Study on Using High Temperature Steam Preparation of Ultra Light Foam TPU Pellets Based Supercritical CO2

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Abstract. This paper mainly introduces the technology of supercritical CO2 pretreatment and high temperature steam preparation of super mild foaming TPU pellets. Mainly discusses the supercritical CO2 pretreatment preparation ultra mild foaming TPU pellets process in high temperature steam condition change of TPU micro foaming granule structure and properties of impact. Experimental results show that the high temperature steam temperature, processing time will influence TPU granules of microporous quantity, structure, resulting in pellets of different physical properties.

Keywords: Supercritical CO2, High Temperature Steam, Micro-Foam, TPU Pellet.

1. Introduction

The use of supercritical carbon dioxide "permeability", the preparation of ultra-light pore composite materials based on the batch method and the heating and pressure reduction method is a research boom in recent years. It is the preparation of ultra-light, high gas barrier, high temperature insulation new materials and their composite materials an interdisciplinary subject [1-2]. Supercritical CO2 is the most common physical blowing agent used in the preparation of micro-foaming materials. Using a high-pressure inert gas (such as CO2, N2, etc.) as a foaming method, the cell size of the material obtained is on the order of ten zero micrometers. This preparation process is usually called "microfoaming" The resulting material is also called "microfoamed" material or "microcellular foam".

Carbon dioxide has unique advantages. Its critical temperature (31.1 ℃) is close to room temperature, and its critical pressure (7.37 MPa) is also low. It does not require high equipment [3]. It has a solubility similar to a liquid and a diffusion coefficient similar to that of a gas. The high mass transfer system is easy to diffuse in the polymer and can reach the equilibrium concentration in the polymer in a short time [4]. The feasibility of the above industrial application based on supercritical carbon dioxide makes the industrial application of microporous polymer preparation possible [5]. In addition, due to the environmental friendliness of carbon dioxide, during its use, it has good solubility for most organic substances, low viscosity, high diffusion coefficient, non-toxic, non-flammable, chemically inert, no solvent residues, safe use, and no pollution to the environment. And other unique advantages [6]. Compared with other supercritical inert gases (such as N2), supercritical CO2 is easier to prepare and has a stronger interaction with polymers [7]. Supercritical CO2 can reduce the interfacial tension of the polymer system, and has a good plasticizing effect on the polymer melt, so it
can reduce the glass transition temperature (Tg) of the polymer, and can reduce the viscosity of the polymer melt and increase the fluidity of the melt reduces the extrusion temperature [8-9]. The many advantages of supercritical CO2 make it an ideal physical foaming agent for microcellular plastics.

2. Experimental Part

2.1 Experimental Materials
CO2 gas, purity 99.9%, Cixi Jinkang Gas Co., Ltd.;
Thermoplastic polyurethane elastomer (TPU), 58887 grade, density: 1.13 g/cm3, Nuoyu Chemical Asia Pacific Co., Ltd.;

2.2 Instruments and Equipment
Supercritical fluid reaction device: Model HL-5L/25 MPa, Ningbo Green Mobil New Material Technology Co., Ltd.;
Specific gravity meter: DH-300 type, Hongtuo Instrument Co., Ltd.;
Ultra-high temperature steam generator: DCZF-F50-0.7 type, Ningbo Green Mobil New Material Technology Co., Ltd.
Scanning electron microscope (SEM): Model S4700, Hitachi, Ltd.

2.3 Experimental Process
2.3.1. Pretreatment. Put the TPU particles into the autoclave, and then fill the autoclave with CO2 gas to make the pressure in the autoclave reach 10MPa, and keep the temperature in the autoclave at 35℃ through heating cycle, hold the pressure for 2h, and quickly release Press to obtain pretreated TPU particles.

2.3.2. Foaming. Put the pretreated TPU particles into a self-made foaming device, and carry out foaming treatment at 80℃, 85℃, and 90℃ respectively. The foaming time is 60s, 80s, 105s, 115s, 150s, and the final result is different. Expanded TPU particles with foam ratio [10].

2.4 Structure Characterization and Density Test
The microscopic cell structure of the foamed TPU was observed with S4700 scanning electron microscope. First, cut the foamed TPU particles into thin slices, then spray gold on the sample under vacuum conditions, and observe its structure with SEM. The density of the foamed particles is tested with a DH-300 specific gravity meter [11].

3. Experimental Principle

3.1 The Basic Principle of Supercritical CO2 Foaming
In the supercritical state, the polymer is dissolved in supercritical CO2. Supercritical CO2 can plasticize the polymer, reduce the Tg of the polymer, and form a homogeneous system of polymer melt/gas mixture. By controlling the pressure and temperature of the mixed system (such as rapid pressure relief or rapid heating), the CO2 is in a supersaturated state, thereby inducing a large number of gas nuclei to form in the polymer matrix at the same time to obtain a microporous structure [12], as shown in Figure 1. Show.
3.2 Principle of Pretreatment Process
As shown in Figure 2, the TPU particles are placed in an autoclave, filled with 10 MPa CO\textsubscript{2} gas, and the autoclave is maintained at a temperature of about 35°C through thermal cycling, and the pressure is maintained for at least two hours to make supercritical CO\textsubscript{2} Fully saturate the sample to form a polymer/supercritical CO\textsubscript{2} homogeneous system, and then quickly release the pressure to normal pressure. Driven by thermodynamic instability, the polymer/supercritical CO\textsubscript{2} homogeneous system phase separates and forms a bubble core.

3.3 Basic Principles of Heating Process
Compared with air at the same temperature, high-temperature water vapor has a higher enthalpy value. Heating the particles by high-temperature water vapor will provide more heat to the particles, which is conducive to the thermal movement of gas molecules and the gas core. Grow.

Pass high-temperature steam into the foaming device and set a certain amount of air leakage, which is conducive to the circulation of high-temperature steam. After reaching the set temperature, put the pretreated TPU particles into the device. The temperature rises and the bubbles Expand, control the planned foaming time, and take out the particles. Figure 3 shows a schematic diagram of processing pretreated TPU particles in a foaming device.
4. Results and Discussion

4.1 Appearance of Samples at Different Stages
During the entire experiment, the appearance and morphology of the particles will change significantly. Figure 4 records the appearance and morphology of TPU particles at different stages. The original TPU particles (Figure 4a) are colorless and transparent particles with excellent light transmittance, olive-shaped in shape, and relatively uniform size. After the pretreatment, the shape and size of the particles remain unchanged, but because the gas penetrates into the inside of the particles, the light transmittance of the particles becomes poor, and the particles change from colorless and transparent to turbidity, as shown in Figure 4b.

After the particles are processed in the foaming device, the foamed TPU particles are obtained. The foamed particles are shown in Figure 4c below. By comparing with the pre-expanded samples and raw material samples, it can be found that the TPU particles have changed from initial transparency to White is opaque, the volume is 2-5 times of the original sample, the surface is smooth, flexible, and the shape remains unchanged.

![Figure 4. Appearance and morphology of TPU particles at different steps](image)
(a, before experiment; b, after pretreatment; c, after foaming)

4.2 Microscopic Morphology Analysis
The cross-sectional SEM test of the foamed particles at different temperatures is carried out, and the scanning photos are shown in Figure 5. Comparing the different scanned photos, it can be seen that at 80°C, the cell diameter is the smallest and the cell size is not uniform; with the increase of temperature, at 85°C, the cell diameter increases significantly and the size becomes more uniform; when foaming When the temperature reaches 90°C, the cell diameter becomes larger, but the number of cells is significantly reduced. This once again shows that the increase in temperature is conducive to the thermal movement of gas molecules, and is more conducive to entering the bubble core and promoting the growth of the bubble. In addition, it can be seen from Figure 5b that there is a relatively dense film on the surface of the foamed particles. This layer of film helps prevent the escape of gas inside the particles, and also helps to maintain the shape of the foamed particles. The overflow of gas inside the foam particles causes the foam particles to shrink.
4.3 Density Test

According to ASTM-D792, the DH-300 instrument is used for density test. The relevant data is shown in the following table:

| Temperature/℃ | Time/s | 60  | 80  | 105 | 115 | 150 |
|---------------|--------|-----|-----|-----|-----|-----|
| 80            |        | 0.556 | 0.509 | 0.473 | 0.353 | 0.365 |
| 85            |        | 0.392 | 0.341 | 0.324 | 0.312 | 0.358 |
| 90            |        | 0.309 | 0.298 | 0.291 | 0.335 | 0.369 |

Figure 6 is a graph showing the relationship between the density of expanded particles, the expansion temperature and the expansion time. It can be seen from the figure that under a suitable foaming time, as the temperature increases, the density of the foamed particles gradually decreases; similarly, at a suitable temperature, with the extension of the foaming time, the density of the bubble particles also gradually decreases. However, a suitable foaming temperature needs to be matched with a suitable foaming time, otherwise the foaming will be excessive, and the foamed particles will eventually become deflated and shrunk, resulting in an increase in density.

When the foaming temperature is 80℃, the foaming time gradually increases from 60s, and the density of the foamed particles gradually decreases. When the foaming time is 60s, the density of the foamed particles is the largest, 0.556g/cm³, and the foaming ratio is only about twice, which is particularly undesirable. The reason for the analysis is that the foaming time is not enough and the bubbles have not grown to the maximum value, which leads to this situation. When the foaming time is increased to 150s, compared with the previous foaming time of 115s, the density increases. This is because the foaming time is too long, the bubbles grow too much, and the bubbles are a little broken. After the gas overflows, the particles shrink and the density increases.

When the foaming temperature is increased to 90℃, the foaming time required to achieve the same foaming ratio is significantly shorter than that at 80℃. The increase in temperature makes the gas molecules move violently and can quickly enter the bubble nucleus, which is conducive to the growth of the bubble nucleus and the formation of cells. Similarly, at this foaming temperature, with the extension of the foaming time, the density will also have a minimum value.

In addition, we carried out a higher temperature of 120℃ foaming, the foaming time is only 10
seconds, the expansion ratio is larger when taken out, and there is slight adhesion between the particles. After being left for a period of time, the particles became wrinkled and shrunk to a large extent. The reason is that the temperature is too high or the time is too long, which will lead to the melting of the surface film of the foamed particles, so that the gas overflows, and at the same time, it will also cause the destruction of the internal cell structure of the foamed particles. The structure collapses and the particles become deflated.

![Figure 6. The relationship between foaming particles' density and foaming temperature and time](image)

5. Conclusion
This paper uses a two-step method to achieve the foaming of TPU particles with supercritical carbon dioxide technology, and investigates the effects of foaming temperature and foaming time on the density of foamed particles and cell structure, and finally draws the following conclusions:

In a certain foaming time, with the increase of foaming temperature, the density of foamed particles gradually decreases;

With the extension of the foaming time at a suitable foaming temperature, the density of the foamed particles will gradually decrease;

If the foaming temperature is too high or the foaming time is too long, the foamed particles will break. The foaming of TPU particles requires a suitable foaming temperature and foaming time. In this experiment, the suitable foaming temperature and foaming time of TPU particles are 90 °C, 105s.

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