

Research article

Influence of different ratio of CO₂/N₂ and foaming additives on supercritical foaming of expanded thermoplastic polyurethane

Wei Peng Zhong, Zhen Yu, Tongyu Zhu, Yongxian Zhao, Ajit Dattatray Phule, Zhen Xiu Zhang* 

Key Laboratory of Rubber–Plastics, Ministry of Education/Shandong Provincial Key Laboratory of Rubber–Plastics, Qingdao University of Science and Technology, 266042 Qingdao, China

Received 21 July 2021; accepted in revised form 24 October 2021

Abstract. Expanded thermoplastic polyurethane (ETPU) foam materials with superelasticity for footwear application were developed and investigated. ETPU foams with different ratios of CO₂/N₂ as foaming agents and ETPU foams prepared by pure nitrogen foaming with different kinds of foaming additives were prepared by supercritical (Sc) foaming technology, which further made into sheet forms through the steam molding process. TPU foam exhibits better cell structure, crystallization performance, and mechanical strength with the increased CO₂ proportion. Further, the foams using 25% CO₂–75% N₂ and 50% CO₂–50% N₂, showed a lower density and excellent resilience and cyclic-compression performance. However, an increase of N₂ ratio improves the dimensional stability and compression set of the foam. The introduction of foaming aids enhances the interaction between Sc-N₂ and TPU. The ETPU foam prepared under the same conditions has a smaller density and a larger expansion ratio. Especially the ETPU foam prepared by Sc-N₂ using monofluorodichloroethane as the foaming assistant as a co-blowing agent, the decrease in cell size (from 117.9 to 19.6 μm) and density (from 0.175 to 0.139 g/cm³) has observed. The study revealed the high potential of these materials in footwear applications and offered sound evidence for mass production in the industry.

Keywords: mechanical properties, thermoplastic polyurethane, CO₂/N₂ blowing agent, footwear application, resilience

1. Introduction

In recent years, the research of foam material applied in sports shoes has received much attention due to the improvement of people's requirements for sports and life comfort. Expanded thermoplastic polyurethane (ETPU) foam has become a popular choice of polymer in this field due to its excellent mechanical performance. The mechanical and thermal properties of ETPU foam material depends on their microstructure, which is closely related to the foaming process [1–5]. ETPU foaming materials can be prepared by using different kinds of foaming agents, such as Azodicarbonamide, butane, and NaHCO₃ [6]. However, it is worth noting that most of these foaming agents

may lead to degradation of polymer matrix and degradation of performance of the material [7]. Supercritical (Sc) foaming has developed rapidly in polymer foaming as it is eco-friendly, which has become a popular process to prepare lightweight material [8–10]. As a foaming agent, Sc-fluid has the advantages of high efficiency, environmental protection and economy, adjustable solvent consumption, complete separation from polymer and so on. Carbon dioxide [11–14] and nitrogen [15–18] are often used as blowing agents, which are nontoxic, green, nonflammable and cost effective. Thus, it has been widely used in the foaming of plastics, rubber and elastomer. Among these two physical foaming agents, CO₂ has a high

*Corresponding author, e-mail: zhangzhenxiu@qust.edu.cn
© BME-PT

foam expanding ability. It has a strong diffusion rate and strong interaction with the polar groups in the polymer, which can induce the crystallization of the material and enhance the performance of the polymer matrix. However, N₂ has strong nucleation power and superior chemical stability [19, 20]. In the study of ETPU supercritical foaming, TPU has higher elastic shrinkage due to its low strength in the molten state. There are many other problems such as cell coalescence, the collapse of pores, less nucleation point, and high density in the process of foaming. Therefore, supercritical foaming of ETPU is a more challenging task in comparison with other conventional polymers. Wang *et al.* [5] controlled the foam structure of TPU by controlling temperature and CO₂ pressure, and the density range of TPU was 0.16–0.18 g/cm³. To solve these problems, along with enhancement in TPU foam properties, is one of the major concerns in the current research scenario.

Foaming aids, such as some small molecules, are aimed at regulating the foaming and lowering the pore size and/or density of the foams, and can significantly promote the nucleation rate of the foam, improve the cell structure, and the foaming efficiency and also act as a blowing agent. Foaming aids can be introduced through the simple process and process control without the need to modify the polymer, which has advantages in the preparation of high-porosity and high-performance foams [21, 22]. The synergistic effect of Sc-CO₂ with foaming aids and the ratio of Sc-N₂ to Sc-CO₂ have been a research hotspot. Chen *et al.* [23] studied the shrinking and aging behavior of TPU foams prepared by mixed CO₂-N₂ by experimental and simulation methods. However, the synergistic effect of Sc-N₂ and foaming aids is rarely reported. Due to the low solubility of Sc-N₂ in some polymers, slow diffusion rate, and poor foaming performance, finding appropriate foaming aids can help to improve foaming performance, foam structure, material performance, and reduce material density. Nistor *et al.* [24] used n-pentane (nC5) and cyclopentane (cC5) as foaming aids, pre-impregnated polystyrene (PS), and prepared microporous polystyrene foam using Sc-CO₂. The results of this study found that n-pentane and cyclopentane can significantly increase the porosity of the foam and improve the structure of the PS foam. The ionic liquid is a substance that is completely composed of specific anions and cations and it is liquid at a certain temperature. It has the characteristics of no vapor pressure,

electrical conductivity, hard to volatilize, good thermal stability, and recyclability [25, 26]. It has a good solubility for many inorganic salts and organic substances and has a good absorption capacity for CO₂. It can be used as a medium for separation and green reaction [27, 28]. The good dissolution and gas absorption of ionic liquid may play a positive role in the polymer foaming process. The fluorocarbon foaming agent is one of the commonly used physical foaming agents for polyurethane materials. Among them, monofluorodichloroethane has become the first choice for preparing foaming materials because of its high environmental protection, non-flammability, low boiling point and heat of vaporization, low surface tension, and high fluidity [29]. Therefore, in the current research experiment, we preferred using cyclopentane, ionic liquid (1-ethyl-3-methylimidazole hexafluorophosphate) and monofluorodichloroethane (HCFC-141B) as Sc-N₂ foaming auxiliaries. Further, the influence of three different foaming assistants on the density, cell structure, thermal properties, physical and mechanical properties and cyclic compression performance of TPU foam prepared with Sc-N₂ has been investigated. It is anticipated that the nucleation rate in the foaming process of TPU Sc-N₂ can be improved; the defects of small and uneven foam size, small foaming ratio and high density can be overcome.

2. Experimental section

2.1. Materials

Thermoplastic polyurethane (TPU9385AU DPS350), received from Covestro Polymers, Germany, which had a specific density of 1.12 g/cm³ and a hardness of Shore 86A. The N₂ and CO₂ with a purity of 99.99% were obtained from Qingdao Tongda Air Co., Ltd, China. Cyclopentane, purchased from Tianjin Damao. Monofluorodichloroethane, purchased from Dongguan Qixing Chemical Co., Ltd. Ionic liquid, purchased from Onstar New Carbon Material Changzhou Co., Ltd.

2.2. Samples preparation

2.2.1. Preparation of ETPU foam

Preparation of ETPU Foam with different ratios of CO₂-N₂. First of all, TPU was dried at 80 °C for 4 h (Constant temperature oven, 101/0A, Nanjing Jayent Company). 400 g TPU pellets and 1.5 l water were enclosed in a high-pressure vessel equipped with a heating system (Self-made). The parameter of the

stirring system was set to 300 rpm. The water was used as a medium to transfer heat and even dispersion of TPU. After which, gas (CO_2 or N_2 or a different gas mixture) was charged into the vessel to obtain the desired pressure. Then the chamber was heated to the set foaming saturation temperature (in the range of 120–140 °C). In the next step, the depressurization occurred by opening the shut-off valve (<1 s), and the TPU foams were obtained in the receiving device. Figure 1 is a schematic description of the supercritical foaming and the steam molding process. Figure 1a is a schematic description of the supercritical foaming. In order to control the experimental variables and explore the influence of different gas components on ETPU, it is necessary to ensure that the saturation time is 80 min along with the same foaming pressure. The final density of ETPU foam particles prepared under different gas components was within $0.15 \pm 0.03 \text{ g/cm}^3$ by adjusting the foaming temperature. In the process of supercritical foaming of TPU, there is a suitable foaming temperature called as foaming window, which is vital for the foaming. In this experiment, the best foaming window was found under four different gas conditions. As shown in Table 1, the foaming window required for pure CO_2 foaming is relatively low. With the increase of N_2 content in the gas component, the temperature of the foaming window increases gradually. ETPU foam with different foaming additives was prepared. 400 g of dried TPU particles, 1.5 l of water, and 20 g of foaming aid (cyclopentane/monofluorodichloroethane/ionic liquid) were enclosed in a

Table 1. ETPU/Sc- CO_2 - N_2 experimental matrix and foaming conditions; gas composition, T_{foam} (foaming temperature), and p_{foam} (foaming pressure).

Sr. No.	Composition [%]		T_{foam} [°C]	p_{foam} [MPa]
	Sc- CO_2	Sc- N_2		
1	100	0	122	12
2	50	50	130	12
3	25	75	134	12
4	0	100	138	12

high-pressure vessel. Turned on the control box and set the stirrer speed to 300 rpm, checked the airtightness after passing in N_2 and exhaust 2–3 times. The temperature and pressure in the reactor were controlled by the control box and the gas booster pump. The foaming temperature was 138 °C, the saturation and foaming pressure kept 12 MPa, and the saturation time was 80 min. The pressure (<1 s) was released quickly after meeting the conditions of the foaming process and collected the ETPU foam particle samples, cleaned the samples and dried in a ventilated place.

2.2.2. Steam chest molded ETPU samples

Figure 1b shows the schematic for the steam molding process. ETPU foam sheet was prepared by using steam chest molding equipment. The mold consists of a fixed side and a moving side. Both of the mold sides have ports for the injection of steam into the mold cavity. The basic process of steam chest molding process consists of three main steps. In the first step, the beads are charged into the mold cavity by using

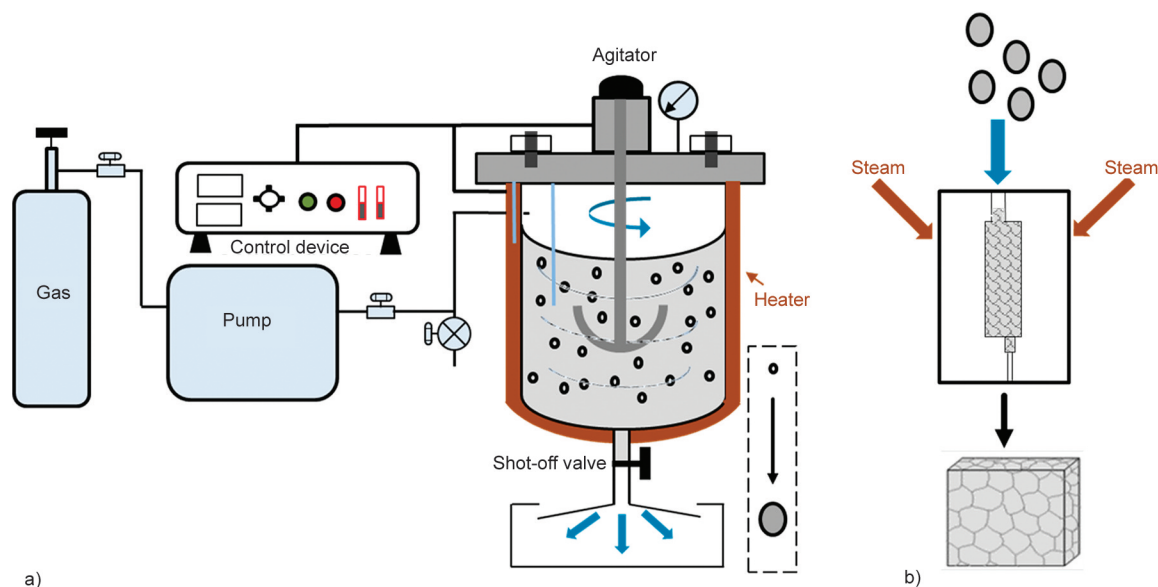


Figure 1. Schematic description of (a) the supercritical foaming and (b) the steam molding process.

a negative pressure of -0.09 MPa. The charging rate depends on the distance between molds, and the parameter used in this study was 17 mm. In the second step, the steam was injected from the fixed mold at the desired processing steam pressure (2.3 MPa) for 20 seconds. Then the steam was injected from the moving mold (2.3 MPa pressure, 20 seconds). Finally, the steam injected from both molds with 2.3 MPa pressure for 30 seconds followed by depressurization. The third step consists of cooling the mold with water for about 80 s followed by vacuuming to remove the remnant water, and then the sample was ejected.

2.3. Characterization of different ETPU foam materials

2.3.1. Physical and mechanical property

The density of different ETPU foam materials was measured using the water displacement method according to ASTM D792 (Density meter, GTXB320M, Gotech Testing Machines Co., Ltd.). The volume expansion ratio was calculated by the measured foam density with the Equation (1):

$$\phi = \frac{\rho_{\text{polymer}}}{\rho_{\text{foam}}} \quad (1)$$

where ϕ is volume expansion ratio [%], ρ_{polymer} and ρ_{foam} are the densities [g/cm^3] of the non-foamed and foamed ETPU samples, respectively.

The Shore C hardness (Shore Hardness Tester Type C, GS-MBI, Gotech Testing Machines Co., Ltd.) and resilience of the specimens (MTS Elastomer Test System, 831.50, Gotech Testing Machines Co., Ltd.) were measured by ASTM D2240-2015 and ASTM D3574-2017, respectively. All the measurements were carried out at room temperature and the average value reported was derived from at least five measurements.

HG/T2876-2009 test standard is used to test the compression set of ETPU foam sheet (Permanent compression distortion tester, GW-059, GuoFeng Testing machine Co., Ltd.). Testing the height before and after compression, calculated according to the following formula (Equation (2)):

$$K = \frac{H_0 - H}{H_0} \cdot 100\% \quad (2)$$

where K is the compression set [%]; H_0 is the thickness of the sample before compression [mm]; H is the thickness after parking at the end of the compression test [mm].

Tensile and tear testing

In order to test the strength and quality of ETPU, The tensile testing and tear testing of the ETPU samples were performed in a universal testing machine (AI-7000S, Gotech Testing Machines Co., Ltd.) following GB/T528-2009 and GB/T529-2008. The tensile properties such as the modulus and the tensile strength were tracked at a tensile speed of 500 mm/min. For these tests, the average value was used in this work were obtained from at least five samples. Before testing, all samples were conditioned at 23 ± 2 °C with $50 \pm 10\%$ RH for 24 h.

2.3.2. Foam structure

Cell morphology and structure were analyzed using a scanning electron microscope (SEM JSM-7500F, JEOL). The vacuum chamber pressure is maintained at 0.5 torr and the acceleration voltage is set to 20 kV. To prepare the SEM samples, first the ETPU was cut with a thin blade, and the fracture surface of samples was coated by gold to enhance conductivity. The image processing software Image-Pro plus 6.0 was used to calculate the average cell diameter (D) and cell density (N_0) (Equations (3) and (4)):

$$D = \frac{\sum d_i n_i}{\sum n_i} \quad (3)$$

$$N_0 = \left(\frac{n}{A}\right)^{\frac{3}{2}} \cdot \phi \quad (4)$$

where n_i is the number of cells calculated, d_i is the diameter [μm] of every cell. ϕ is the expansion of ETPU. n is the number of cells in the SEM image, and A is the area [cm^2] of the image region.

2.3.3. Shrinkage properties

The shrinkage ratio was calculated by the initial expansion ratio measured after pressure released and final expansion ratios measured at 168 h after pressure released (Equation (5)):

$$S = \frac{\phi_i - \phi_f}{\phi_i} \cdot 100\% \quad (5)$$

where S is shrinkage ratio [%], ϕ_i , ϕ_f are the initial and the final expansion ratios [%] of ETPU, respectively.

2.3.4. Thermal property

The thermal behaviors of different ETPU bead foams were studied by differential scanning calorimeter (DSC) measurements (DSC204C, NETZSCH

Scientific Instruments Trading (Shanghai) Ltd.). For each measurement, a 5 to 10 mg specimen was scaled in an aluminum pan and the melting temperature (T_m) and the enthalpy of fusion (ΔH_m) were measured by heating the foamed samples from 25 to 220 °C (without eliminating thermal history) at the heating rate of 10 °C/min in a N₂ environment.

2.3.5. Solubility and desorption property

The desorption behavior of the blowing agent was determined by the gravimetric method. First of all, TPU samples were molded and cut into 40 mm × 40 mm × 4 mm dimensions, then placed in a high-pressure vessel after drying in an oven at 80 °C for 6 h. The different gas components (100% CO₂; 75% CO₂–25% N₂; 50% CO₂–50% N₂; 25% CO₂–75% N₂; 100% N₂) was injected in vessel, the saturation condition was 15 MPa pressure, 120 °C temperature for 4 h. After pressure release, the sample was put on the analytical balance quickly and recorded the data. The diffusion coefficient (D), adsorption capacity (m) of blowing agent, and time (t) fit to the Equation (6) [21, 22]:

$$\frac{m_t}{m_0} = 1 - \frac{4}{d} \left(\frac{Dt}{\pi} \right)^{\frac{1}{2}} \quad (6)$$

where m_t is the total adsorption concentration of blowing agent at time t , m_0 is fitted from the desorption curve by linear extrapolation, and d is the thickness of the sample.

2.3.6. Cyclic compressive testing

Cyclic compressive testing can evaluate the mechanical state and elasticity of elastomer foam under cyclic compression, which was tested with the MTS 831.50 (Gotech Testing Machines Co., Ltd.) elastomer test system. The testing can simulate the frequent pressure of foam in the middle of shoes while running and standing. The mode with a thousand loading-releasing cycles was used. The diameter of the test sample was 50 mm, and the thickness was 16 mm. Testing procedures were designed as follows: (1) Loading: the initial load was 0 N, and the maximum load was 1400 N; the sample was loaded to 1400 N in 100 ms. (2) Releasing: the load was reduced to 0 N in 100 ms after loading. (3) Cycle: the cycle time for each load-release process was 710 ms, and the sample needs to go through 1000 cycles. The corresponding stress and strain were recorded

at different moments. The Origin software was used to draw the compression curve.

All the tests were carried out at room temperature (20±3 °C) with humidity between 50±10%, and the specimen thickness was 16 mm. Moreover, to avoid the effects of the residual gas and the environmental condition change on measurements, all samples were placed in the required environment for more than a week before testing.

2.4. Statistical analysis

Statistical data analyses were performed by using Origin 8.0 software (Origin Lab, Massachusetts, USA). One-way ANOVA method was used to determine significant differences between sample means, where the level of significance was set at $p < 0.05$. All data from the multiple separate experiments were expressed as the mean ±SD.

3. Results and discussion

3.1. Diffusion behavior and solubility of blowing agents

It is vital for the preparation of foaming materials that the solubility and desorption rate of blowing agent, which affects the nucleation and growth of cells, the saturation time of batch foaming, as well as dimensional stability [23–25]. In this experiment, the pure TPU sample with 40 mm × 40 mm × 4 mm dimension was saturated with five gas components under the condition (120 °C temperature, 15 MPa pressure for 4 h), then the pressure was rapidly released and the mass was measured by the analytical balance.

Because TPU had a mass loss from the depressurization to weighting, the desorption curve was determined from 40 s. Figure 2 shows the desorption curve of ETPU with different gas components. The solubility of gas components can be approximately measured (as shown in Table 2) by using ORIGIN for curve fitting. It can be seen from the chart that the gas desorption rate and the gas solubility increase and accelerate with the increased CO₂ content in the blowing agents. The desorption process can be divided into three stages: rapid diffusion stage of 0–100 s, stable diffusion stage of 100–90 000 s, and slow diffusion stage. The formation of rapid diffusion stage is due to the fact that gas is dissolved on the surface of the ETPU sample under high pressure put the value with dynamic equilibrium. After pressure

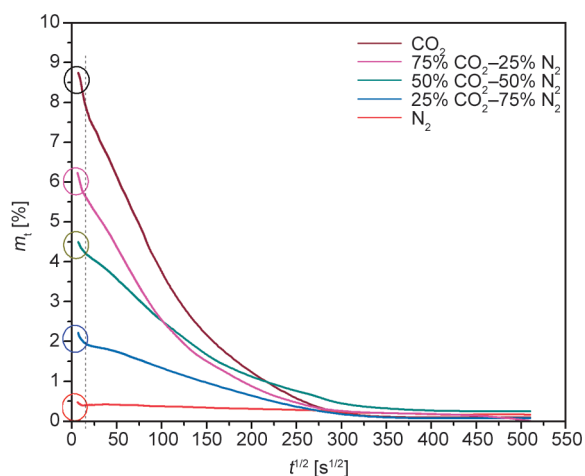


Figure 2. Desorption curves of different ratios of CO₂-N₂ in ETPU.

Table 2. Solubility of different ratios of CO₂-N₂ in ETPU.

Gas component	Solubility (total blowing agent/100 g polymer) [g]
100% CO ₂	9.57
75% CO ₂ -25% N ₂	6.75
50% CO ₂ -50% N ₂	5.38
25% CO ₂ -75% N ₂	2.45
100% N ₂	0.56

drops, they escape rapidly from the surface. The stable diffusion stage is the diffusion of gas dissolved in the ETPU sample, which fits Fick’s diffusion law. The slow diffusion stage is the last stage, while most of the gas has diffused from the material matrix and the mass of the sample is close to the initial mass. The desorption curve illustrates that the desorption rate of N₂ is much lower than that of CO₂, which is of great significance to the study of the dimensional stability of foamed materials.

The solubility of CO₂ is much higher than that of N₂ at the same temperature and pressure conditions. The N–H bond in the urethane groups and oxygen atoms in CO₂ will form intermolecular hydrogen bonds, which are stronger than that between the non-polar nitrogen atoms in N₂ and the N–H bonds. Meanwhile, CO₂ has a better affinity with polar polymers. If the blowing agent has good solubility, it will be more conducive to the formation of the homogeneous system (polymer/Sc-fluid) in the foaming process, which helps to improve the nucleation density.

High-pressure Sc-CO₂ is also often used for the devolatilization of polymers (*i.e.* extraction of impurities from polymers) because of its higher solubility and faster diffusion rate. However, the rapid diffusion of

CO₂ is also the key reason for the shrinkage of ETPU foam.

3.2. Density change and Shrinkage ratio of ETPU prepared with different ratios of CO₂-N₂

Figure 3 shows the density change of the ETPU in a week after foaming. Obviously, the density of ETPU foamed with pure CO₂ began to increase gradually after foaming, reaching 0.24 g/cm³ after 3 h of foaming; later it has started decreasing and stabilizing with the extension of time. However, the density of ETPU changed more smoothly with the increase of N₂ content in the blowing agents, especially for the ETPU foamed with 100% N₂, where the initial density and final density basically did not change significantly. But the density of 100% N₂ foamed sample is relatively high, about 0.175 g/cm³. From the final density of the four samples, the density of ETPU prepared by 50% CO₂-50% N₂ and 25% CO₂-75% N₂ is smaller, which is 0.115 and 0.134 g/cm³.

Figure 4 shows the shrinkage ratio of ETPU with different ratio of CO₂/N₂. The shrinkage rate of ETPU decreases with the increase of N₂ content. The shrinkage rate of 100% CO₂ is as high as 24.3%, 25% CO₂ + 75% N₂ is 2.8%, and 100% N₂ is only 1.1%. The changes in the morphology of ETPU foamed with 100% CO₂ has shown in Figure 5.

These phenomena are mainly caused by the difference of the diffusion rate of CO₂ and N₂ in the polymer. After foaming, CO₂ escapes and diffuses rapidly from the cell, and air cannot enter into the cell quickly, which creates a negative pressure that the strength of the cell cannot support. The cell of ETPU will temporarily collapse, and the density increases

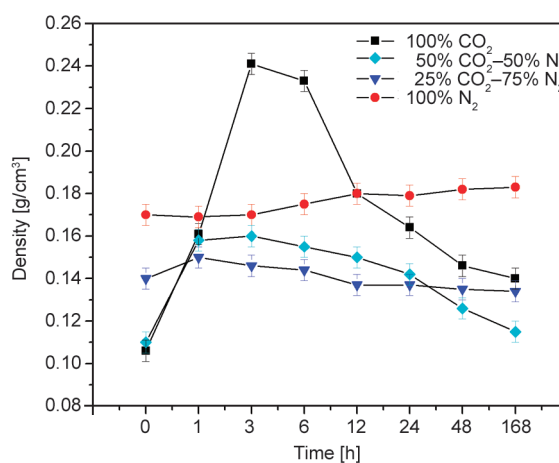


Figure 3. The density of ETPU foams with different ratios of CO₂-N₂.

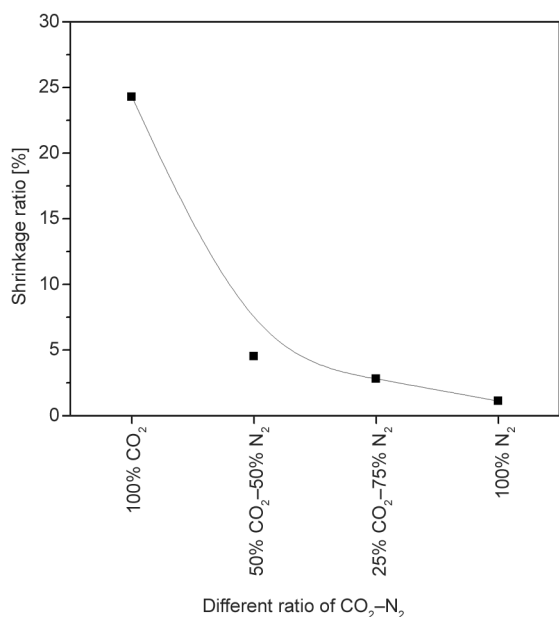


Figure 4. The shrinkage ratio of ETPU foams with different ratios of CO₂-N₂.

abruptly. As time goes on, air will enter into the cell to support the cell and expand the cell again, which makes density to get dropdown. However, the properties and diffusion rate of N₂ and air are similar; there is no negative pressure without replacement or imbalance of gas. Although CO₂ can be used to produce highly expanded ETPU foams, the lower shrinking ETPU foam can be obtained by using N₂.

The use of mixed gas can reduce shrinkage while preparing low-density foam products.

3.3. Cell structure analysis of ETPU prepared with different ratios of CO₂-N₂

Figure 6 shows the cellular morphology of the ETPU foamed by different gas components. There are obvious differences in the cell structures between the ETPU foamed with 100% N₂ and others. The ETPU foamed by 100% N₂ (Figure 6b) shows larger cell size, disordered cell shape, and thick cell walls. The solubility of the blowing agent determines the density of nucleation [21]. On the other hand, solubility and diffusivity of N₂ are worse than CO₂ in TPU at the same pressure and saturation time, which leads to a low density of nucleation. On the other hand, the higher temperature reduces the resistance of bubble expansion, which makes competition between the bubbles weaker. The two effects finally lead to the results of large bubble size, smaller bubble density, and wall thickness of the bubbles.

Figure 7 shows a plot of cell diameter and cell density of the ETPU foam with different CO₂-N₂ ratios. The cell density and the average cell size have obvious dependence on gas content when the CO₂ content increases in the blowing agents, the average cell size and cell wall thickness decrease significantly,

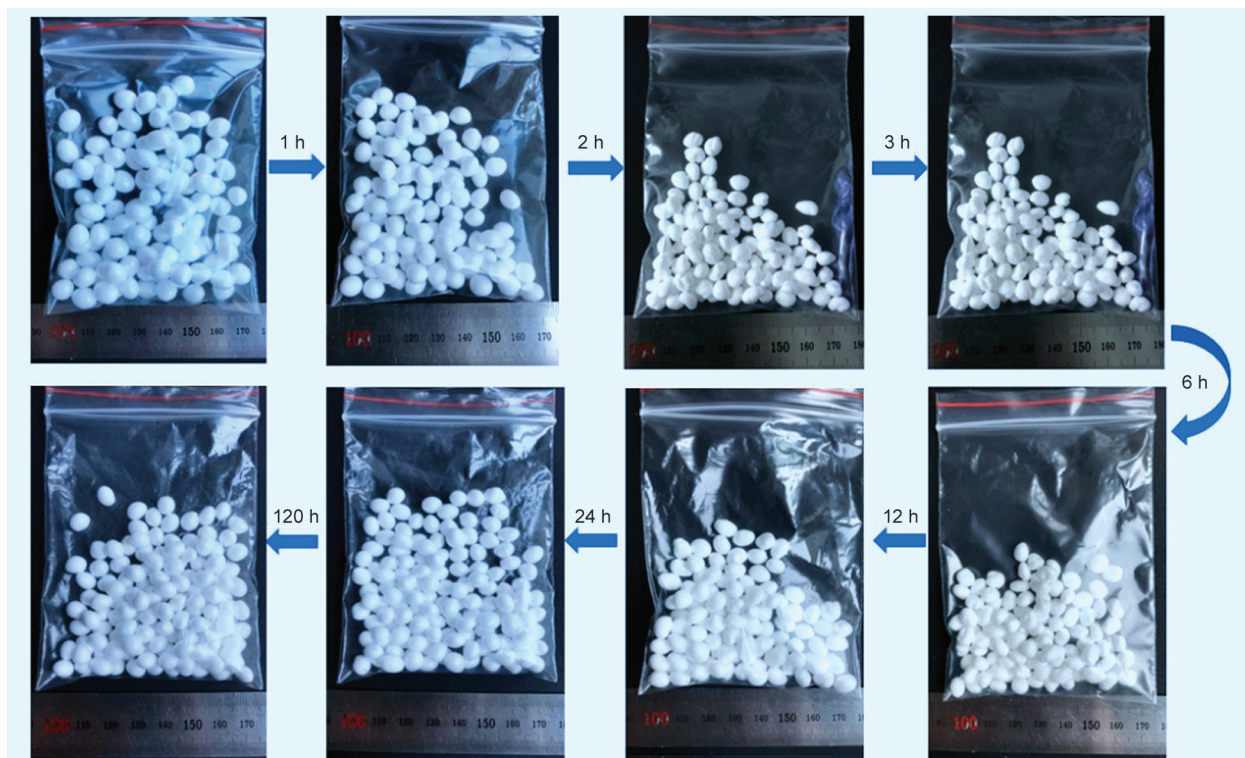


Figure 5. Change of ETPU morphology after foaming via Sc-CO₂.

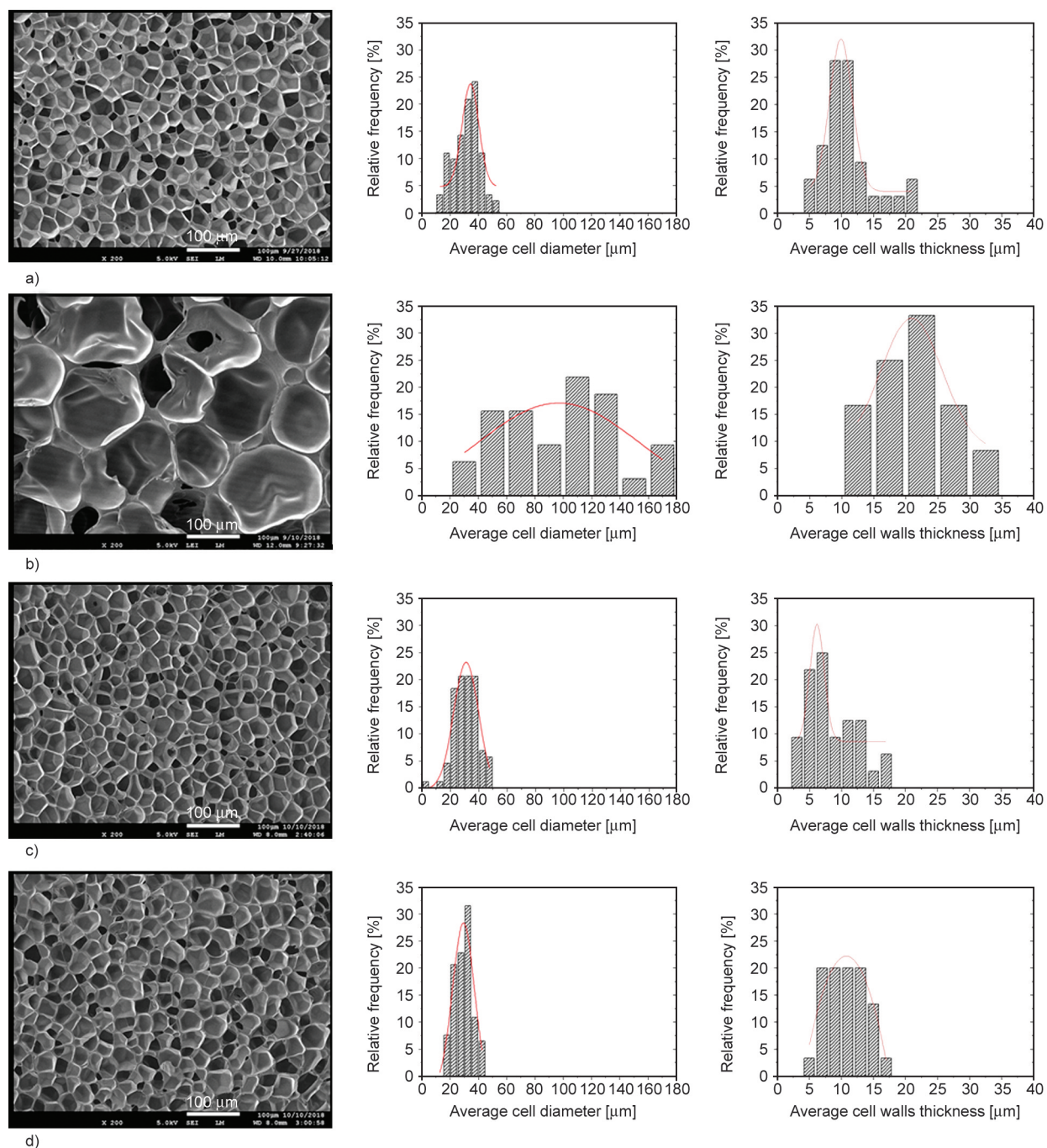


Figure 6. The SEM images (left), average cell diameter (middle) and average cell walls thickness (right) of the ETPU foamed by (a) 100% CO₂; (b) 100% N₂; (c) 50% CO₂-50% N₂; (d) 25% CO₂-75% N₂.

where the cells show a homogeneous polygonal structure with the improved cell density and nucleation – those phenomena related to the effect of CO₂ on polymer. Sc-CO₂ can also make TPU swelling similar to solvent, which promotes the increase of polymer's free volume and plays a certain role in plasticization. It is beneficial for foaming to reduce the energy barrier, which is required in the process of bubble nucleation and growth. Meanwhile, CO₂ can assist in permeation [11], which is beneficial to the increase

of solubility and diffusion adsorption rate of other small molecules (such as N₂), and improving the foaming performance of the TPU. As a result, (1) increased nucleation points at the stage of cell nucleation; (2) at the stage of cell growth, the expand resistance decreases, and the competition between cells is fiercer; (3) improved the foaming property of material matrix. For foaming system, a small amount of CO₂ (e.g., 25% CO₂-75% N₂, Figure 6d) can be used to obtain microporous materials with better cell

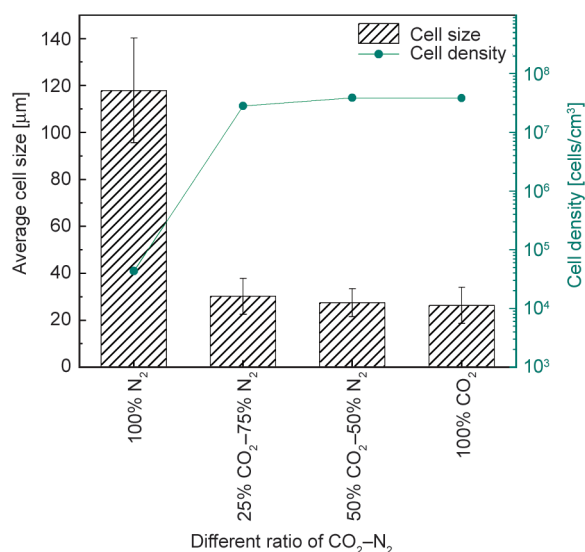


Figure 7. The cell size and cell density of ETPU foam at different ratios of CO₂-N₂.

structure. With the increase of CO₂ in the gas component, the final effect does not change significantly (e.g., Figure 6a, 6c and 6d), but it affects the density and shrinkage stability of the materials.

3.4 Thermal property analysis of ETPU prepared with different ratios of CO₂-N₂

Figure 8 shows the DSC heating thermograms of the various ETPU bead foams (without eliminating thermal history). Table 3 summarizes the melting temperature (T_m), melting range and the heat of fusion (ΔH_m). The difference of melting peaks was associated with the melting of the hard segment crystalline domains [26, 27]. T_m and crystallization of samples are affected by different gas compositions. Obviously, the heating curves of four ETPU samples showed

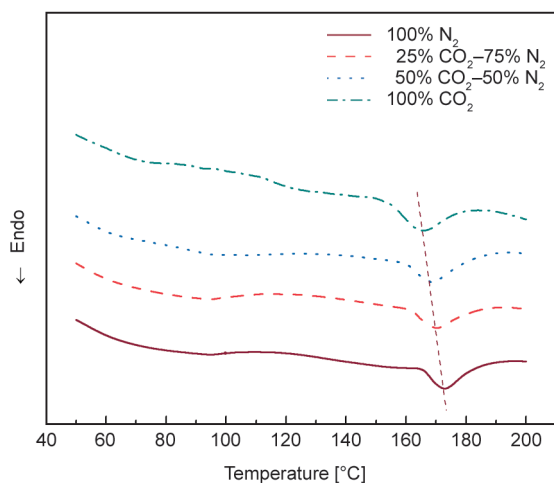


Figure 8. The DSC heating curve of ETPU foams by using different ratios of CO₂-N₂.

Table 3. The thermal parameter of ETPU samples with different ratios of CO₂-N₂.

Samples	T_m [°C]	Melting range [°C]	ΔH_m [J/g]
100% CO ₂	165.6	29.0	2.683
50% CO ₂ -50% N ₂	169.1	24.9	2.366
25% CO ₂ -75% N ₂	170.2	28.3	2.221
100% N ₂	173.0	18.6	1.779

a single melting peak. The ETPU foamed by 100% N₂ had a high T_m of about 173.0 °C and a low ΔH_m of about 1.779 J/g. However, with the increase of CO₂ in the blowing agents, the T_m of the ETPU sample decreases, the melting range becomes wider, and the ΔH_m slightly increases.

Sc-CO₂ has better solubility and diffusion than Sc-N₂. The Sc-CO₂ can act as a plasticizer in polymers since the movement ability of the chain segment was enhanced with changes of free volume when CO₂ diffused into polymers. Moreover, Sc-CO₂ is easy to interact with the polar groups in the polymer matrix, which can induce the crystallization of the polymer and promote the nucleation of the crystal. Therefore, in the gas component of foaming, more CO₂ can help to reduce the T_m and improve the perfection of the crystallization zone of ETPU.

3.5. Physical and mechanical properties of ETPU prepared with different ratios of CO₂-N₂

Steam molding means that high-temperature steam enters into the gap between foam beads as a heating medium to soften and fuse the beads. The key contribution of steam forming is that the polymer chains will diffuse to the interface area of the foam bead and rearrange under high-temperature steam [28]. There are differences in cell structure and movement ability of the polymer chain of the ETPU sheet foamed by different gas components, which affects the performance and strength.

Figure 9 shows the comparison of hardness and resilience of different ETPU plates. The hardness of four kinds of samples (Shore C) is basically in between 30–40, and the resilience is about 70%. In contrast, the sample with component (100% N₂) has the highest hardness and the worst resilience, which is closely related to its density and cell structure: the final density of the ETPU reaches 0.175 g/cm³, which is higher than the other three samples, so its hardness is relatively high. Moreover, the cell structure with

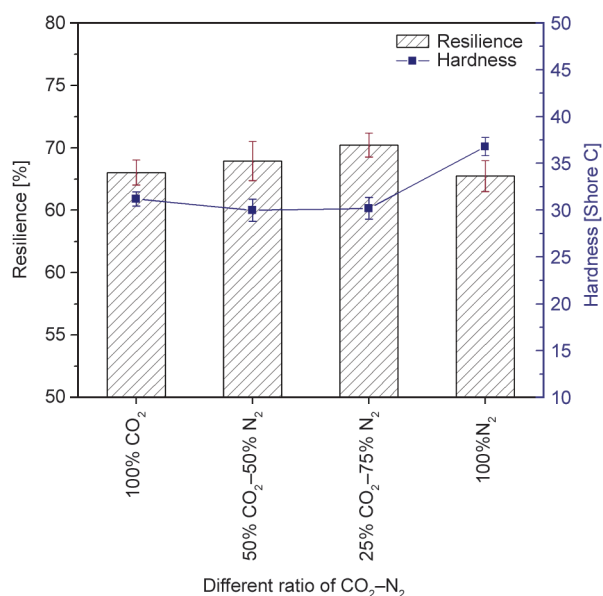


Figure 9. Hardness and resilience of ETPUs plate foamed with different ratios of CO₂-N₂.

large cell size, poor uniformity and thick cell wall also makes its resilience slightly worse than others. The samples foamed by mixed components (50% CO₂-50% N₂) and (25% CO₂-75% N₂) are relatively good in density and cell structure, so they have smaller hardness and higher rebound rate.

In order to quantify the compression recovery behavior of ETPU foam, the compression deformation test of steam formed sheet was carried out. The compression set of the sample has shown in Figure 10. With the increase of CO₂ and the decrease of N₂ in blowing agents, the compression set of the ETPU plate tends to increase. There are some reasons for the result; First, when the proportion of CO₂ in the blowing agent is large, the density of ETPU changes greatly after foaming. After the diffusion and replacement of foaming gas and air, the cells can not completely return to their original state. The bubbles are equivalent to the process of expansion, collapse, and re-expansion, resulting in poor compression performance. However, the density of ETPU prepared by the blowing agent with a large proportion of N₂ changes gently after foaming, and the bubbles can maintain the original well morphology and state. Secondly, the stronger plasticization effect of the Sc-CO₂ on polymer will increase the free volume of polymer and enhance the motion ability of polymer segment and chain, which makes it easy for foam material to get permanent deformation under compression. Besides, there are three main stages, namely, elastic bending, elastic buckling of cell walls, and densification of

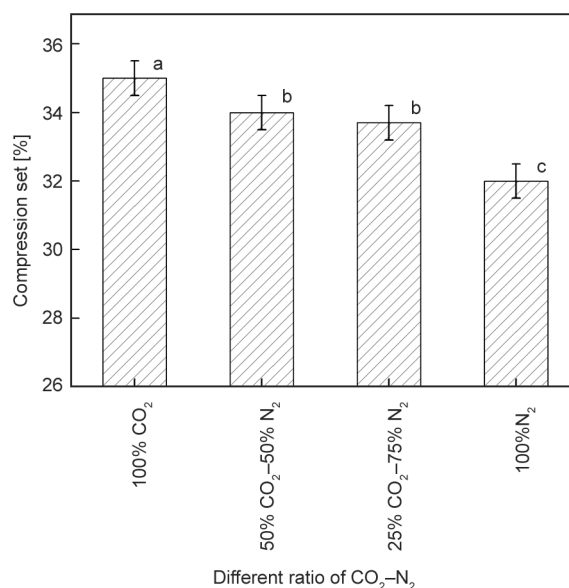


Figure 10. The compression set of ETPUs plate foamed with different ratios of CO₂-N₂.

cell walls which are clearly visible in the compression response. The elastic buckling stage of cell walls is the most sensitive and has the maximum energy consumption. The plastic deformation produced by foam under compression is related to the cell wall in the elastic buckling stage. The thicker the cell wall, the greater the energy required for elastic buckling. In other words, under the same external force, the thicker cell wall is less prone to elastic buckling and densification, which will lead to weaker plastic deformation. Therefore, the ETPU plate foamed by 100% N₂ has thicker wall than others, which has a lower compression set.

After steam molding, the adhesion between foam beads often determines the mechanical properties of steam molded products because the products are fractured, or broken paths usually form and develop in the inter bead bonding regions [30]. The bond quality and strength of ETPU beads can be characterized by tensile and tear tests. Figure 11 and Figure 12 show the tensile strength, tear and split tear strength of the four samples. The tensile strength of the specimen prepared by 100% CO₂ is 0.93 MPa, which is higher than other samples, while the tensile strength of the specimen prepared by 100% N₂ is the lowest, *i.e.*, 0.79 MPa. In terms of tear and split tear strength, the strength of the specimen prepared by 100% CO₂ is the largest. The tear strength of the samples decreased with the decrease of CO₂ in the blowing agent, but no regular change pattern has been observed in split tear strength.

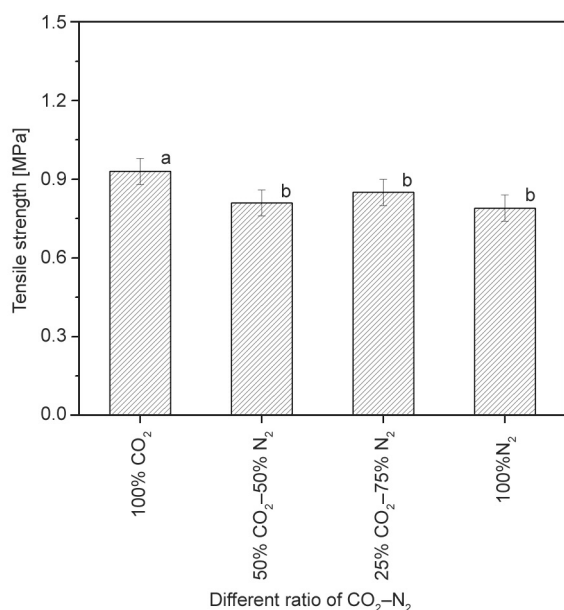


Figure 11. Tensile strength of ETPUs plate foamed with different gas ratios.

During the steam molding of foam beads, the vapor temperature does not reach the T_m of ETPU, the hard segment of TPU remains in the original state, while the diffusion efficiency of the soft segment chain increases between the beads because of Sc-CO₂ as the plasticizer of ETPU, that can form a more stable binding area. Sc-CO₂ increases the crystallinity of ETPU, which has a positive effect on the strength of the material. So, the ETPU sheet made by using only Sc-CO₂ has better bonding quality and strength. However, the density of foam has a positive effect on its strength [30, 31]. The ETPU foamed by 100% Sc-N₂ has a relatively larger density than others,

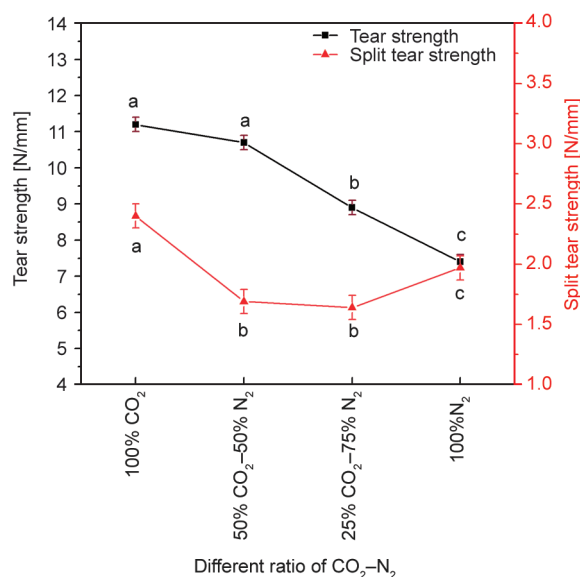


Figure 12. Tear strength and split tear strength of ETPUs plate foamed with different gas ratios.

which may be the reason for the irregular change of tensile strength and split tear strength.

3.6. Cyclic compression analysis of ETPU prepared with different ratios of CO₂-N₂

Figure 13 is the schematic diagram of the cyclic compression process (Figure 13a) and the dynamic compression curve of the foam (Figure 13b). According to the curve, the average stiffness (AS), energy absorbed per unit volume (EA/Vol), the ratio of energy returned/energy absorbed (EE), stiffness I (when $F < 700$ N, it represents the stiffness of humans in jogging or standing state), stiffness II (when $F > 700$ N, it represents the stiffness of human in running state) can be calculated, showed in Table 4. Based on these data, we can evaluate the performance of the micro-cellular elastomeric foam.

Energy absorption efficiency is one of the important factors affecting the resilience of elastomers. According to the data, the energy absorption efficiency of four kinds of ETPU board samples is all in the range of $86 \pm 1\%$, which explains why the resilience difference of four kinds of samples is small. The average stiffness of the ETPU plate prepared by the mixed component (50% CO₂-50% N₂) is 137 N/mm, which is the smallest of the four samples, and the ETPU sample prepared by the component (100% N₂) is the largest. Compared with the stiffness I under low load, the stiffness I of 100% N₂ ETPU sample is also significantly higher than other samples, and the sample of (50% CO₂-50% N₂) also is the smallest, which may be related to the final expansion ratio, density, and cell wall thickness of different samples. The former has a small expansion ratio, thick cell wall, and sufficient strength, while the latter has the largest expansion ratio and thin and regular cell wall. Therefore, if the samples will have the same deformation under external force load, the former requires a bigger external force. Compared with the stiffness II data under high load, the ETPU of (25% CO₂-75% N₂) is the smallest, but there is no significant difference among the four samples. This is because, under a load of large external force, the samples are greatly deformed, and the cells of samples are in a state of high compression. The difference in cell structure does not affect the stiffness II easily in this state.

Generally, the higher the energy absorption efficiency, the better the cushioning property of foam materials with better durability. The less stiffness will make people feel more comfortable while standing,

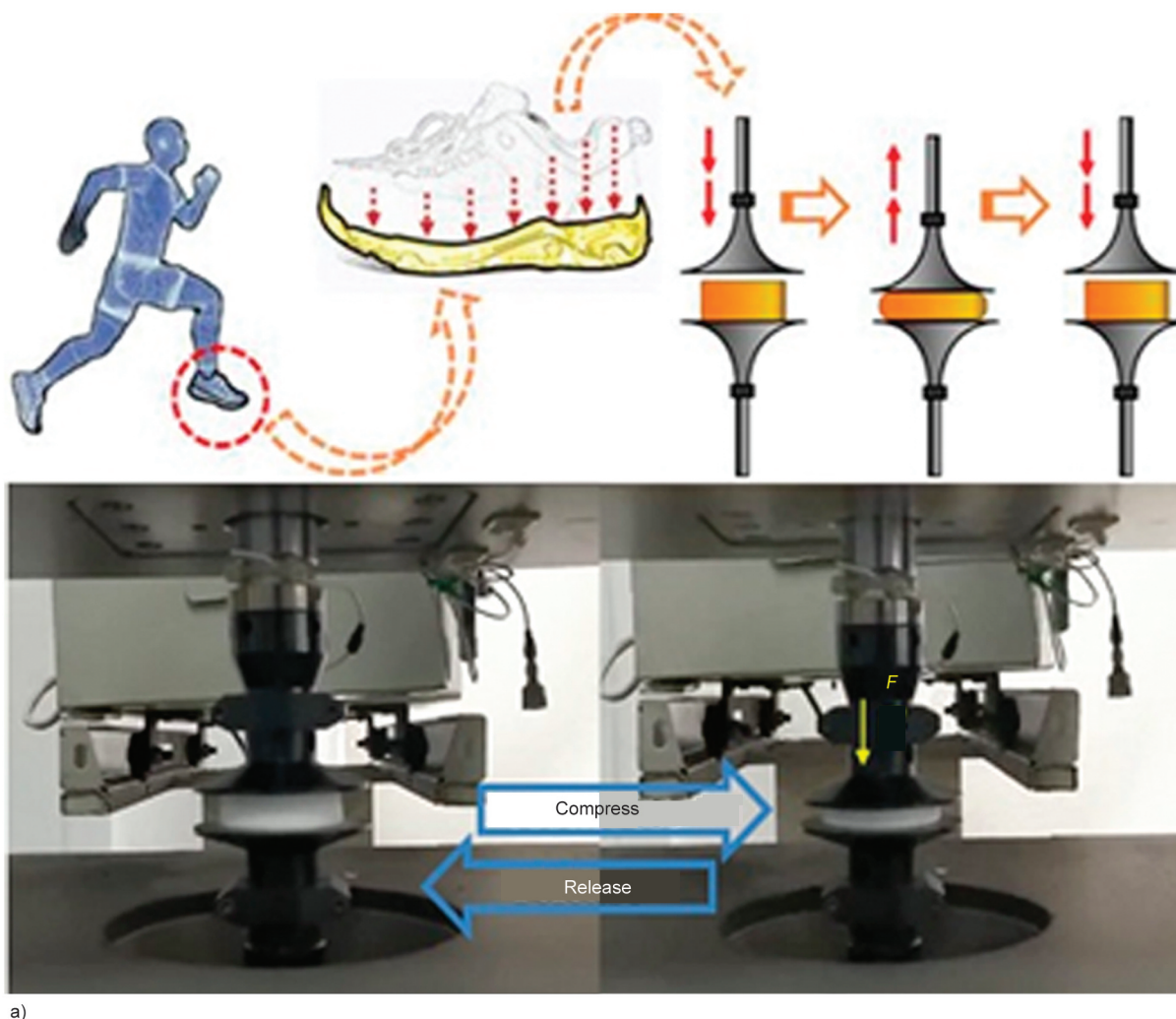


Figure 13. (a) Schematic diagram of the cyclic compression process and (b) force-deformation curves of ETPUs foamed with the different gas components under 1000 compressions cycle.

Table 4. Information of cyclic compressions.

Specimen	ϵ_{\max}	EA/Vol [mJ/cm ³]	AS [N/mm]	Stiffness I [N/mm]	Stiffness II [N/mm]	EE [%]
100% CO ₂	0.590±0.028	118±9	142.9±8.6	75.7±5.6	431.2±8.9	85.38
50% CO ₂ -50% N ₂	0.608±0.030	111±8	137.0±7.6	66.6±7.6	437.2±7.8	86.06
25% CO ₂ -75% N ₂	0.581±0.012	111±5	141.1±5.5	72.7±4.5	418.3±5.6	86.56
100% N ₂	0.545±0.058	113±10	154.4±5.0	84.7±8.6	435.3±6.6	86.50

walking, or running. Therefore, from the experimental results, the samples prepared by the mixed components (50% CO₂–50% N₂) and (25% CO₂–75% N₂) have better performance and are more suitable for the insole materials.

3.7. The influence of different foaming additives on the dimensional stability of ETPU

It can be seen from Figure 14 that the density of TPU foams treated with foaming aids is more stable than the untreated samples. The final expansion ratio of TPU foams with different foaming aid has shown in Figure 15. Under the same foaming conditions (T , P , t), the density of ETPU without foaming assistant is 0.175 g/cm³, and the foaming ratio is 6.4; the ETPU using the foaming aid monofluorodichloroethane (HCFC-141B) has the smallest density (0.139 g/cm³) and the largest expansion ratio (8.1); the density of

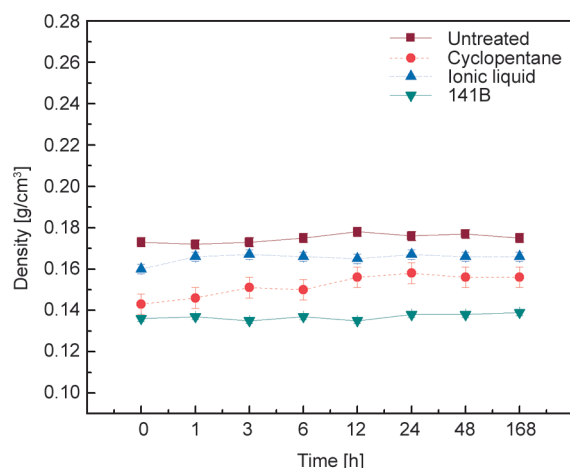


Figure 14. The density of TPU prepared with different co-blowing agents.

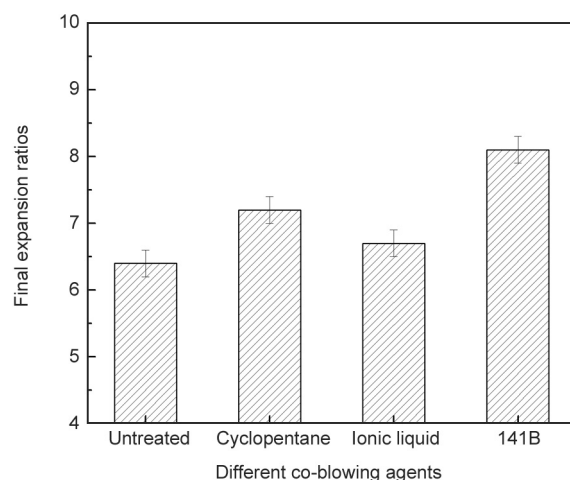


Figure 15. The final expansion ratio of TPU prepared with different co-blowing agents.

ETPU with cyclopentane as foaming assistant is 0.156 g/cm³ and the foaming ratio increased to 7.2. The density of the ETPU using ionic liquid as the foaming aid is 0.166 g/cm³, and the foaming ratio is 6.7. The ionic liquid has the least promotion effect on foaming among the three foaming aids. The reason for these changes is mainly ascribed to the influence of these additives on the foaming process. When the temperature of the foaming system is close to or higher than the glass transition temperature of the sample, the presence of these foaming additives will increase the free volume of TPU and reduce the resistance to the dissolution and diffusion of N₂ in TPU, and the increase in the solubility of nitrogen will accelerate the diffusion of nitrogen. The formation of a TPU/Sc-N₂ homogeneous system is promoted due to these effects, which positively affect the nucleation and growth of cells and increase the foaming rate to a certain extent, and expand the foaming temperature window. It concludes that the density has decreased, and the expansion ratio has increased in the macroscopic aspect.

3.8. Analysis of cell morphology of ETPU prepared with different foaming additives

The microscopic cell morphology and structure of ETPU prepared with different co-blowing agents are shown in Figure 16. It is obvious that the cell sizes of Figures 16b, 16c, and 16d are significantly reduced under the same magnification of 200 times. Figure 16a is a control group without adding foaming aids and Figures 16b, 16c, and 16d are ETPUs using cyclopentane, ionic liquid, and monofluorodichloroethane as foaming aids, respectively. Figure 17 is a data comparison chart of cell size and cell density. The average size of the control group (Figure 16a) is 117.9 μm, the cell density is 4.38·10⁴ cells/cm³, the cells are large, the cell walls are thick, not full, and the shape regularity is poor. The average cell size of ETPU reduces to 46.4 μm, the cell density increases to 6.9·10⁷ cells/cm³, the cell size distribution is more uniform, and the shape is more regular after using cyclopentane as a foaming aid (Figure 16b). Figure 16c shows the cell structure of ETPU treated with ionic liquid. Compared with the control group, the cell size is significantly reduced to 38.2 μm, and the cell density increases to 7.82·10⁷ cells/cm³. The uniformity and regularity of the cells are also improved and the thickness of the cell wall is reduced at the same time. The cell size (19.6 μm) of ETPU after

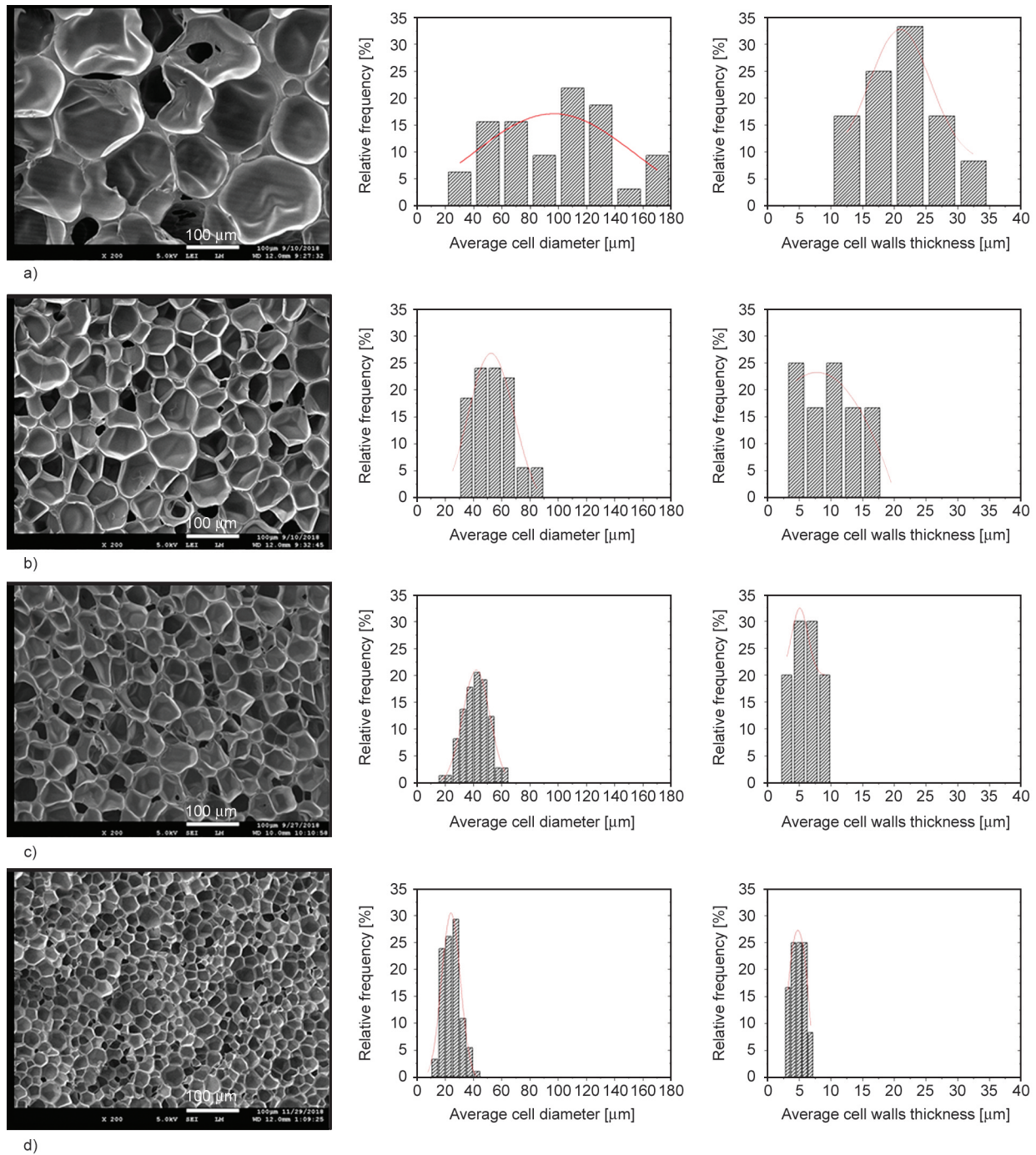


Figure 16. The SEM images (left), average cell diameter (middle) and average cell walls thickness (right) of the ETPU prepared with different foaming aids: (a) untreated, (b) cyclopentane, (c) ionic liquid, (d) HCFC-141B.

using monofluorodichloroethane as the foaming aid (Figure 16d) is the smallest among the four samples, the uniformity of the size distribution is also the best, and the cell density reaches $6.59 \cdot 10^8$ cells/cm³, the cell wall is also significantly thinner, and the cell shape is polygonal with relatively few broken holes. The SEM image of the cells shows that the addition of these three foaming additives can improve the cell structure of the foam, reduce the cell size, increase the cell density, reduce the cell wall thickness, and

improve the cell uniformity and regularity. This is due to the fact that the free volume between TPU molecular chains will increase with the introduction of foaming aids in the foaming system, which plays a certain plasticizing effect, reduce the melt viscosity, and reduces the dissolution of N₂ in the TPU matrix. The activation energy of diffusion increases the solubility of N₂ and promotes the rate of diffusion of N₂. This also leads to an increase in the nucleation density of N₂ during the cell nucleation process and

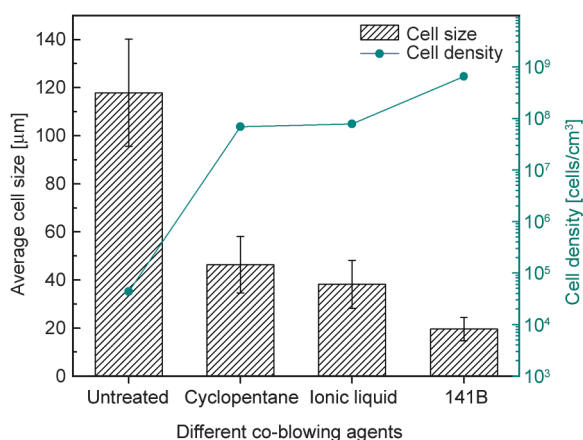


Figure 17. The effects of different co-blowing agents on cell size and cell density of ETPU foams.

a decrease in the resistance to bubble expansion during the cell growth process. On the other hand, cyclopentane and HCFC-141B solvent endothermic vaporization at high temperature dissolve and diffuse in the matrix and form effective bubbles, which play a synergistic foaming effect. In this way, a large number of bubbles will compete in the foaming process, which will eventually lead to an increase in cell density, the cell size becomes smaller, the cell wall becomes thinner, and the shape is more regular and full of the material. But relatively, the effect of HCFC-141B is better. This is because it has good compatibility with the isocyanate and polyol of TPU, and it is easier to dissolve and diffuse in the TPU matrix, which has a greater impact on the foaming performance of TPU.

3.9. Thermal performance analysis of ETPU prepared with different co-blowing agents

Figure 18 shows the DSC curve of ETPU prepared by using different co-blowing agents at an elevated temperature and melting, and its important thermodynamic parameters have shown in Table 5. The T_m of the ETPU using a foaming aid has decreased compared with the control group's ETPU with a melting point of 173 °C. This is mainly because the foaming aid plays a plasticizing role in the foaming process, which increases the free volume between the molecular chains of the polymer matrix and enhances the mobility of the molecular chains. Comparing the three foaming aids, the effect of cyclopentane is more significant. The T_m of the sample prepared with cyclopentane is 169.1 °C, and its melting enthalpy ΔH_m is nearly doubled compared to the control group, which better reflects the plasticizing effect and inducing

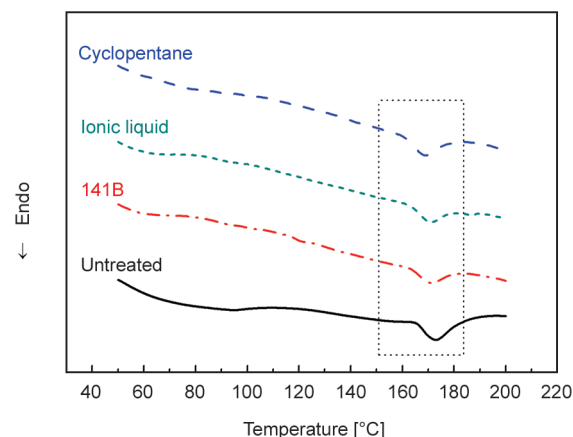


Figure 18. The DSC thermogram of ETPUs foamed with different co-blowing agents.

Table 5. Thermodynamic parameters of samples.

Samples	T_m [°C]	ΔH_m [J/g]
Untreated	173.0	1.779
Cyclopentane	169.1	3.369
Ionic liquid	171.2	1.645
141B	171.4	1.720

crystallization of cyclopentane on the TPU molecular chain; where the effect of HCFC-141B and ionic liquid is very small. The melting points of these two samples dropped to 171.4 and 171.2 °C, respectively, and the enthalpy of fusion ΔH_m had no obvious mutation. Therefore, cyclopentane has a greater impact on the thermal properties of the material matrix for TPU.

3.10. Physical and mechanical properties of ETPU prepared with different co-blowing agents

Figure 19 shows the effect of different co-blowing agents on the hardness and resilience of the ETPU foam sheet. The hardness of the blank control sample is 36.8, and the rebound rate is 67.73%. The hardness of the sample dropped to 33, and the resilience increased to 71.4% after using cyclopentane. The sample of ETPU also dropped to 33, and the resilience increased slightly after using ionic liquid; however, the hardness of the sample dropped to 24.6 and the resilience was 70.52% after using HCFC-141B. The reason for this effect is that the foaming aid dissolves and diffuses into the TPU matrix under high temperature and high pressure, which affects the foaming process and changes the cell structure. Generally, for the same foam material, the smaller the density, the smaller the hardness (Shore C). Therefore,

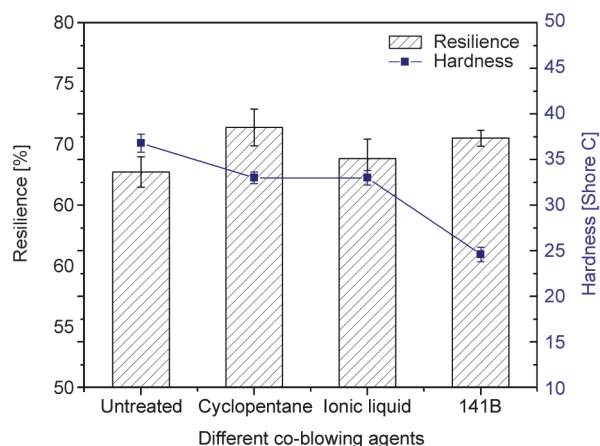


Figure 19. The effects of different co-blowing agents on hardness and resilience of ETPU foams sheet.

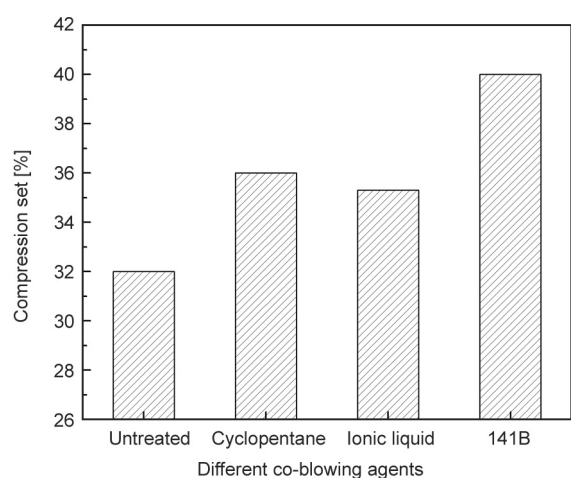


Figure 20. The effects of different co-blowing agents on the compression set of ETPU foams.

the use of foaming aids will reduce the hardness of ETPU under the same foaming conditions.

The compression set rate of ETPU has shown in Figure 20. The compression set rate of ETPU is getting

larger and larger with the introduction of foaming aids. It may be because the introduction of foaming aids reduces the density of ETPU. The compression performance of the foam will be worse with the smaller the density. Secondly, the plasticizing effect of the foaming aid makes the foam prone to greater plastic deformation when it has compressed for a long time. Moreover, the smaller the thickness of the cell wall, the resistance to compression will be worse. All three foaming aids negatively impact the compression performance and increase the permanent deformation rate of ETPU. HCFC-141B has the most significant impact because of its high polarity and good compatibility with isocyanates and polyols, which are the main raw materials of TPU. It may slightly dissolve the cell walls during the foaming process and destroy the compressive strength of the cells.

The bonding quality of steam-formed sheets can be measured by tensile strength and tear strength. Figure 21 shows the effect of different foaming additives on the tensile strength, tearing and peeling tearing strength of ETPU sheets. Compared with the control group (pure nitrogen foaming), the three strengths of the sample using cyclopentane foaming aid are all the highest. This is because cyclopentane plays a plasticizing effect similar to CO₂ in the foaming process, and improves the movement efficiency of polymer molecular chains under high-temperature steam, so that it can quickly diffuse to form a more stable bonding area. However, the strength loss of samples using HCFC-141B is greater. This is because, within a certain range, the density of the foam beads is proportional to the strength of the board. Although HCFC-141B also has a softening and plasticizing

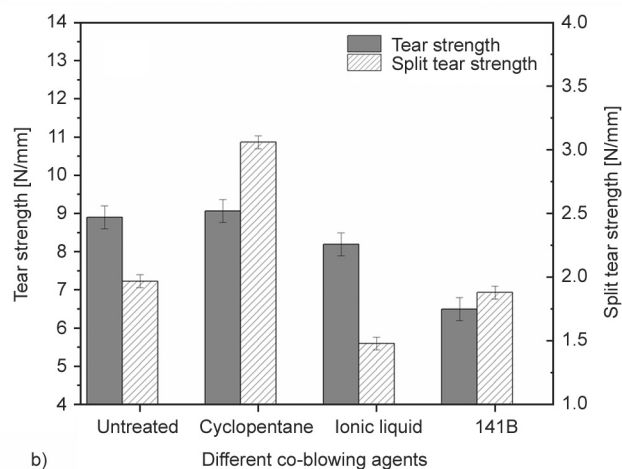
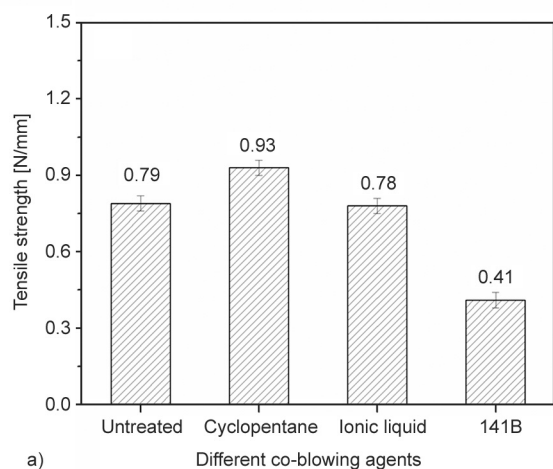


Figure 21. The effects of various co-blowing agents on (a) tensile strength and (b) tear strength and split tear strength of ETPU.

effect on TPU, it also significantly changes the foam density (decreased from 0.175 to 0.139 g/cm³). At the same time, HCFC-141B has good swelling and dissolving ability for TPU, which may damage the cells during the foaming process. The combined effect of two factors leads to a decrease in the strength of the sample. The strength of the sample decreased slightly after using an ionic liquid, and the reason may be related to the decrease of foam density. In summary, the foaming aid cyclopentane has a positive impact on foam steam forming and improves the bonding quality of the foam sheet.

3.11. Cyclic compression analysis of ETPU prepared with different co-blowing agents

Figure 22 shows the cyclic compression test results of ETPU prepared with different co-blowing agents. Table 6 displays the calculated data of the maximum deformation, rigidity and energy absorption efficiency of the sample. It can be seen from the graph that the curve of samples prepared with HCFC-141B under the same compressive load shifts significantly to the right, ϵ_{max} is the largest, the average rigidity and rigidity I and II are the smallest, and the energy absorption efficiency can reach nearly 88.41%. The

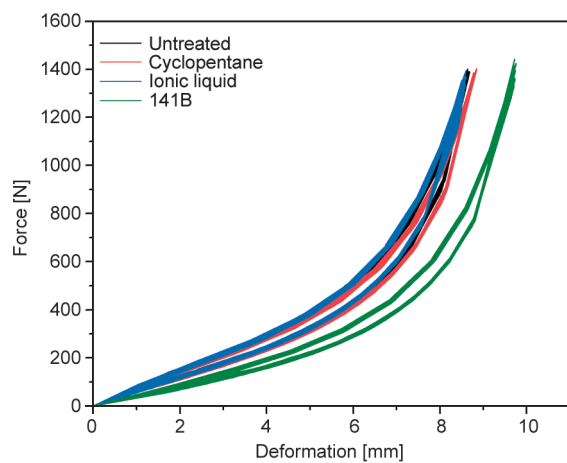


Figure 22. Force-deformation curves of ETPUs foamed with different co-blowing agents under 1000 compressions cycle.

reason is that HCFC-141B can significantly reduce the density and hardness of ETPU, which makes the foam softer and less rigid, and ϵ_{max} increases accordingly. At the same time, HCFC-141B can optimize the cell structure, and the small size and high-density cell structure is more conducive to the improvement of energy absorption efficiency. In contrast, the effect of cyclopentane is inferior to that of HCFC-141B, the ϵ_{max} of the sample is 0.555, the rigidity data is higher than that of HCFC-141B, and the energy absorption efficiency is 87.97%. The ionic liquid has the least influence on the reciprocating compression performance. From the analysis of the results, HCFC-141B as a foaming aid can make the elastomer foam have better comfort, impact resistance and feedback when used as a shoe soles or cushioning materials.

4. Conclusions

In summary, the saturation time can be shortened, and the temperature required for ETPU foaming can be reduced as the proportion of CO₂ in the foaming gas component increases. The mixed gas components (50% CO₂–50% N₂) and (25% CO₂–75% N₂) can prepare ETPU with lower density, which is more conducive to improving the resilience and cyclic compression performance of ETPU. The higher solubility and diffusion rate of CO₂ are powerful to foaming and also play an important role in poor shrinkage and stability. However, the dimensional stability of ETPU during the curing process has enhanced, and the shrinkage rate of ETPU has decreased as the proportion of N₂ in the gas component increases. The foaming aid can significantly promote the nucleation rate of the foam, improve the cell structure as well as the foaming efficiency. All three kinds of foaming aids cut down the hardness, elevated the resilience, and increased the compression set rate of the N₂ prepared ETPU foam. The cell density has greatly increased, the rigidity is small, and the energy absorption efficiency is the best-up to 88.41% of the N₂ prepared ETPU foam when monofluorodichloroethane

Table 6. Information of cyclic compressions.

Specimen	ϵ_{max}	EA/Vol [mJ/cm ³]	AS [N/m]	Stiffness I [N/m]	Stiffness II [N/mm]	EE [%]
Untreated	0.545±0.026	118±7	142.9±5.6	84.7±2.2	435.3±7.2	86.50
Cyclopentane	0.555±0.035	111±4	137.0±4.3	80.6±5.8	437.8±8.8	87.97
Ionic liquid	0.540±0.026	111±2	141.1±9.6	81.6±9.7	424.6±5.6	86.63
141B	0.606±0.037	113±6	134.4±7.7	61.4±4.8	419.8±9.1	88.41

is used as the foaming aid. It has good feedback and comfort, and it is more suitable for shoe soles or cushioning materials. Cyclopentane increases the tensile strength, tear and peel strength of the ETPU sheet, while the ionic liquid and monofluorodichloroethane caused a greater strength loss of the sheet sample. It shows that it is easier to prepare foams with better bonding quality by using cyclopentane as a foaming aid.

References

- [1] Hossieny N., Shaayegan V., Ameli A., Saniei M., Park C. B.: Characterization of hard-segment crystalline phase of thermoplastic polyurethane in the presence of butane and glycerol monostearate and its impact on mechanical property and microcellular morphology. *Polymer*, **112**, 208–218 (2017).
<https://doi.org/10.1016/j.polymer.2017.02.015>
- [2] Zhang R., Huang K., Hu S., Liu Q., Zhao X., Liu Y.: Improved cell morphology and reduced shrinkage ratio of ETPU beads by reactive blending. *Polymer Testing*, **63**, 38–46 (2017).
<https://doi.org/10.1016/j.polymertesting.2017.08.007>
- [3] Huang A., Peng X., Turng L-S.: *In-situ* fibrillated polytetrafluoroethylene (PTFE) in thermoplastic polyurethane (TPU) *via* melt blending: Effect on rheological behavior, mechanical properties, and microcellular foamability. *Polymer*, **134**, 263–274 (2018).
<https://doi.org/10.1016/j.polymer.2017.11.053>
- [4] Ge C., Wang S., Zheng W., Zhai W.: Preparation of microcellular thermoplastic polyurethane (TPU) foam and its tensile property. *Polymer Engineering and Science*, **58**, E158–E166 (2018).
<https://doi.org/10.1002/pen.24813>
- [5] Wang G., Wan G., Chai J., Li B., Zhao G., Mu Y., Park C. B.: Structure-tunable thermoplastic polyurethane foams fabricated by supercritical carbon dioxide foaming and their compressive mechanical properties. *Journal of Supercritical Fluids*, **149**, 127–137 (2019).
<https://doi.org/10.1016/j.supflu.2019.04.004>
- [6] Nema A. K., Deshmukh A. V., Palanivelu K., Sharma S. K., Malik T.: Effect of exo- and endothermic blowing and wetting agents on morphology, density and hardness of thermoplastic polyurethanes foams. *Journal of Cellular Plastics*, **44**, 277–292 (2008).
<https://doi.org/10.1177/0021955x07088326>
- [7] Kharbas H. A., McNulty J. D., Ellingham T., Thompson C., Manitiu M., Scholz G., Turng L-S.: Comparative study of chemical and physical foaming methods for injection-molded thermoplastic polyurethane. *Journal of Cellular Plastics*, **53**, 373–388 (2017).
<https://doi.org/10.1177/0021955x16652107>
- [8] Ghariniyat P., Leung S. N.: Development of thermally conductive thermoplastic polyurethane composite foams *via* CO₂ foaming-assisted filler networking. *Composites Part B: Engineering*, **143**, 9–18 (2018).
<https://doi.org/10.1016/j.compositesb.2018.02.008>
- [9] Yu C-T., Lai C-C., Wang F-M., Liu L-C., Liang W-C., Wu C-L., Chiu J-C., Liu H-C., Hsiao H-T., Chen C-M.: Fabrication of thermoplastic polyurethane (TPU) / thermoplastic amide elastomer (TPAE) composite foams with supercritical carbon dioxide and their mechanical properties. *Journal of Manufacturing Processes*, **48**, 127–136 (2019).
<https://doi.org/10.1016/j.jmapro.2019.09.022>
- [10] Yang Z., Hu D., Liu T., Xu Z., Zhao L.: Strategy for preparation of microcellular rigid polyurethane foams with uniform fine cells and high expansion ratio using supercritical CO₂ as blowing agent. *Journal of Supercritical Fluids*, **153**, 104601 (2019).
<https://doi.org/10.1016/j.supflu.2019.104601>
- [11] Liu Y., Jian L., Xiao T., Liu R., Yi S., Zhang S., Wang L., Wang R., Min Y.: High performance attapulgite/polypyrrole nanocomposite reinforced polystyrene (PS) foam based on supercritical CO₂ foaming. *Polymers*, **11**, 985 (2019).
<https://doi.org/10.3390/polym11060985>
- [12] Wei L., Huang A., Sun J.: Isotactic polypropylene/polyethylene terephthalate in situ microfibrillar composites foams using supercritical CO₂ (in Chinese). *Polymeric Materials Science and Engineering*, **34**, 66–71 (2018).
<https://doi.org/10.16865/j.cnki.1000-7555.2018.07.012>
- [13] Salerno A., Domingo C.: Polycaprolactone foams prepared by supercritical CO₂ batch foaming of polymer/organic solvent solutions. *The Journal of Supercritical Fluids*, **143**, 146–156 (2019).
<https://doi.org/10.1016/j.supflu.2018.08.006>
- [14] Yang C., Xing Z., Zhao Q., Wang M., Wu G.: A strategy for the preparation of closed-cell and crosslinked polypropylene foam by supercritical CO₂ foaming. *Journal of Applied Polymer Science*, **135**, 45809 (2018).
<https://doi.org/10.1002/app.45809>
- [15] Zhang Z. X., Dai X. R., Zou L., Wen S. B., Sinha T. K., Li H.: A developed, eco-friendly, and flexible thermoplastic elastomeric foam from SEBS for footwear application. *Express Polymer Letters*, **13**, 948–958 (2019).
<https://doi.org/10.3144/expresspolymlett.2019.83>
- [16] Wang G., Zhao G., Dong G., Mu Y., Park C. B., Wang G.: Lightweight, super-elastic, and thermal-sound insulation bio-based PEBA foams fabricated by high-pressure foam injection molding with mold-opening. *European Polymer Journal*, **103**, 68–79 (2018).
<https://doi.org/10.1016/j.eurpolymj.2018.04.002>
- [17] Zou L., Li H., Wang D., Ma L., Prakashan K., Zhang Z. X.: Micro/nanocellular polypropylene/trans-1,4-polyisoprene (PP/TPI) blend foams by using supercritical nitrogen as blowing agent. *Polymer Engineering and Science*, **60**, 211–217 (2020).
<https://doi.org/10.1002/pen.25274>

- [18] Zhang Z. X., Zhang T., Wang D., Zhang X., Xin Z., Prakashan K.: Physicomechanical, friction, and abrasion properties of EVA/PU blend foams foamed by supercritical nitrogen. *Polymer Engineering and Science*, **58**, 673–682 (2018).
<https://doi.org/10.1002/pen.24598>
- [19] Li R., Lee J. H., Wang C., Mark L. H., Park C. B.: Solubility and diffusivity of CO₂ and N₂ in TPU and their effects on cell nucleation in batch foaming. *Journal of Supercritical Fluids*, **154**, 104623 (2019).
<https://doi.org/10.1016/j.supflu.2019.104623>
- [20] Wong A., Mark L. H., Hasan M. M., Park C. B.: The synergy of supercritical CO₂ and supercritical N₂ in foaming of polystyrene for cell nucleation. *Journal of Supercritical Fluids*, **90**, 35–43 (2014).
<https://doi.org/10.1016/j.supflu.2014.03.001>
- [21] Haurat M., Dumon M.: Amorphous polymers' foaming and blends with organic foaming-aid structured additives in supercritical CO₂, a way to fabricate porous polymers from macro to nano porosities in batch or continuous processes. *Molecules*, **25**, 5320 (2020).
<https://doi.org/10.3390/molecules25225320>
- [22] Qiang W., Hu D.-D., Liu T., Zhao L.: Strategy to control CO₂ diffusion in polystyrene microcellular foaming *via* CO₂-philic additives. *Journal of Supercritical Fluids*, **147**, 329–337 (2019).
<https://doi.org/10.1016/j.supflu.2019.01.002>
- [23] Chen Y., Li D., Zhang H., Ling Y., Wu K., Liu T., Hu D., Zhao L.: Antishrinking strategy of microcellular thermoplastic polyurethane by comprehensive modeling analysis. *Industrial and Engineering Chemistry Research*, **60**, 7155–7166 (2021).
<https://doi.org/10.1021/acs.iecr.1c00895>
- [24] Nistor A., Topiar M., Sovova H., Kosek J.: Effect of organic *co*-blowing agents on the morphology of CO₂ blown microcellular polystyrene foams. *Journal of Supercritical Fluids*, **130**, 30–39 (2017).
<https://doi.org/10.1016/j.supflu.2017.07.026>
- [25] Perkin S., Kirchner B., Fayer M. D.: Preface: Special topic on chemical physics of ionic liquids. *Journal of Chemical Physics*, **148**, 193501 (2018).
<https://doi.org/10.1063/1.5039492>
- [26] Hayes R., Warr G. G., Atkin R.: Structure and nanostructure in ionic liquids. *Chemical Reviews*, **115**, 6357–6426 (2015).
<https://doi.org/10.1021/cr500411q>
- [27] Watanabe M., Thomas M. L., Zhang S., Ueno K., Yasuda T., Dokko K.: Application of ionic liquids to energy storage and conversion materials and devices. *Chemical Reviews*, **117**, 7190–7239 (2017).
<https://doi.org/10.1021/acs.chemrev.6b00504>
- [28] Horne W. J., Shannon M. S., Bara J. E.: Correlating fractional free volume to CO₂ selectivity in [Rmim][Tf₂N] ionic liquids. *Journal of Chemical Thermodynamics*, **77**, 190–196 (2014).
<https://doi.org/10.1016/j.jct.2014.03.012>
- [29] Yin Y., Wang F., Sun Y.: Development situation of HCFC-141b alternative techniques in polyurethane panel and matching foam stabilizers and catalysts. *Chemical Propellants and Polymeric Materials*, **2019**, 17–19 (2019).
- [30] Qiang W., Zhao L., Liu T., Liu Z., Gao X., Hu D.: Systematic study of alcohols based *co*-blowing agents for polystyrene foaming in supercritical CO₂: Toward the high efficiency of foaming process and foam structure optimization. *The Journal of Supercritical Fluids*, **158**, 104718 (2020).
<https://doi.org/10.1016/j.supflu.2019.104718>
- [31] Pinto J., Reglero-Ruiz J. A., Dumon M., Rodriguez-Perez M. A.: Temperature influence and CO₂ transport in foaming processes of poly(methyl methacrylate)-block copolymer nanocellular and microcellular foams. *Journal of Supercritical Fluids*, **94**, 198–205 (2014).
<https://doi.org/10.1016/j.supflu.2014.07.021>