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# Influence of Surfactants on Supercritical $CO_2$ Foaming Polyurethane Materials

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## Abstract

**Thermoplastic polyurethane elastomer (TPU) foam materials have been widely used in various fields due to their excellent characteristics such as light weight, high elasticity, and non-toxicity. Supercritical $CO_2$ foaming technology, as an environmentally friendly and efficient physical foaming method, has become the mainstream development direction of polyurethane foaming. However, the traditional process often has problems such as large pores and uneven distribution. Some existing studies have shown that surfactants can improve the foaming performance. This paper systematically analyzes the current development status of polyurethane foaming technology, the advantages and limitations of supercritical $CO_2$ foaming technology, and focuses on the research progress and results of surfactants on the pore structure of supercritical $CO_2$ foamed polyurethane materials. It also looks forward to the future prospects and research directions in this field. Relevant studies have shown that surfactants can significantly reduce pore diameter and increase pore density by reducing the surface tension of bubbles and the free energy of gas dispersion, providing an effective technical method for improving the performance of polyurethane foam materials. The related research provides new directions and thoughts for promoting the technological development of the industry.**

## Keywords

**Surfactants; Supercritical $CO_2$ foaming; Thermoplastic polyurethane elastomer; Cell structure; Literature Review.**

## 1. INTRODUCTION

Polyurethane is formally known as polyamino carboxylate and is a general term for macromolecular compounds with repeating methacrylate groups in their main chain. Polyurethane materials possess excellent mechanical properties, weather resistance, and processing adaptability. Its foaming products are widely used in various fields such as automotive manufacturing, packaging protection, medical health, and building insulation due to their light weight, good elasticity, and excellent sound insulation and vibration reduction effects. The mainstream foaming methods for polyurethane materials include chemical foaming, physical foaming, and mechanical foaming. Supercritical $CO_2$ foaming technology, as a typical representative of physical foaming methods, has gradually replaced traditional chemical foaming and mechanical foaming technologies due to its significant advantages such as non-toxic foaming agent, environmental friendliness, low cost, and better elasticity. It has become the most popular polyurethane foaming method nowadays. This technology utilizes the properties of $CO_2$ in the supercritical state, which combines the high diffusivity and low viscosity of a gas, as well as the unique properties of close to liquid density and solvation, allowing the gas to uniformly integrate into the polymer matrix. Through depressurization, gas

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is induced to escape and form a cellular structure, resulting in foam materials with excellent elasticity and high purity[1]. However, the polyurethane materials produced solely by the supercritical $CO_2$ foaming technology often have problems such as excessive pore diameters, uneven distribution, etc., which seriously affect the mechanical properties, thermal insulation performance, and service life of the materials, restricting their application and promotion. Surfactants, as a class of substances that can significantly reduce the surface tension of a system and improve the compatibility of phase interfaces, have a significant impact on foam structure and size, physical properties, and manufacturing processes[1]. In recent years, the application research of surfactants in supercritical $CO_2$ foaming polyurethane has attracted widespread attention. By regulating the interaction at the gas-liquid interface and adjusting the size of pores, it provides new ideas and directions for addressing the bottlenecks of traditional processes. Based on the existing research results, this article systematically reviews the development and current status of polyurethane foaming technology, the mechanism of surfactants in supercritical $CO_2$ foaming, and research progress. It analyzes the current research deficiencies and looks forward to future research directions and development, providing preliminary references for academic research and application in related fields.

## 2. CURRENT STATUS OF POLYURETHANE FOAMING TECHNOLOGY

### 2.1. Traditional Foaming Technology

Over the past few years, polyurethane materials have undergone continuous technological advancements, resulting in three major foaming systems - chemical foaming, mechanical foaming, and physical foaming. Among these, chemical foaming and mechanical foaming are traditional foaming technologies that were widely used in the past, but they also have significant shortcomings and limitations[2]. The chemical foaming method is a technology that utilizes the chemical reaction between polymer raw materials and foaming agents to generate gas and achieve foaming. This method is simple in process and has low costs, making it suitable for large-scale production. However, it also has obvious drawbacks. Li Guo found in his research on the application of plastic foaming processes in product packaging that the polyurethane foam materials prepared by the chemical foaming method have a loose pore structure, poor compressive strength and rebound performance, and are only suitable for low-end packaging scenarios, unable to meet the strict material performance requirements of high-end applications[2].

The mechanical foaming method introduces air into the polymer emulsion or melt through intense mechanical stirring, forming a foam system. Its core advantage lies in the fact that no additional chemical foaming agents are required. However, this technology not only has extremely high requirements for parameters such as the rotational speed of the stirring equipment, but also has high costs and is difficult to achieve large-scale production. The foam stability is also poor. During the molding process, problems such as bubble rupture are prone to occur. Its application scope is limited and it is difficult to meet the diverse market demands[2].

### 2.2. Supercritical Physical Foaming Technology

Supercritical $CO_2$ foaming technology, as the core technology of physical foaming methods, is an environmentally friendly foaming technology that uses $CO_2$ as the physical foaming agent to prepare polymer micro-foamed materials[3-6]. Compared with traditional foaming technologies, supercritical carbon dioxide foaming technology has significant advantages: Firstly, the foaming agent $CO_2$ is non-toxic, odorless, non-flammable, has a wide source and low cost, which is in line with the development trend of environmental protection; Secondly, the foaming materials produced are free of chemical residues, have high purity, good elasticity, and

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mechanical properties are significantly better than those produced by traditional methods[1, 7].

However, the supercritical $CO_2$ foaming technology still has some bottlenecks that need to be addressed: during the gas nucleation process, the surface tension is relatively high, resulting in insufficient bubble nucleation density, and it is prone to form a few large bubbles rather than a large number of small bubbles, thus causing the problem of uneven bubble diameters [1]. These defects make it difficult for polyurethane foam materials to meet the comprehensive performance requirements of high-end applications, and limit the industrialization promotion of the supercritical carbon dioxide foaming technology[1].

## 3. RESEARCH PROCESS AND RESULTS

### 3.1. Research Process

At present, although the research on the surface active agents of supercritical $CO_2$ foaming in polyurethane foaming is still in its infancy, some achievements have been made. Among them, the research conducted by Zhang Yunlong from South China University of Technology is representative. In this study, polyether polyol R090 was used as the raw material for polyurethane production, and three surface active agents - B8474, B8534, and TN1078 - were selected as the research objects. A control group without surface active agents was also established. Through supercritical $CO_2$ foaming experiments, the influence of surface active agent types on pore structure was systematically studied.

The foaming device used in the experiment is mainly composed of a $CO_2$ cylinder, a pressurization system, an air compressor, a constant temperature bath, a high-pressure reactor, and a stirring motor. It can precisely control key parameters such as temperature, pressure, and stirring rate, ensuring the stability and accuracy of the experimental conditions[1]. The bubble structure of the foaming samples is observed using a scanning electron microscope (SEM), and the indicators such as bubble distribution, average pore diameter, and bubble density are analyzed to provide reliable data support for evaluating the effect of surfactants[1].

### 3.2. Research Results

The research results indicate that, compared with the control group that did not add any surfactants, the pore size distribution range of the polyurethane foaming samples after adding three surfactants (namely B8474, B8534, and TN1078) was significantly reduced[1]. The pore distribution of the control group samples was disordered, with significant differences in pore size, and there were obvious large pores and voids; while the samples with added surfactants had more regular pore shapes and more uniform sizes, among which the improvement effect of the TN1078 surfactant was the most significant, with the most concentrated pore size distribution[1]. This result confirmed that surfactants can effectively inhibit pore merging and promote the uniform growth of pores, providing structural support for the stability of material properties[1]. Secondly, the pore size was refined and the density increased. Quantitative analysis showed that the addition of surfactants could significantly reduce the average pore size and increase the pore density[1].

Overall, all three surfactants were able to achieve the effects of pore refinement and density increase. Among them, TN1078 had the most ideal regulatory effect, followed by B8474, while the effect of B8534 was relatively weaker. However, they all outperformed the control group[1]. This result indicates that the type of surfactant has a significant impact on the regulatory effect, and the compatibility of the molecular structure with the foaming system is the key factor determining the effect.

The experimental results further verified the mechanism of the surfactant's action: The surfactant reduced the surface tension between the polyol and carbon dioxide, decreased the

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nucleation free energy, and increased the nucleation rate, thereby forming more bubble cores in the system; at the same time, the surfactant also promoted better mixing of the various components, resulting in a more uniform reaction in the reactor during the bubble formation stage. During the bubble growth phase, the polymer system around the bubbles was stronger, thereby limiting the growth of the bubbles. Therefore, the bubble diameters of the foaming samples containing surfactants were smaller. The clarification of this mechanism provides theoretical support for the selection of surfactants and process optimization in the future[1].

### 3.3. Research Significance

The conduct of this research has filled the research gap in the field of surface active agents for the foaming process of polyurethane foam using supercritical $CO_2$, providing an effective technical path to address the bubble structure defects existing in traditional processes[1]. By adding an appropriate amount of surface active agents, the bubble structure of polyurethane foam materials can be significantly improved, thereby enhancing the mechanical properties, thermal insulation performance, and durability of the materials, and expanding their application scope in high-end automotive interiors, precision electronic packaging, medical equipment, and other fields[1, 7].

Furthermore, the relevant research results are of great significance for promoting the industrial application of supercritical $CO_2$ foaming technology[1]. The introduction of surfactants does not require major modifications to the existing foaming equipment; it is only necessary to optimize the process parameters to significantly improve product performance, which has the advantages of low cost and easy promotion, and is in line with the actual needs of industrial production[1].

## 4. RESEARCH STATUS AND LIMITATIONS

Although the research on surfactants in supercritical $CO_2$ foaming polyurethane has achieved some initial results, there are still many limitations: Firstly, the research scope is narrow. Currently, related studies only focus on a few types of surfactants (such as B8474, B8534, TN1078) and specific raw materials (polyether polyols R090), lacking systematic research on different types and structures of surfactants, and also not involving the compatibility analysis of different polyurethane raw material systems [1]. Secondly, The basic design principle of surfactants is in the water system. When they are applied in the carbon dioxide system, it is necessary to take into account the differences between the carbon dioxide medium and the water medium, and then design more suitable surfactants specifically. The effect and impact will be more significant.

## 5. CONCLUSION

Polyurethane foam materials, as a versatile material, play an irreplaceable role in various fields. Supercritical $CO_2$ foaming technology, as a green and environmentally friendly foaming method, has become an inevitable trend in the industry development. Surfactants, as effective regulators of the pore structure, can significantly improve the pore structure of supercritical $CO_2$ foamed polyurethane materials by reducing the surface tension of the system, optimizing the nucleation process, and enhancing the stability of the pores. This can refine the pore diameter, increase the pore density, and improve the uniformity of distribution, providing an effective technical path for the improvement of material performance.

Although the current research has achieved some initial results, there are still deficiencies in the research system and the differences in medium characteristics. Further in-depth exploration is needed. In the future, by expanding the research system, improving the evaluation methods, deepening the mechanism research, and promoting industrial verification,

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it is expected to achieve precise application of surfactants in the field of supercritical $CO_2$ foaming of polyurethane, promoting the development of the polyurethane foam material industry towards a green and efficient direction, and providing effective support for the technological upgrading and sustainable development in related fields.

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