

EXPERIMENTAL STUDIES OF BIOPOLYMERS IN PRESENCE OF HIGH PRESSURE CARBON DIOXIDE

Sulamith Frerich*, Sabine Kareth, Andreas Kilzer, Marcus Petermann, Eckhard Weidner,
Institute of Thermo- and Fluidynamics, Chairs of Particle Technology and Process Technology,
Ruhr-University Bochum, Germany
Email to: frerich@vtp.rub.de

ABSTRACT

Foams based on biodegradable polymers are sustainable packaging materials. High pressure carbon dioxide (CO₂) is recently applied as foaming agent. There are at least two possible ways of polymer foaming: For the one method, the polymer is first saturated with CO₂, then depressurised and therefore expanded. In the second method, the foaming agent is a low boiling substance that is dissolved in the polymer. By heating, the foaming agent evaporates and creates a foam of the plasticized polymer. This latter method is also likely to work with encapsulated foaming agents. But in order to successfully design foaming procedures, investigations in the behaviour of the involved components at process conditions have to be carried out.

INTRODUCTION

Polymers made of renewable sources are a chance to reduce the consumption of fossil fuels. In addition, biodegradable polymers allow a sustainable recycling economy. Their quality of biological degradation helps to avoid waste. Therefore, several products and procedures already contain or work with biopolymers, especially in packaging [1,2]. In order to prevent goods during transportation, polymer foams are used. As sustainable foaming agent, high pressure carbon dioxide is applied in recent years [3]. In addition, CO₂ is used as auxiliary in several spraying processes. E.g. with the PGSS-process (Particles from Gas Saturated Solutions), polymeric particles with an encapsulated second phase are possible to obtain [4]. In principle, two substances referred to as shell and core material are provided in separate vessels. If necessary, they are heated up before being delivered into a high pressure mixing device. Here, a third line providing a compressed and preheated fluid is entering. All three substances are mixed together, then atomised through a nozzle into a spraying tower at atmospheric pressure. Due to the sudden expansion, the temperature drops rapidly (Joule-Thomson effect). Therefore, the small droplets of shell and core material are cooled down. Usually, the shell material is solid at ambient temperature. Once the temperature in the spraying tower drops below its crystallisation point, the droplets solidify. Thus, a two phase composite powder is obtained.

A designed two step foaming process could consist of blowing agents encapsulated in biodegradable polymeric particles and would be used to foam different forms. In a first step, the biodegradable polymer and the blowing agent are mixed together and atomised creating powder composites of the latter as core material in shells of biopolymer particles. Then, the composites are filled into a hollow form which is preheated under pressure near the melting temperature of the biopolymer. Now, during depressurisation, the polymer is flexible enough to be blown up due to the evaporating blowing agent. Thus, biopolymer foam is created whose shape is easily diversified. For a schematic of this process, see figure 1.

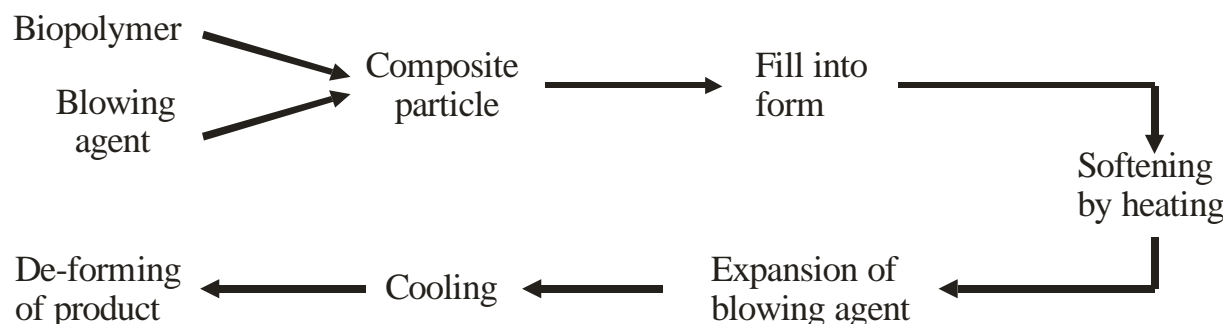


Figure 1: Schematic of a two step foaming process

Several considerations have to be taken into account in order to ease the foaming process. The requirements, especially for the properties of biopolymer and blowing agent are listed in table 1.

Table 1: Requirements for the two step foaming process

	Requirement	Explanation
Biopolymer	solid at room temperature	no particles obtained
	good mechanical properties	suitable for packaging
	low melting point	energetic advantages
	low glass transition temperature	softening starts earlier, better foaming
	fast crystallisation	enables fast de-forming of product
Blow agent	high vapour pressure	less blowing agent required
	non-toxic, non-flammable	safety reasons
In combination	no chemical reaction	no reduction of the two substances
	not miscible	no single fluid phase

The biopolymer has to be chosen by investigating its melting and crystallisation behaviour. As it is shown above, low glass transition and melting temperatures show energetic advantages. Combined with fast crystallisation, the whole process is less time consuming. The blowing agent should show a high vapour pressure at the glass transition temperature of the polymer to enable a sufficient foaming. If biopolymer and blowing agent are miscible, the mechanical properties of the product still have to be sufficient for foaming. A single fluid phase would inhibit the blowing up of the biopolymer as shell material. Concerning the PGSS-process, a rapid crystallisation of the biopolymer in the spraying tower is necessary; otherwise agglomeration of non-solidified biopolymer instead of powder is obtained. In addition, a low temperature in the spraying tower is needed to avoid great loss of the blowing agent due to evaporation. A high solubility in the compressible gas would result in a loss of

the blowing agent either, as it would be removed from the spraying tower with the gas extracted by suction. Because of the mixing of biopolymer and compressible fluid, and the addition of a blowing agent, the behaviour of these three substances under spraying conditions has to be investigated.

MATERIALS AND METHODS

As biodegradable polymers, GS Pla AZ91T[®] from Mitsubishi Chemical Corporation, Japan (based on polybutylene succinate), NatureWorks PLA from Cargill Dow LLC, USA (based on polylactide acid), and Biograde[®] 200C from FKuR, Germany (based on cellulose acetate), were used. Delivered as granules obtained from extrusion, the substances were investigated in their initial state as well as in presence of carbon dioxide (YARA, 99,9 % purity) which is used as compressible gas in the PGSS-process. The melting behaviour of each polymer was analysed first per differential scanning calorimetry (DSC) analysis (Setaram DSC 131 evo) with nitrogen (Air Liquide, 99,9 % purity) as protective gas. Each sample experienced heating and cooling rates from 2 K/min to 10 K/min. Compared with a reference, changes in heat flow between two crucibles in one furnace were recorded. Thus, the melting temperature of each polymer and its crystallisation behaviour was determined. In addition, a high pressure view cell was used to investigate the melting behaviour due to dissolved gas (see figure 2). The cell shows two high pressure windows mounted at opposite sides and is designed to operate up to 35 MPa and 300 °C. Each measurement started with preheating the view cell and its sample up to a temperature below the melting point. Depending on the temperature chosen, the preheating lasted between 35 min and 90 min. The addition of CO₂ into the view cell increased the pressure. In order to keep the temperature constant during pressurisation, the pressurisation was accomplished in steps about 0,1 MPa after at least a 30 min break. Once the polymer melted, the decrease of melting temperature at that pressure was obtained.

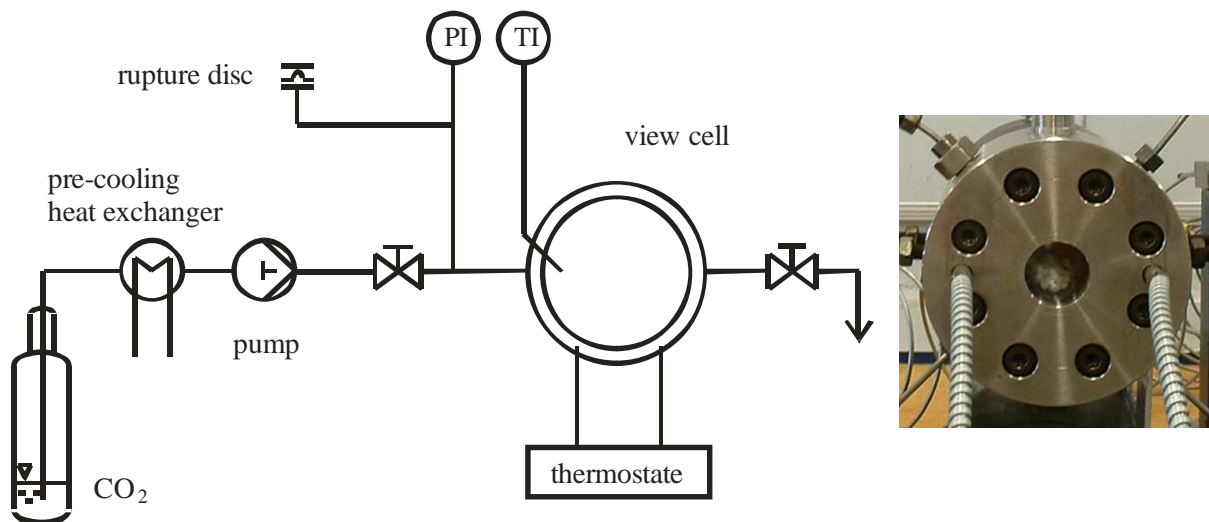


Figure 2: Schematic of the high pressure view cell apparatus and a picture of the view cell

In order to start the encapsulating experiments, preliminary investigations of the PGSS-process parameters for obtaining biopolymer particles have been carried out. An existing PGSS-plant was slightly modified to sufficiently melt the biopolymer. As it is shown in

figure 3, a single-screw extruder (MAGME, KSP 18B) is providing the biopolymer, so the polymer granules are melted due to its heat transfer and shear stress.

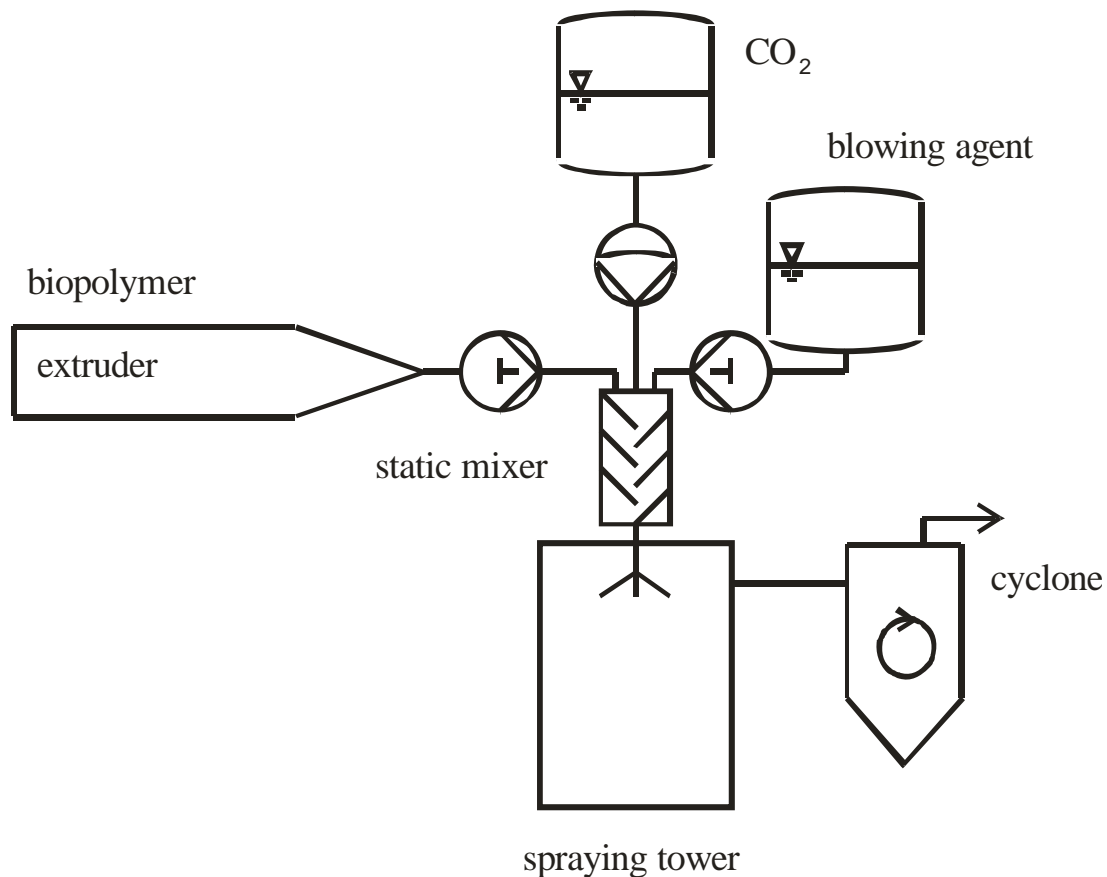


Figure 3: Modified PGSS-plant with a single-screw extruder

The blowing agent is provided in a container, and the compressible gas, CO₂, is stored in a tank under 5 MPa. CO₂ is withdrawn in its liquid state and delivered by a high pressure dosing pump (LEWA), biopolymer and blowing agent are delivered by piston pumps (LEWA resp. Bran Luebbe). All substances are mixed together in the static mixer (0 to 4 mixing elements from Fluitec, diameter: 6 mm) before being atomised into the spraying tower (diameter: 1,20 m, height: 2 m). Parameter studies were carried out by varying pre-expansion pressure, pre-expansion temperature, gas-to-polymer ratio, number of static mixing elements, and nozzle diameter. In general, a pressure increase results in higher shear stress experienced by the biopolymer while atomised through the nozzle. In addition, high pre-expansion pressure levels increase the pressure drop during expansion. That is, the biopolymer is divided in smaller droplets in the spraying tower while the post-expansion temperature in the tower is lowered. Nevertheless, the temperature in the tower is influenced by the pre-expansion temperature as well. However, a higher temperature of the biopolymer (both the temperature of biopolymer and CO₂ yield into the pre-expansion temperature) lowers its viscosity and reduces therefore the shear stress forces at the nozzle. Thus, the parameter studies had to consider these mutual influences. Once the PGSS-experiments with pure biopolymer are finished, encapsulation tests start. In order to choose a blowing agent, databases were screened, and solubility experiments investigated the behaviour of possible substances with the chosen biopolymers. For first experiments, deionised water was chosen.

RESULTS

The thermal analysis of GS Pla AZ91T and NatureWorks PLA with DSC and view cell yield 115 °C resp. 146 °C as melting temperatures at ambient pressure. Unfortunately, Biograde 200C did not show a melting temperature at any thermal heating rate neither in DSC analysis nor in the view cell. Further investigations in the high pressure view cell show a decrease in the melting temperature of GS Pla AZ91T and NatureWorks PLA about 15 °C resp. 50 °C in the presence of carbon dioxide (see figure 4). The thermal analysis of Biograde 200C in presence of carbon dioxide showed polymeric decomposition instead of a melting point decrease. Although its decomposing temperature was determined with 250 °C, the cellulose acetate based polymer started to decompose already at 180 °C if the operating time lasted 2 h or more.

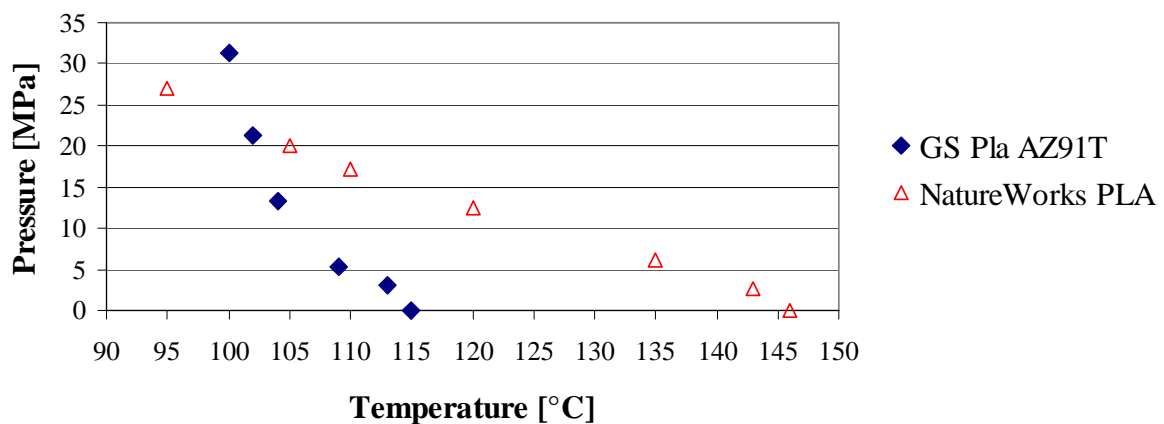


Figure 4: Melting behaviour due to dissolved carbon dioxide

After the thermal analysis of biopolymers in presence of CO₂, the view cell was depressurised. Therefore, the previously dissolved carbon dioxide in the biopolymer was set free, and the liquefied polymer was blown up. Depending on the dissolution time during the previous experiment as well as on the rate of depressurisation, different biopolymer foams were obtained. It was e.g. possible to foam a cylindrical shape (inner diameter: 27 mm, height: 25 mm) with Biograde 200C granules. The biopolymer was filled into the form closed with the lid while the CO₂ dissolved into the granules through the mesh wire. After 1 h at 190 °C and 15 MPa operating conditions, the view cell was depressurised. The granules sintered together and expanded to more than two times of their initial volume (see figure 5).



Figure 5: Foaming of Biograde 220C

According to the preliminary analysis of thermal behaviour, the PGSS-experiments refrain from spraying Biograde 200C. Its non-melting but decomposing behaviour precluded its delivery by the extruder. Until now, the experiments in the PGSS-process were accomplished with GS Pla AZ91T. It was found that pre-expansion pressures between 25 MPa and 28 MPa in combination with pre-expansion temperatures around 120 °C and 130 °C yield biopolymer particles. With lower pressures and higher temperatures, the created biopolymer droplets are not completely cooled down before they meet the bottom of the spraying tower. Therefore, agglomeration can be observed. As the encapsulation of water as blowing agent just started, the preliminary parameter alignments served as orientation values. But because of the changing properties of the system consisting of biopolymer and blowing agent, the parameters have to be adjusted in order to maintain particles as a product.

CONCLUSION

With GS Pla AZ91T, NatureWorks PLA and Biograde 200C, several biopolymers were chosen as model substances for future foaming procedures. Their melting behaviour under ambient pressure was studied per DSC analysis as well as in a high pressure view cell. In presence of CO₂, the analysis in the view cell showed a decrease of melting temperatures. With pressures up to 30 MPa, it was possible to melt GS Pla AZ91T about 15 °C and NatureWorks PLA about 50 °C below their initial melting temperature. Due to its non-melting but decomposing behaviour, Biograde 200C was excluded from further investigations. During depressurisation, all chosen biopolymers were foamed because of the dissolved gas evaporating. The liquefied granules expanded, sintered together, and the shape of the created foam could be varied. First PGSS-experiments with GS Pla AZ91T proved the possibility to obtain biopolymer particles. In order to encapsulate water as blowing agent into GS Pla AZ91T, process parameters have to be adjusted.

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