

BIOPOLYMER PARTICLES AND FOAMS BY PGSS TECHNOLOGY

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ABSTRACT

The availability of fossil resources is shrinking. Polymers based on renewable resources are considered as an alternative to synthetic polymers based on olefins. If the polymers are biodegradable, their short life cycle enables a sustainable disposal. The applicability of biodegradable polymers is limited, however, their use in packaging and transportation protection is approved. Polymeric foams are appropriate to meet the requirements of low weight combined with good stability. In addition, foamed polymers are shock absorbing and insulating. They are manufactured by dissolving a gas within the polymer and subsequent expansion. High pressure carbon dioxide is increasingly applied as blowing gas in recent years. Moreover, it is used as auxiliary substance in the PGSS-process, an established high pressure micronisation and encapsulation process suitable for viscous polymer melts.

In this work, the potential of creating biopolymer foams via the PGSS-process was investigated. Several biopolyesters were chosen as model polymers. Their melting behaviour was determined by experiments in both a differential scanning calorimeter (DSC) and a high pressure view cell up to $p \leq 25$ MPa and $T \leq 300$ °C. For a process design, additional fluid dynamic parameters as viscosity are necessary. The dynamic viscosity of the biopolymers was determined by using a shear rheometer. Spray experiments with the PGSS-process were accomplished at various parameters, and different particle morphologies of the polymer were achieved. The influence of the parameters on the morphology of the samples was studied. A new approach of foaming polymers in porous moulds to yield light construction or packaging elements is presented. The foaming behaviour of the biopolymers at various conditions was studied.

INTRODUCTION

Biopolymers recently obtain increasing interest, due to their properties. The definition of a biopolymer includes polymers based on renewable resources and biodegradable polymers. Packaging and transportation protection are preferential applications [1]. Polymeric foams show densities from $1,6 \text{ kg/m}^3 \leq \rho \leq 960 \text{ kg/m}^3$ [2]. Their manufacturing consists of three different steps. First, a gas has to be dissolved or mixed into the polymer. Second, the foam is created by gas expansion, and third, the foam is stabilised by cooling or cross-linking of the polymer. High pressure carbon dioxide is applied as blowing agent in recent years [3]. Moreover, carbon dioxide is used in several spray processes. The PGSS process enables the powderisation of polymers, and the creation of particle composites [4]. However, the encapsulation of a blowing agent requires special characteristics. Another approach to foam polymers is to use porous moulds. Carbon dioxide dissolves into the polymer. During depressurisation, the liquefied polymer is blown up and sintered together, creating foam moulded parts.

MATERIALS AND METHODS

The biopolymers chosen as model polymere were GS Pla AZ91T[®] from Mitsubishi Chemical Corporation, Japan (based on polybutylene succinate), NatureWorks PLA from NatureWorks LLC, USA (based on polylactic acid), and a polyester blend, based on polylactic acid and polyhydroxy butyrate. The substances were investigated in their initial state as well as in presence of carbon dioxide (YARA, 99,9 % purity). 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. As the sample is compared with a reference, changes in heat flow between two crucibles in one furnace were recorded. To eliminate thermal history of each sample, it was run two times from room temperature to $T_{\max} = 250\text{ }^{\circ}\text{C}$. Thus, the melting and crystallisation temperature of each polymer was determined. A rheometer (Thermo Scientific RheoStress 75) was used to determine the complex viscosity of each polymer at different temperatures. In addition, a high pressure view cell was used to investigate the melting behaviour due to dissolved gas. The cylindrical shaped view cell is an autoclave with two high pressure windows mounted at the opposite sides. It is designed to operate at $p_{\max} \leq 25\text{ MPa}$ and $T_{\max} \leq 300\text{ }^{\circ}\text{C}$. Each measurement in the view cell started with preheating up to temperatures below the melting point, determined by DSC measurements. The preheating took $35\text{ min} \leq t \leq 90\text{ min}$, depending on the temperature chosen. By adding CO_2 into the view cell, the pressure was increased in steps of around 0,1 MPa every 60 min in order to keep the temperature constant. Once the polymer melted, the decrease of melting temperature at the given temperature and pressure was obtained.

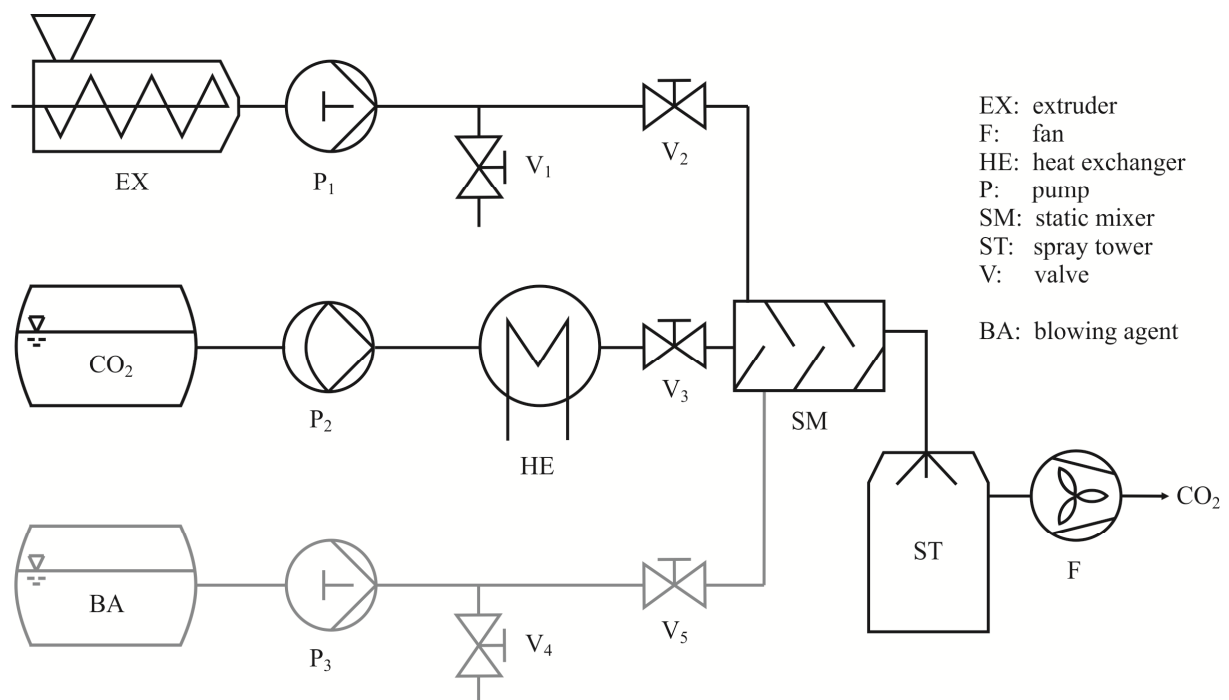


Figure 1 : PGSS-plant used for micronizing the biopolymers

The PGSS-process has been carried out to obtain biopolymer particles. As it can be seen in figure 1, a single-screw extruder (MAGME, KSP 18B) is providing the biopolymer. The compressible gas, CO_2 , is stored in a tank under 5 MPa. CO_2 is withdrawn in its liquid state

and delivered by a high pressure dosing pump (LEWA), the biopolymer is delivered by a piston pump (LEWA). The substances are mixed together in the static mixer (0 to 4 mixing elements from Fluitec, diameter: 6 mm) before being atomised through a nozzle into the spray tower (diameter: 1.20 m, height: 2 m). Due to the sudden expansion, the temperature drops rapidly (Joule-Thomson effect). The droplets solidify if the temperature is below their crystallisation point. The CO₂ is withdrawn by a fan and can be recycled. 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 addition, a third substance referred to as blowing agent was sprayed with the biopolymer in order to obtain particle composites. In this work, deionised water was chosen. It was provided in a separate tank and delivered by another piston pump (Bran Luebbe). The three substances were mixed together and atomised into the spray tower as explained above. The obtained particle composites were characterised and their ability to create foams was examined.

A new approach of a direct foaming procedure was developed. Cylindrical shaped porous moulds were filled with the polymer, and placed into an autoclave at various temperatures and pressures. Besides the amount of polymer used, the times of pressurisation and depressurisation were varied. The obtained foam moulded samples were compared in density and mechanical properties.

RESULTS

The DSC analysis of the three polymers yield melting temperatures of $T = 115\text{ }^{\circ}\text{C}$ (PBS), $T = 157\text{ }^{\circ}\text{C}$ (PLA), and $T = 172\text{ }^{\circ}\text{C}$ (polyester blend), respectively. Further investigations in the high pressure view cell show a decrease in the melting temperature of $\Delta T = 15\text{ }^{\circ}\text{C}$ (PBS), $\Delta T = 42\text{ }^{\circ}\text{C}$ (PLA), and $\Delta T = 32\text{ }^{\circ}\text{C}$ (polyester blend), respectively, in the presence of carbon dioxide (see figure 2).

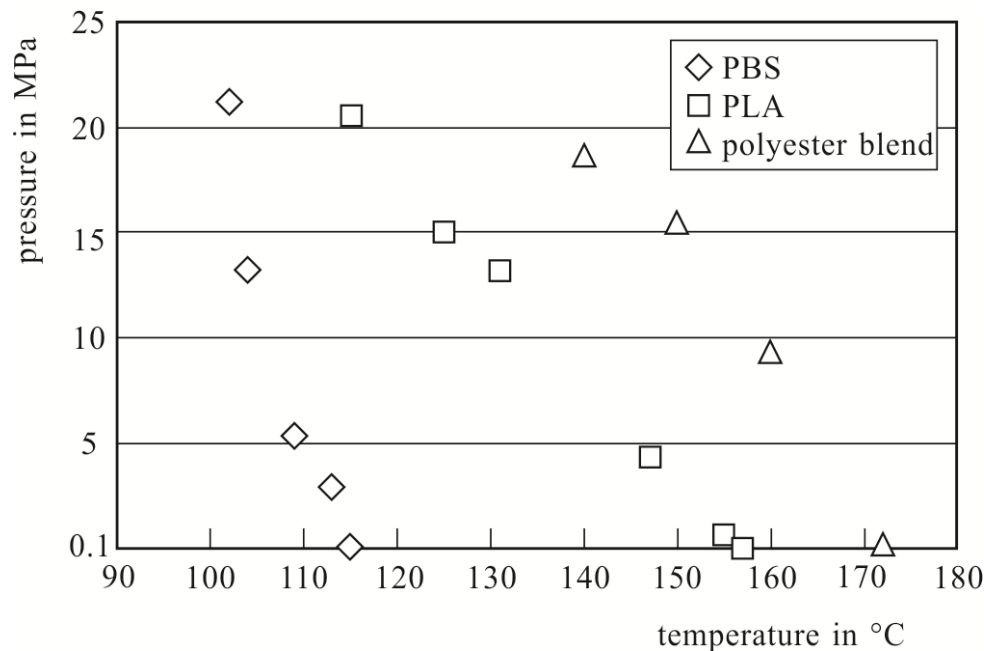


Figure 2 : Pressure-induced melting of the biopolymers in presence of carbon dioxide

The viscosity of the biopolymers was determined as shear thinning and is decreasing at increasing temperatures. While PBS got values as $3200 \text{ Pas} \leq \eta^* \leq 5100 \text{ Pas}$ at temperatures $T = 160 \text{ }^\circ\text{C}$ and $T = 120 \text{ }^\circ\text{C}$, resp., PLA is determined with $700 \text{ Pas} \leq \eta^* \leq 12000 \text{ Pas}$ at $T = 200 \text{ }^\circ\text{C}$ and $T = 160 \text{ }^\circ\text{C}$, resp. The polyester blend did show the lowest viscosity, with values as $75 \text{ Pas} \leq \eta^* \leq 400 \text{ Pas}$ at temperatures $T = 200 \text{ }^\circ\text{C}$ and $T = 180 \text{ }^\circ\text{C}$, resp.

In order to investigate the potential of obtaining polymer particles and particle composites, two of the three biopolymers were processed via PGSS technology. 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 CO_2 yield into the pre-expansion temperature) lowers its viscosity and reduces therefore the shear stress forces at the nozzle. As it can be seen in table 1, the process parameters are varied for each polymer according to the preliminary results. PBS was processed at moderate temperatures, due to its low melting behaviour. Pre-expansion pressures at $200 \text{ bar} \leq p_{\text{pre}} \leq 300 \text{ bar}$ were used to obtain spherical particles, but the specific gas amount was relatively high. The polyester blend was processed at a broader range of temperatures and pressures. Due to its distinct pressure-induced melting at lower temperatures, even pre-expansion temperatures at $T = 135 \text{ }^\circ\text{C}$ combined with higher pre-expansion pressures are possible.

Table 1 : PGSS-parameters of PBS and polyester blend

Parameters	PBS	polyester blend
pre-expansion pressure	$200 \text{ bar} \leq p_{\text{pre}} \leq 300 \text{ bar}$	$150 \text{ bar} \leq p_{\text{pre}} \leq 375 \text{ bar}$
pre-expansion temperature	$108 \text{ }^\circ\text{C} \leq T_{\text{pre}} \leq 175 \text{ }^\circ\text{C}$	$135 \text{ }^\circ\text{C} \leq T_{\text{pre}} \leq 220 \text{ }^\circ\text{C}$
post-expansion temperature	$12 \text{ }^\circ\text{C} \leq T_{\text{post}} \leq 160 \text{ }^\circ\text{C}$	$20 \text{ }^\circ\text{C} \leq T_{\text{post}} \leq 76 \text{ }^\circ\text{C}$
number of mixing elements	$0 \leq N \leq 4$	$0 \leq N \leq 4$
nozzle diameter	$0,55 \text{ mm} \leq d \leq 1,2 \text{ mm}$	$0,64 \text{ mm} \leq d \leq 1,2 \text{ mm}$
specific amount of gas	$64 \leq SG \leq 198$	$36 \leq SG \leq 175$

The encapsulation of deionised water in both PBS and the polyester blend was accomplished at ratios up to 4 times water to polymer amount. It was possible to obtain composite particles containing 30 weight per cent to 70 weight per cent water, as detected during drying experiments at $80 \text{ }^\circ\text{C}$ in an oven. However, it was not possible to observe any foaming due to the expansion of water in subsequent experiments. Therefore, a new approach of designing a foaming procedure was undertaken.

The tool used for these experiments is shown in figure 3, a cylindrical shaped porous mould coated with PTFE (Huth & Soehne). Placed into an autoclave and heated up, carbon dioxide was dissolved into the polymer. By depressurisation, a foam is created. In general, high processing temperatures liquefy the biopolymer which is needed for sintering. Inefficient cooling of the foam causes negative results, due to a collapsing polymer. The pressure present

during the experiment has an influence on diffusion and solubility of the gas into the polymer. At low pressures, the solubility of gas is lower, but the dissolution takes longer. Therefore, the pressurisation time is crucial. In addition, the depressurisation rate has a great influence in the shape of the achieved foam moulded samples, too. As the solubility of gas is reduced, the gas separates from the polymer. Thus, a high depressurisation rate causes deviations of shape, as the polymer is withdrawn from the mould.



Figure 3 : Cylindrical shaped porous mould used for foaming

This foaming procedure was accomplished for all three polymers. The achieved foam moulded samples show a porosity of 50 volume per cent to 80 volume per cent. PBS showed a good foam quality at $110\text{ }^{\circ}\text{C} \leq T \leq 116\text{ }^{\circ}\text{C}$ and $20\text{ MPa} \leq p \leq 30\text{ MPa}$, PLA was processed best at $125\text{ }^{\circ}\text{C} \leq T \leq 140\text{ }^{\circ}\text{C}$ and $20\text{ MPa} \leq p \leq 30\text{ MPa}$, and the polyester blend results were optimal at $136\text{ }^{\circ}\text{C} \leq T \leq 146\text{ }^{\circ}\text{C}$ and $20\text{ MPa} \leq p \leq 30\text{ MPa}$.

CONCLUSION

In this work, the foaming of the biopolymers GS Pla AZ91T (PBS), NatureWorks PLA (PLA) and a polyester blend based on PLA and PHB was investigated. Preliminary experiments of thermal and mechanical properties were accomplished to determine their melting and crystallisation behaviour and dynamic viscosity. In addition, the pressure-induced melting behaviour in presence of carbon dioxide was studied. The PGSS-process was used to powderise two polymers by taking these results into account. In addition, particle composites were achieved by encapsulating water. As the foaming ability of those composites was unsatisfying, a different approach was carried out by using carbon dioxide as blowing agent. This second foaming procedure has been using the polymer granules as delivered. However, it is possible to use the particles manufactured via PGSS-process in porous moulds, too. If mass is constant, the surface of particles is enhanced, compared to bulk polymer. That is, the saturation time during gas dissolution is shorter, and therefore, the foaming ability is enhanced. In order to avoid any discharge of particles out of the mould, its pore size has to be adjusted.

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