (Waters 2414), $M_n=54000$. The test matrix was prepared by drying the solvent. A 40mm×10mm and 3 mm thick was used as foaming sample. CO₂ (99/9%) was purchased from Yuan Ann, Taiwan.

2.2 Apparatus and Procedure

All the foaming experiments were carried in batch mode. The experimental apparatus is schematically shown in Fig.1. A cuboid of water-base polyurethane is closed in a 316 stainless steel high pressure vessel to soak at various foaming conditions until saturation conditions were reached. The vessel consists of three view windows to record the procedure of foaming and heat transfer jacket to maintain desired temperature. The vessel was preheated and filled with scCO₂ to desired operation condition. The temperature was controlled by using a circulating silicon oil thermostat bath. CO₂ from a cylinder with siphon attachment is passed through a cooling coil and compressed to the operating pressure by a high pressure diaphragm pump (LEWA, EK-1). At the end of foaming period, the vessel was depressurized at constant temperature. A wet flow meter (Ritter-TG1) was used to measure the rate of overall supercritical CO₂ delivered.

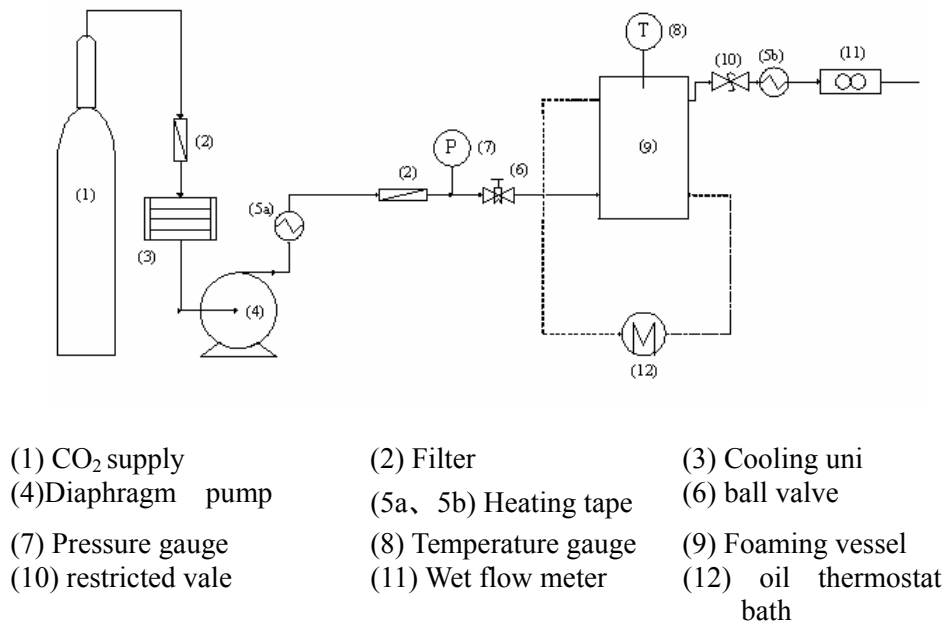


Fig. 1. Flow diagram of water-base polyurethane foaming process.

2.3 Characterization

Foamed water-base polyurethane matrix were fractured by using liquid nitrogen, each sample was cut to 10 mm×30 mm. these were studied under scanning electron microscope(JSM-5410, HITACHI) for a qualitative appraisal of the microstructures. The mechanical properties were measurement by using universal tester(TYPE 4482 , INSTRON).Density was measurement by using precisa 125A balance assembled with pycnometer kit. SigmaScan Pro image analysis software was used to measure the value of cell size. The number of cell were counted using the method suggested by Nam et al.[12].

3. RESULTS AND DISCUSSION

The important variables in our process are as following: (a) foaming temperature, (b) depressurization rate, (c) foaming pressure and (d). soaking time. The influence of these variables on the foam morphology was thoroughly studied to build the foaming process.

3.1 The effect of foaming temperature

In order to study the effect of temperature, water-base polyurethane was foamed at a series of temperature. Fig.2 presents the morphology of water-base polyurethane foamed matrix that were foamed under pressure of 4000psi and during 2hr at various temperatures 30°C, 40°C and 50°C, respectively. The effect of foaming temperature has direct influence on the morphology of foamed matrix. Despite the temperature above 40°C appears microcellular foam. In general, the foaming of polymer takes place above the T_g of polymer. Although the T_g of water-base polyurethane used in this study is 46.3°C for soft segment, but the T_g of polymer can be reduced by supercritical CO₂ was established. Thus, the result of water-base polyurethane should be best foamed at temperature 40°C is reasonable. The temperature under 50°C which was over the T_g, water-base polyurethane became soften, lead to bubble aggregated easily. Then the size of foam cell became large than that under 50°C. From the results, the better foaming temperature is between 40°C and 50°C. During this range, the cell size increases with a decrease of temperature. The result is consistent qualitatively with the previous researches such as Han et al.[12], Arora et al.[13], Reverchon and Cardea[14] etc. It was known that the higher temperature, polymer will be had higher plasticity. The factor leads to more supercritical CO₂ penetrated into the matrix. Furthermore, Arora et al.[13] suggested that the density of CO₂ decreases with a increase of temperature. This leads to a lower degree of swelling of matrix, allowing for fewer nuclei generated. In addition, increasing the temperature decreases the viscosity of the matrix, causing the retractive force restricting cell growth to decrease and the diffusivity of CO₂ within the matrix to increase. These factors lead to more rapid cell growth. Consequently, all the discussion in this work has been achieved at temperature 40°C.

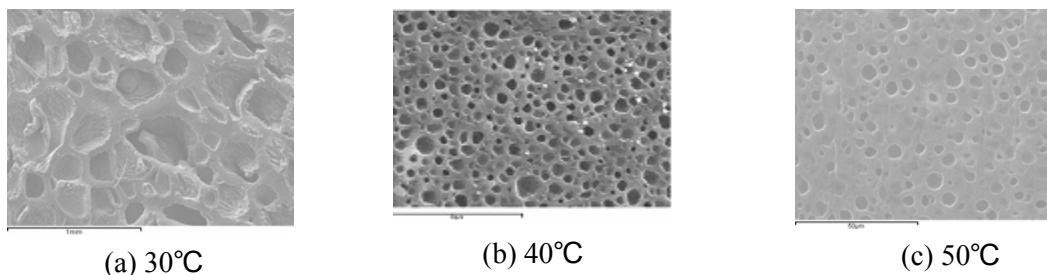


Fig. 2 SEM micrographs of the cross section of water-base polyurethane foamed matrix under various temperature.

3.2 The effect of depressurization rate

The influence of the decompression rate on the foam morphology has been studied at temperature and pressure of 40°C , 4000psi and during 2hr soaked. The obtained results are shown in Fig. 3 as depressurization rate 22 psi/s, 66.5psi/s and 133 psi/s, respectively. The results reveal an increase in pore size and uniformity with increasing depressurization rate. The significant change is between the depressurization rate 66.5psi/s and 133 psi/s. The homogeneous nucleation theory is generally used to explain these phenomena. Nalawade et al. [15] suggests that the energy barrier and the interfacial tension decrease as the pressure drop increases. Consequently, the nucleation rate increases and a large number of small cells were obtained. In fact, both the pressure drop rate and the magnitude of the pressure drop determine the cell density and cell size in microcellular foaming. The higher the pressure drop rate the greater is the nucleation rate due to the high supersaturation rate. This allows only a short time for existing cells to grow and, consequently, favors formation small cells. A similar result about influence of depressurization rate has been obtained for the polystyrene foaming by Arora et al.[13].

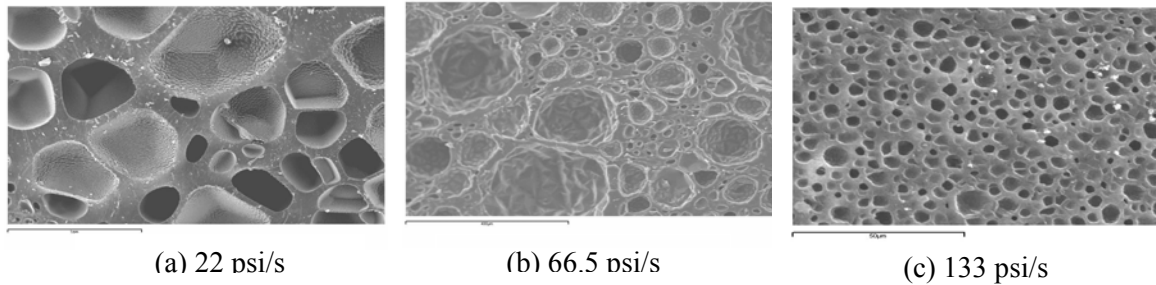


Fig. 2 SEM micrographs of the cross section of water-base polyurethane foamed matrix at various depressurization rate.

3.3 The effect of foaming pressure

The influence of foaming pressure on the foam morphology has been studied at constant temperature 40°C and during soaking time 2hr. The foam morphologies are shown in Fig.4. Fig.4 presents the foamed matrix that were foamed under various pressure 2000psi, 3000psi and 4000psi, respectively. The effect of foaming pressure has direct influence on the morphology of foamed matrix. Although the foamed matrix will not be formed completely at low pressure 2000psi, the pressure under 4000psi appears uniform microcellular foam. Furthermore, Fig.4 shows that cell size decreases with increasing foaming pressure. With increasing pressure, supercritical CO₂ will be liquidlike to enhance the solubility of supercritical CO₂ and reduce the energy barrier. According to homogeneous nucleation theory ([8], [16]) suggests that, the energy barrier for nucleation decrease with increasing foaming pressure, leading to higher nucleation density. This would result in smaller cell size. Consequently, all the discussion in this work has been achieved at pressure of 4000 psi.

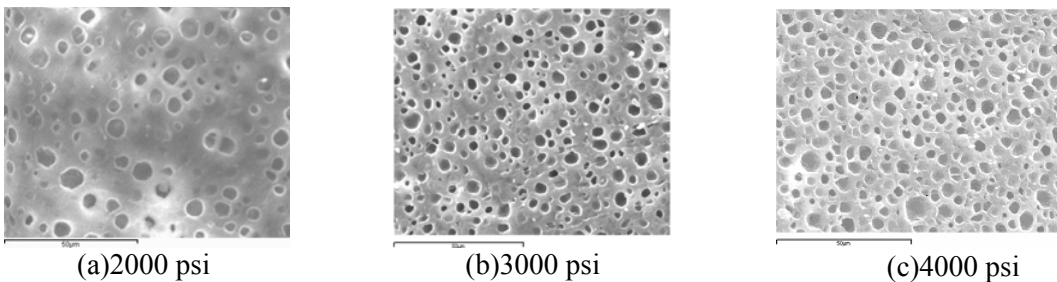


Fig. 4 SEM micrographs of the cross section of water-base polyurethane foamed matrix under

various pressure.

3.4 The effect of soaking time

In order to study the influence of soaking time on foam morphology, the soaking time was varied from 0.5 to 3 hr at temperature 40°C and under pressure of 4000psi. The morphology of water-base polyurethane foamed matrix is shown in Fig.5. The matrix formed completely seems onset from 2 hr. It is clear that the cell number increases with increasing soaking time and cell size decreases with increasing soaking time. Furthermore, the structure of foamed matrix expanded from both close and isolate to both open and connect. This results of which soaking time has contributed to the foam matrix structure as well as previous studies such as Goel and Beckman [8] and Xu et al.[16] etc..

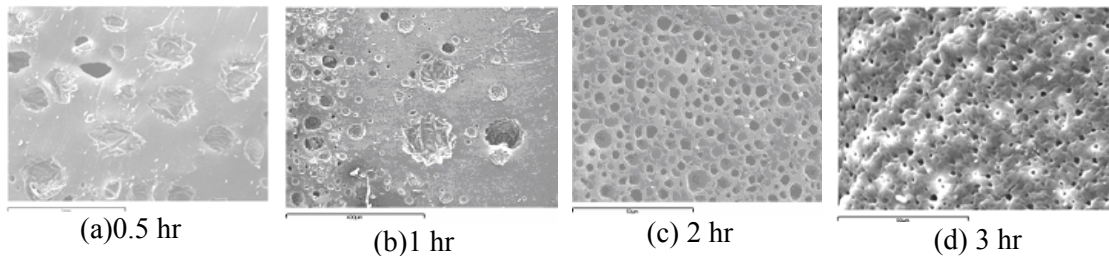


Fig. 5 SEM micrographs of the cross section of water-base polyurethane foamed matrix under soaking time.

The comparison of cell density and cell size at different foaming condition are summarized in Table 1 and Table 2. It can be found that both characteristics increased with soaking time, but that decreased with temperature. It may be caused by higher temperature, polymer will be had higher plasticity. The factor leads to growth of cell, then the number of cell in unit volume was reduced. Under the operation at 40 °C and during 3 hr, the max. cell density as 2.58×10^{11} and min. size as $2.7 \pm 0.31 \mu\text{m}$ can be obtained in this study.

Table 1 The comparison of cell density at different temperature and soaking time under pressure 4000psi and depressurization rate 133psi/s

Soaking time	Temp.	40°C	50°C	60°C
	Cell density (cell/cm ³)			
2hr		7.08×10^9	5.55×10^9	4.59×10^9
3hr		2.58×10^{11}	1.21×10^{11}	1.9×10^{10}

Table 2 The comparison of cell size at different temperature and soaking time under pressure 4000psi and depressurization rate 133psi/s

Soaking time	Temp.	40°C	50°C	60°C
	Cell size (μm)			
2hr		7.3 ± 2.25	8.7 ± 4.8	11.2 ± 3.59
3hr		2.7 ± 0.31	3.78 ± 1.15	6.85 ± 1.13

3.4 Thermal conductivity of the foamed matrix

The thermal conductivity of the original water-base polyurethane is 6.97W/mK. The property of foamed water-base polyurethane obtained at different conditions was shown as Fig.6. For all of the foamed materials, thermal conductivity was lower than that of the original matrix around one order. The thermal conductivity is inverse proportion with cell density, and the min. thermal conductivity is 0.19W/mK.

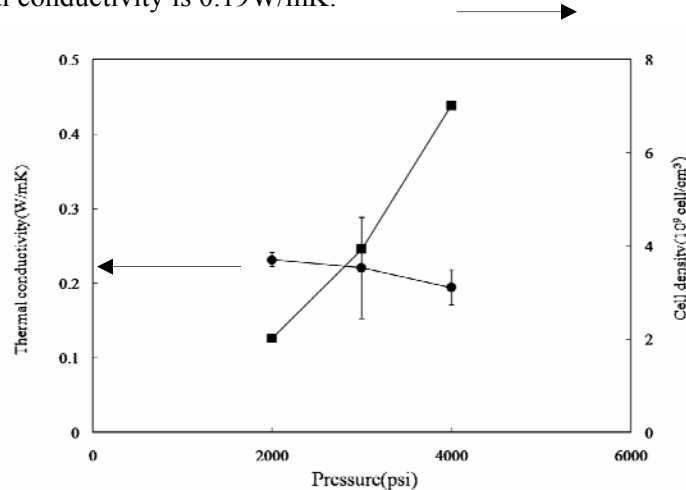


Fig. 6 The thermal conductivity change with cell density and pressure.

4. CONCLUSION

The foaming process using supercritical CO₂ was successfully applied to water-base polyurethane. The important foaming factors, viz., foaming temperature, depressurization rate, foaming pressure, and soaking time, were thoroughly discussed. The better foaming temperature is between 40°C and 50°C. The soaking time has a substantial influence on the morphology of the foamed matrix. With increasing soaking time, denser foamed matrix with smaller cell size was obtained. In this study, the minimum cell size of foam material is 2.7 μm , and the max. cell density is around 10^{11} cell/cm³. Both characteristics were satisfied the industrial specification for microcellular which size 20-70 μm and the cell density 10^9 cell/cm³. The thermal conductivity is inverse proportion with cell density, and the min. thermal conductivity is 0.19W/mK.

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