Sustainable foaming using supercritical carbon dioxide and biopolymers

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In 1907, Leo Baekeland introduced synthetic polymers, marking a pivotal moment in material science. These polymers, renowned for their durability, heat resistance, and mass production capabilities, revolutionized numerous industries. As technology advanced, the addition of blowing agents became a natural extension of polymer processing. Combining chemistry and engineering principles, foaming methodology continued to expand during and after World War II. Foams are essentially porous structures with gaseous voids surrounded by a dense phase. The drastic differences in nature between gases and solids make foams unique combinations that have special properties. The presence of a porous structure can regulate flow velocity, dissipate disturbance, and enlarge mass transfer area. The limitless possibilities of plastics fueled an optimistic vision of a future abundant in material wealth, given their affordability, safety, and adaptability. However, by the 1960s, the unintended consequences of improper disposal began to surface, with the first signs of plastic pollution emerging. Observations of plastic accumulation in oceans and landfills raised concerns about their environmental impact.

Despite these challenges, synthetic polymers, including polymeric foams, have played an important role in shaping the modern era, facilitating access to products that would have otherwise been economically or functionally unfeasible with alternative materials. However, it is essential to acknowledge and address the environmental issues associated with synthetic polymers, including their production, processing, and disposal.

The advantages and tunability of foam materials make them suitable for diverse applications such as protection, insulation, comfort, structural support, and biological uses. However, the conventional processes for producing foams often involve methods that are not environmentally friendly. Moreover, some chemical reactions to produce foam may introduce additional chemicals, complicating the recycling process and potentially releasing more toxic components into the environment. The use of supercritical fluids emerges as a promising solution to address some environmental challenges. Supercritical fluid foaming processes operate on a physical basis, eliminating the need for chemical reactions. In Chapter 1, the environmental impacts of traditional foaming processes are discussed alongside alternative methods for foam production. Among the proposed alternatives, supercritical carbon dioxide (scCO2) stands out as one of the promising techniques for mitigating issues related to polymer foam production. The energy input required to reach the critical point is relatively low, as CO2 enters its supercritical condition at 31 °C and 73 bar. Chapter 1 highlights the environmental benefits and ease of using scCO2 and emphasizes its tunability with temperature and pressure to achieve different foam morphologies. This study provides several illustrations of polymeric foams synthesized using scCO2. The chapter further describes the practical applications of these tailored foams, such as heat conservation, protection, sound insulation, filtration, energy storage, bone scaffolds, electromagnetic interference, and agricultural applications.
In Chapter 2, the focus shifts towards addressing environmental pollution through a perspective centered on material characterization with emphasis on foaming with scCO₂. We propose the exploration of biodegradable synthetic polymers derived from both non-renewable and renewable sources. Trying to repair the issue of improper disposal of synthetic polymers, the proposal supports a transition to biodegradable alternatives. Numerous potential biodegradable polymers exist, and for the purpose of foaming with scCO₂, the emphasis lies in selecting thermoplastic types with mild melting temperatures that can be foamed using a physical blowing agent. Noteworthy among these biodegradable polymers are polybutylene adipate terephthalate (PBAT), polybutylene succinate (PBS), poly (3-hydroxybutyrate 3-hydroxyvalerate) (PHBV), and polylactic acid (PLA). Therefore, in Chapter 2, each one of these biodegradable polymers undergoes thorough chemical, thermal, and mechanical characterization. The properties of PBAT, PBS, PHBV, and PLA are individually assessed, and the results are interconnected to their behavior during foaming with scCO₂. Consequently, a consistent foaming protocol is applied to each polymer, resulting in divergent morphologies, given their distinct polymer molecular structures. This systematic approach allows for a comprehensive understanding of how each polymer responds to foaming with scCO₂, paving the way for sustainable material selection and environmentally conscious foaming processes.

In Chapter 3, we study the re-processability of PBAT, promoting the circular economy and mitigating environmental impact. We recognize the urgent shift towards polymers with biodegradable features for the benefit of the environment. While biodegradable materials offer a solution to improper disposal, there is an equal effort to integrate biodegradable polymers into the circular economy through recycling or repurposing. Chapter 3 concentrates on understanding the reprocessing potential of PBAT through conventional extrusion and foaming processes using scCO₂. This chapter describes PBAT reprocessing, focusing on mechanical recycling. This investigation examines the feasibility of sustaining PBAT within the circular economy, studying process methods such as shearing, melting, and reprocessing. Our study starts assessing the stability of PBAT against humidity and oxidation. Subsequently, we employ different processing types of equipment with varied parameters to determine the energy-related factors that significantly influence PBAT properties. Chapter 3 provides insights into the degradation of PBAT, establishing some processing limits that enable multiple recycling cycles with minimal consequences to the polymer properties. Importantly, this analysis is conducted with a focus on the foamed product using scCO₂, considering both the recycling feasibility and the unique characteristics introduced by the foaming process.

Early on, our research revealed a challenge with scCO₂, as its stability proved to be variable under different temperature and pressure settings. The dual nature of scCO₂, exhibiting characteristics of both liquid and gas, meant that adjusting temperature and pressure influenced its behavior, altering the viscosity and density of CO₂. Therefore, Chapter 4 assesses the impact of scCO₂ conditions on polymeric foam, specifically focusing on PBAT and a blend of PBAT/PLA with PLA content of 10, 20, and 30 %. Blending biodegradable polymers introduces plenty of possibilities by proportionally combining the properties of the individual polymers. Blending PLA into the PBAT matrix engineers the biodegradable aspect and tailors its thermal and mechanical properties, expanding potential applications for the blended material. Chapter 4 studies the complex flow be-
behavior of PBAT and PBAT/PLA blends, examining the interaction between polymers and CO$_2$ absorption concerning various process parameters and blending ratios. We conduct a study of the interplay between processing parameters and foam morphology, placing emphasis on pore structure, distribution, density, and compressive properties.

In Chapter 5, we investigate the blending of non-renewable polyesters with poly (3-hydroxybutyrate 3-hydroxyvalerate) (PHBV). PHBV offers a unique balance of rigidity and flexibility, rendering it adaptable for various applications. Blends comprising up to 15% PHBV with PBAT and PBS matrices were thoroughly examined. Chemical, thermal, and mechanical characterizations were conducted to understand the impact of PHBV incorporation on the properties of the blends. Furthermore, the complex flow behavior of the blends was carefully analyzed. Subsequently, foaming experiments were carried out, following a protocol. The foaming process involved creating foam samples from the blended materials to assess foam morphology, pore distribution, pore shape, expansion rate, and compression properties. A comparative analysis of the foam-related findings was undertaken, considering the varying PHBV content and its relationship with the characteristics of the base matrices. Through this comprehensive investigation, insights were gained into the synergistic interactions between PHBV and the base matrices. Such insights help in understanding the relationships that affect the properties of the resulting foams, thereby contributing to the development of tailored materials with desirable characteristics.

Biodegradable polymers hold promise for advancing sustainable materials, yet their susceptibility to degradation throughout the product life cycle poses a significant concern. In Chapter 6, we investigate the degradation rates of PBAT and PBAT blended with PLA (up to 15%). Initial characterization sets baseline parameters before degradation, with a focus on hydrolysis and photodegradation. Hydrolysis tests are conducted over 2, 4, and 6 weeks at 85% humidity and 60 °C, while photodegradation lasts 3, 6, and 9 weeks at 60 °C with UV exposure. Samples are analyzed chemically, thermally, and mechanically to track changes. Our results reveal significant alterations with PLA incorporation, impacting degradation rates. This chapter underscores the diverse degradation profiles observed, providing valuable insights into PBAT/PLA blends and their degradation behavior. Understanding these dynamics is essential for developing environmentally friendly materials with tailored degradation properties.

Numerous alternatives exist to address the issue of synthetic polymer pollution, with materials like PBAT, PBS, PHBV, and PLA emerging as promising examples. Their distinct properties make them suitable for a wide range of uses, including packaging, agricultural mulches, disposable tableware, medical devices, textiles, and apparel. Focusing on foams, which offer incredible advantages due to their versatility and lightweight nature, we have the option of utilizing CO$_2$. ScCO$_2$ has been proven to be beneficial in this thesis, offering adjustability for different foam needs, even when using the same polymer, since temperature and pressure adjustments will produce different morphology. ScCO$_2$ acts as a green solvent with mild processing conditions, providing easy control over its solubility in polymers. The combination of biodegradable thermoplastics processed with scCO$_2$ can integrate with existing polymer industry equipment such as extruders and batch reactors, making a significant impact globally. Biodegradable polymers foamed with scCO$_2$ find applications in energy insulation, automotive components, bedding,
protective materials, aerospace components, and vertical farming. This innovative approach not only addresses environmental concerns but also opens doors to a variety of sustainable solutions across various industries.