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Extrusion assisted by supercritical CO₂: A review on its application to biopolymers

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A B S T R A C T

Extrusion assisted by supercritical CO₂ (sc-CO₂) is an emerging method for the microcellular foaming of polymer. Instead of batch foaming, which requires formation of single-phase polymer/CO₂ solution in long cycle times, the extrusion assisted by supercritical fluids overcomes this issue by providing rapid mixing and dissolution of CO₂ in the polymer melt. Because the sc-CO₂ is soluble in many molten polymers and acts as a removable plasticizer, its introduction in an extruder will permit a decrease of the processing temperature. This technic allows the use of fragile component like active molecule or starchy and proteinaceous materials. At the end of the extruder, the pressure drop will create instability and phase separation with the creation of porosity. This review is dedicated to the extrusion assisted by sc-CO₂ with different types of biopolymer. Industrial application domains include agro-food, biomedical, pharmaceutical, packaging and many others.

Keywords:

Biopolymers
Supercritical fluid extrusion
Foaming
Biomedical applications
Agro-food applications
Consumer plastics applications

1. Introduction

Foams of polymers are used in many fields like cushioning, insulation, packaging, and medical purposes (e.g. scaffolding), because of their specific properties [1]. A porous polymer matrix can be defined by the size distribution of the cells, the cell density i.e. the number of cells per unit volume, and the volume expansion defined as the volume occupied by voids divided by the volume of the polymer [2]. It is combined with a low density and a high porosity.

Classic manufacturing processes use chemical blowing agents (CBAs) like carbonated salts which lead to CO₂ upon thermal decomposition but leave residues in the final product. The main advantage of CBAs lies in the fact that they can be used irrespective of the pressure. However, they are expensive and require high temperature for decomposition [3]. This is why the use of physical blowing agents (PBAs) tends to replace the CBAs utilisation. PBAs are gaseous substances like HFCs, which can be injected under pressure into a polymer melt. PBAs have no decomposition temperature requirements, a reduced cost, and generally produce better cell morphology. However most of these gases can exhibit deleterious effects like the depletion of the ozone layer as well as some hazardous properties [3].

An interesting alternative is the use of supercritical fluids and particularly carbon dioxide (CO₂) as PBA in hot-melt extrusion processes due to their unique properties, such as environmental friendliness, non-flammability, and low cost [3]. This relatively new field of research has developed quickly in the recent years [4,5]. CO₂ is well known for its compatibility with several polymers in which its solubility can be relatively high depending however on the temperature and pressure conditions.

The methodology used can be basically described as an injection of pressurized CO₂ in the barrel of an extruder (see next paragraph). CO₂ acts as a removable plasticizer in the metering zone of the extruder where it modifies the rheological behaviour of the melt. Moreover, it acts as an expansion agent when it returns suddenly to atmospheric pressure at the die exit [6]. This pressure quench is responsible for the supersaturation in the metastable melt phase leading to nucleation and growth of CO₂ bubbles and eventually the final porous 3D-structure.

Nowadays, because of the shortage in fossil resources and environmental concerns over the waste materials, the use of synthetic polymers is disputable. A biobased polymer is a polymer derived from renewable resources. Therefore, it appears that the use of such biopolymers will replace the polymers obtained from petrochemistry and shows a great potential.

Biodegradable polymers are another category of biopolymers. Jeon et al. published in 2013 a review on the microcellular foaming of biodegradable polymers [7]. In their paper, different foaming

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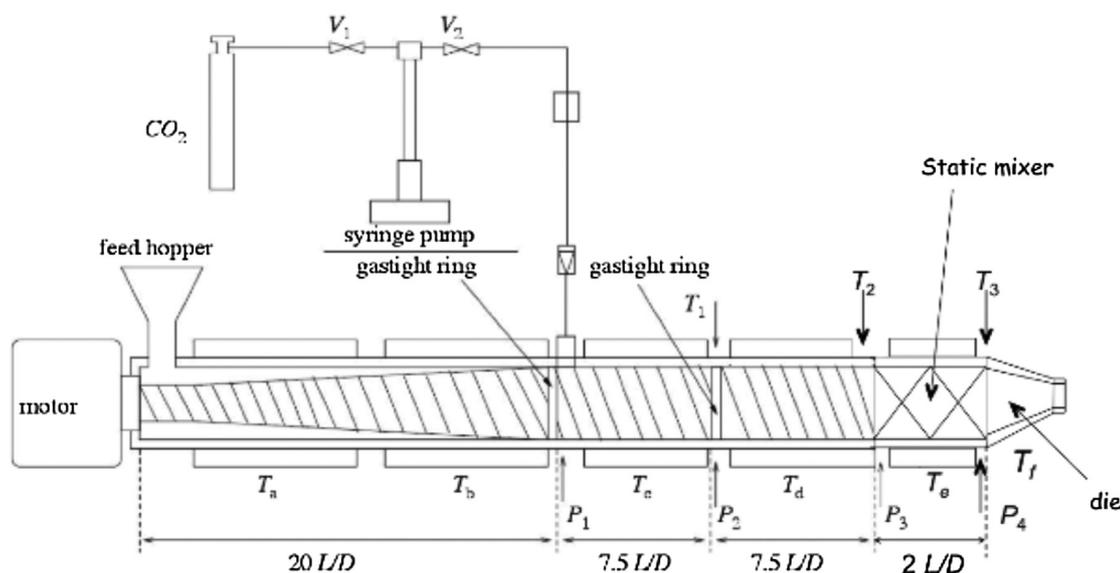


Fig. 1. Schematic of the single-screw extruder used by Fages et al. [15,19–23]. (Reprinted with permission from [15], © 2014 Elsevier).

processes are investigated including batch foaming process, and injection foaming process.

Biocompatibility refers to the ability of a material – including polymers – to be implanted in the human body. In this review biocompatible polymers will be included in the generic term of biopolymer.

In the present paper, we have chosen to focus on the processing of biopolymers by extrusion assisted by supercritical- CO_2 (sc- CO_2) in several application areas with a special emphasis on the pharmaceutical and food domains.

2. The process of extrusion assisted by supercritical CO_2

2.1. The process: rationale

A supercritical fluid is defined as a substance for which both pressure and temperature are above the critical values. The special combination of gas-like viscosity and liquid-like density of a supercritical fluid makes it an excellent solvent or plasticizer for various applications like polymer composites, microcellular foaming or particle production [8,9]. The density of supercritical fluids can be tuned easily by small changes in pressure within the critical region. Sc- CO_2 is most often used because it is non-toxic, non-flammable, chemically inert, and its supercritical conditions are easily reached ($T_c = 31^\circ\text{C}$, $P_c = 7.38\text{ MPa}$) and it can be removed from a system by simple depressurization. Its high solubility enhances plasticizing and expansion of a material, with accompanying modification of mechanical and physical properties. For example, CO_2 decreases the glass transition temperature, T_g , and the viscosity of many polymers without otherwise changing their pseudo-plastic behaviour [9,10].

There are many additional advantages of using sc- CO_2 with the process of extrusion. Not only the sc- CO_2 will change the rheological properties of the material inside the extruder but it also plays the role of an expansion agent. The diminution of viscosity will result in the limitation of mechanical and shear stresses and will allow a decrease in operating temperatures. Therefore, it will be easier to handle molecules having a limited thermal stability. Moreover, its dissolution in the polymer under pressure will be accompanied by large volume expansion during the return to atmospheric pressure [10].

2.2. Experimental devices and modes of operation

According to Sauceau et al. [10], the experimental devices for the extrusion assisted by CO_2 supercritical must allow the steps described here:

- Dosing and conveying the components;
- Development of rheological properties of the melt (preparation and plasticizing);
- Injection of pressurized CO_2 ;
- Homogeneous mixing to obtain a single phase mixture;
- Nucleation, growth and coalescence of pores provoked and controlled by the thermodynamic instability created by the pressure drop through the die;
- Material shaping and cooling at the return to atmospheric pressure.

Depending on the number of screws turning in the barrel, the extruders are available in two different types: the single-screw extruder or the twin-screw extruder. In both types, the polymer is introduced into the feed hopper, conveyed along the barrel and begins to melt in the first section, then, it is pressurized in the last section and is forced through the die. Most of the time, the metered amount of physical blowing agent is injected into the extrusion barrel at a gas injection port by a positive displacement pump and is mixed intensively with the polymer melt stream.

At the end of the extruder screw, before the die, some ancillary devices can be added. A static mixer can be installed for enhancing both distributive and dispersive mixing and to improve the sorption and dissolution of the CO_2 in the polymer melt. Matuana et al. [11,12] and Pilla et al. [13,14] added a diffusion-enhancing device (static mixer Omega FMX8441S). Le Moigne et al. [15] chose to add a static mixer composed of four elements (SMB-H 17/4, Sulzer, Switzerland). Mihai et al. [16–18] added a gear pump placed at the end of the extrusion line to preserve a high-pressure level at the end of the extruder. To control the processing pressure, a two-hole flow restriction nozzle can be mounted like in the study of Rizvi et al. [5] or by constricting the cross-sectional area of the channel in a home-made die by means of a central pin like for Vigh et al. [19]. In these cases, the pressure inside the extruder near the die

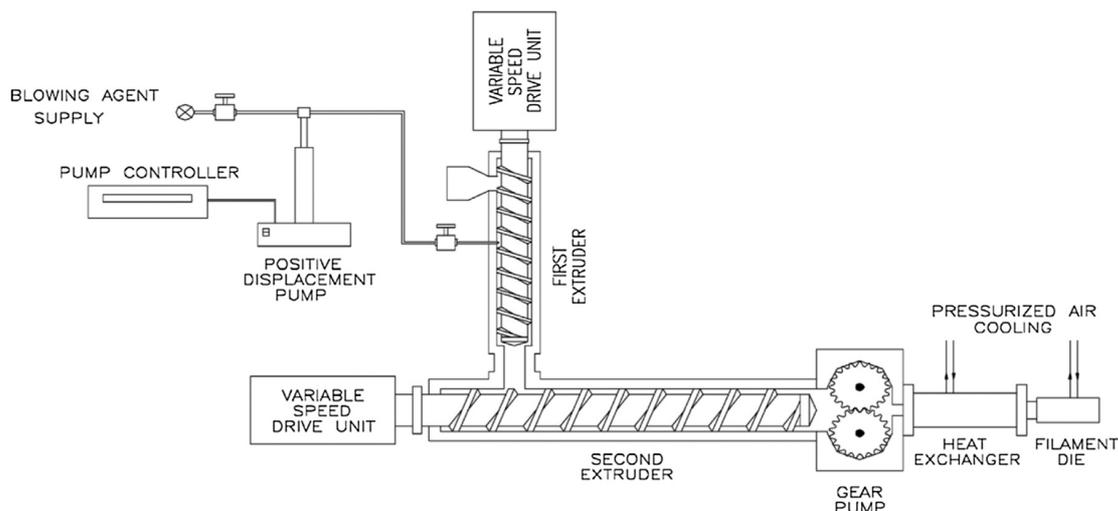


Fig. 2. Schematic of the tandem extrusion line used by Lee et al. [24–26]. (Reprinted with permission from [26], © 2005 American Chemical Society).

was increased or decreased by tuning the opening degree of the restriction, applied to the melt flow.

In the case of a single-screw extruder, like in Fig. 1, a restriction ring can be located between each section to increase the shear and the pressure locally and thus creating a dynamic molten polymer seal, which prevents backflowing of sc-CO₂ [15,19–23]. For a better mixing, a tandem extrusion system can be used. Park and coworkers [24–26] use a tandem extrusion system as shown in Fig. 2. The system consists of a first extruder with a mixing screw, a second extruder with a cooling screw, a syringe pump for injecting the blowing agent, a gear pump, a heat exchanger containing homogenizing static mixers, and a filamentary die. The first extruder plasticizes the polymer and disperses the blowing agent into the polymer melt. The gear pump provides flow rates, which are independent of temperature and pressure. The second extruder provides further mixing and initial cooling of the melt, and the heat exchanger removes the remaining heat for testing at a specific temperature.

In the case of a twin-screw extruder, it is a common thing to add a pair of reverse screw elements, situated upstream from the blowing agent injection point for creating a dynamic melt seal to maintain a high CO₂ pressure in the latter portion of the extruder [16–18].

2.3. Influence of the die geometry

An important point to take in consideration for the extrusion foaming is the die and the pressure drop rate induced by this die. Indeed, the pressure drop rate in the nucleation device plays a strong role in determining the foam cell density. The die has an effect on the thermodynamic instability induced in the polymer/gas solution and the competition between cell nucleation and growth. Park et al. [27] showed that for a given amount of gas, the cell density increased with an increase of pressure drop rate for polystyrene. They also highlighted the fact that regardless of the concentration of CO₂, or nucleating agent in a molten polymer, the die geometry determines the pressure-drop rate and the die pressure, thereby dominantly affecting both the cell density and the cell morphology [28]. Alavi and Rizvi [29] observed similar results with starch-based foams: the bubble density (N_{bubble}) increased while the average bubble diameter decreased with a lower nozzle diameter i.e. a higher pressure drop rate. They also noticed that samples underwent higher expansion rate as the nozzle radius

decreased from 3 to 1.5 mm and piece density decreased by 40%. They explained that as N_{bubble} increased, the effective diffusivity (D_{eff}) of CO₂ is reduced and less gas escaped out, leaving a larger amount for diffusion into the bubbles. This led to an enhanced expansion, although the average bubble diameter was reduced because the CO₂ was distributed over a greater number of bubbles.

2.4. Importance of the operating temperature

If the cell density is mainly determined by the die and the pressure drop, the foam expansion and other foam's characteristics are mainly controlled by the temperature, as shown for several polymers (PLA [13,24,25], PC [26], starch [29], PS [6,30], PP [31], LDPE [32]). Indeed, during the microcellular foam generation through and after the die, there is a loss of CO₂, which limits the volume expansion because the CO₂ easily escapes through the exterior skin of the foam. One way to prevent gas escape from the foam is to freeze the skin of the extrudate by controlling the die temperature. Indeed, the decrease of the die temperature can limit the gas diffusion at the surface and finally, more gas remains in the foam to contribute to the volume expansion [6]. However, if the temperature is further decreased, the expansion decreases because of the increased stiffness of the frozen skin layer [6] (Fig. 3).

Moreover, the polymer melt should be cooled substantially to increase its strength in order to prevent cell coalescence and to insure a high cell density while keeping a sufficient fluidity for bubbles to grow [30]. Therefore, a compromise for die and melt temperatures must be found. It has to be emphasized that, for some polymers, to be able to decrease the melt and die temperatures, the sc-CO₂ content has to be increased ([24,26]). In fact, when the temperature is lowered, the polymer viscosity increased and the pressure upstream the die can be very high. Adding more CO₂ in the extruder will plasticize the polymer and thus decrease both the viscosity and the pressure allowing to operate at lower temperature (Fig. 4).

Because the expansion ratio is also linked to the open-cell content, Park et al. [32], Lee et al. [26] and Huang et al. [33] showed with LDPE/PS and polycarbonate that there was an optimal die temperature for maximizing the open-cell content (Fig. 3). At low temperatures (zone 3), cell walls became too stiff for cell opening, and therefore, the open-cell content increased as the temperature was increased in this low-temperature range (between zone 3 and 2). At higher temperatures, the thickness of cell walls governed cell

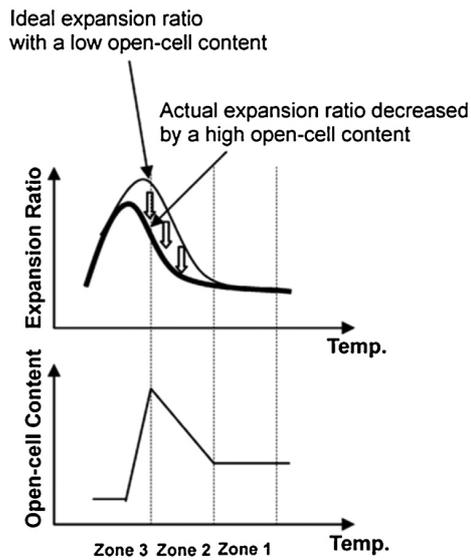


Fig. 3. Comparison between expansion ratio and open-cell content from Ref. [26]. (Reprinted with permission from [26], © 2005 American Chemical Society).

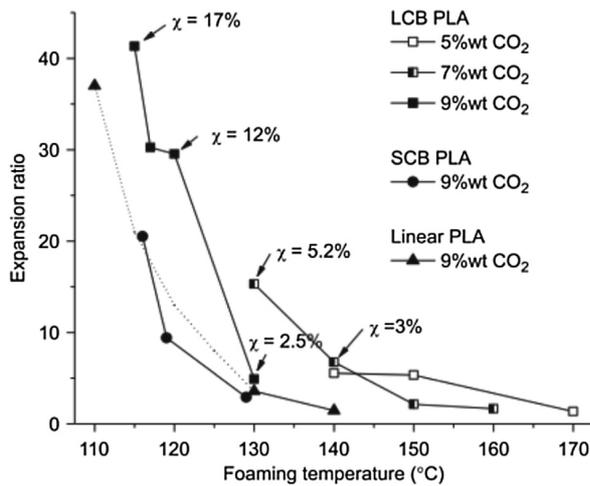


Fig. 4. Expansion ratio and bulk crystallinity of PLA foams as a function of processing temperature and CO₂ concentration by Wang et al. [24]. (Reprinted with permission from [24], © 2012 Elsevier).

opening, and therefore, the open-cell content decreased as the temperature increased in the high-temperature range (between zone 2 and 1).

3. The different types of biopolymer

In 2013, the European plastics consumption was about 46.3 millions tonnes (data from PlasticsEurope [34]). The oil-based and non-biodegradable polyolefins like polypropylene (PP), polyethylene (PE) and polyvinyl chloride (PVC) represent more than 50% of this consumption. These plastics finish often as waste. In 2012, for 25.2 million tonnes of post-consumer plastics wastes, 62% was recovered through recycling and energy recovery processes while 38% went to landfill [34]. In order to decrease the high percentage of wastes ending up in landfill and to preserve the petroleum resource, biopolymers are more and more used. In Europe, the global production capacities of bioplastics increased from 1492 to 1622 millions tonnes in one year (2012–2013) and it is expected that it will reach

6.7 millions tonnes in 2018 (data from Bio-Based Economy [35]). According to different definitions, a biopolymer/bioplastic can be either a biodegradable polymer or a biobased polymer. The biocompatible i.e. implantable in the human body, polymers are also often incorporated in the term biopolymer. Therefore we have chosen to consider that a biopolymer is a polymer having at least one of the following three properties: biobased, biodegradable or biocompatible.

Biodegradation is a natural process by which organic chemicals in the environment are converted to simpler compounds, mineralized and redistributed through elemental cycles such as the carbon, nitrogen and sulphur cycles. Biodegradation can only occur within the biosphere as microorganisms play a central role in the biodegradation process [36]. According to standards definition (ISO 472:2013), a polymer undergoes a biodegradation when the degradation is caused by biological activity, especially enzymatic action, leading to a significant change in its chemical structure. This degradation is an irreversible process characterized most of the time by a change in properties (integrity, molecular mass or structure, mechanical strength). For example, biodegradable polymers are useful for various applications in medical, agriculture, drug release and packaging fields.

A biobased polymer is a polymer derived from renewable resources according to the French Agency of the Environment and Energy Management (ADEME). It can also be synthesized by the polymerisation of natural monomers (Fig. 5). These products can replace petroleum-based polymers in nearly every function from packaging and single use to durable products. They offer the opportunity to reduce fossil resources required to produce the 21 million tons of plastic annually consumed for packaging and non-durable goods, as well as divert the 16.7 million tons of plastic waste entering landfill [37].

Black [39] defined the biocompatibility as the ability of a polymer to perform with an appropriate host response in a specific situation. In the medical field, a biocompatible material must have the ability to exist in contact with tissues of the human body without causing an unacceptable degree of harm to that body [40]. The biocompatible polymers can be used in several applications like tissue engineering, invasive sensors, drug delivery and gene transfection systems.

Fig. 6 shows the different polymer types depending on the biodegradability and the materials origin. For example, starch is a biobased and biodegradable polymer whereas polystyrene is a non-biodegradable and oil-based polymer.

4. Applications

Extrusion assisted by supercritical fluids broadens its field of application and has been called as a revolutionary invention in the polymer industry [9]. Among several advantages, the use of this technology allows a decrease of the processing temperature and thus the use of thermo sensitive components.

4.1. Biocompatible polymers used in the medical field

4.1.1. Enhancing the bioavailability of active molecules

Combining extrusion with sc-CO₂ allows using relatively fragile or thermally sensitive molecules, like pharmaceutical molecules, without any residue in the final material. For instance, these biopolymer foams can be later used in floating drug delivery systems to achieve gastric retention. The use of the injection of pressurized carbon dioxide in an extruder for a number of pharmaceutical grade polymers like polyvinylpyrrolidone-vinyl acetate (PVP-VA-64), Eudragit E100 and ethylcellulose (EC). [18–21,39–43]

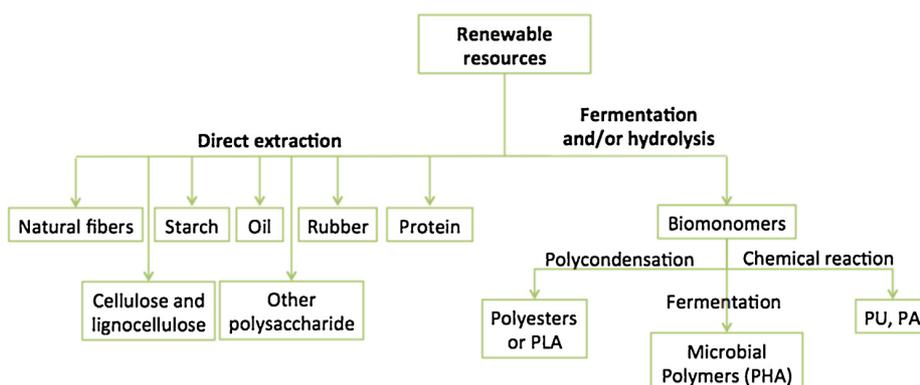


Fig. 5. Different ways for obtaining biobased polymers (adapted from Ref. [38]).

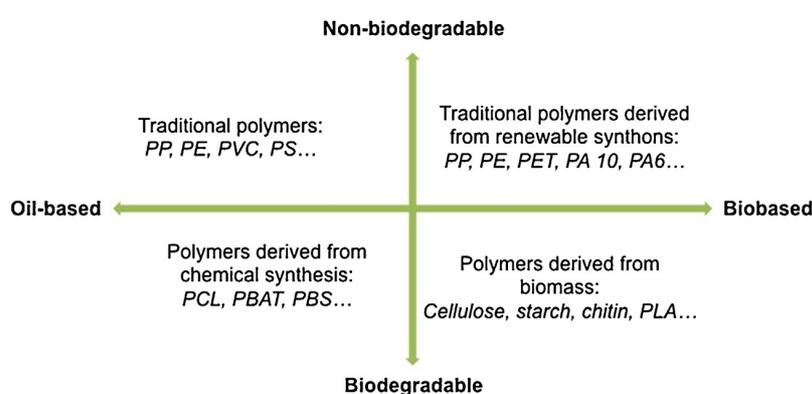


Fig. 6. Biobased and biodegradable polymers (adapted from Ref. [41]).

Table 1

The processing conditions used for the extrusion assisted by sc-CO₂ for enhanced the bioavailability of poorly soluble drugs.

Matrix.	API	Extrusion			Q(sc-CO ₂) or sc-CO ₂ (%)	Ref.
		Screw type	Temperature	Speed		
PVP-VA-64	-	Co-rotating intermeshing twin-screw	120–162 °C	100 rpm	N/A	[42]
Eudragit EPO 100			115–162 °C			
EC 20 cps			75–190 °C			
PVP-VA-64	Itraconazole	Co-rotating intermeshing twin-screw	110–180 °C	100 rpm	N/A	[43]
EC 20 cps			80–130 °C			
EC 20 cps	Acide ρ -Amino Salicylic	Co-rotating intermeshing twin-screw	110–130 °C	100 rpm	N/A	[44]
EC 20 cps			70–180 °C			
PEO+ Eudragit EPO	Carvedilol	Co-rotating intermeshing twin-screw	50–140 °C	N/A	N/A	[46]
Eudragit E100			110–130 °C			
Eudragit E100	-	Single-screw	110–150 °C	40–80 rpm	0.002–0.381%	[20]
Eudragit E100			130–150 °C			
Eudragit E100	Carvedilol	Single-screw	125–130 °C	5–10 rpm	0.25 cm ³ /min	[22]
Eudragit E100			125–130 °C			

has already been reviewed elsewhere [10] and Table 1 below shows the different processing conditions used.

Verreck et al. [42] found that the CO₂ acts as a plasticizer for several pharmaceutical polymers (PVP-VA-64, Eudragit E100 and EC 20cps grade) and allows a decrease of the operating temperatures. For the amorphous PVP-VA 64 and Eudragit E100 polymers, their glass transition temperature were not changed after the extrusion foaming and the dissolution is enhanced thanks to an increase in specific surface area and porosity. This process alters the EC 20cps crystallinity. In all cases, a post-processing milling step is improved due to a morphology change, an increase porosity and because no plasticizer is left in the polymer leaving the T_g in the product at its original value and the polymer in its glassy/brittle state. When Itraconazole was blend with the PVP-VA 64 at 10 or 40%wt [43], the dissolution of Itraconazole was controlled by tem-

perature and pressure during the hot stage extrusion process. In the case of a blend of ρ -Amino Salicylic Acid (ρ -ASA) with EC 20cps at a mass ratio of 10/90 [44], the decomposition of the API was reduced thanks to the CO₂ injection (17% decomposition without the CO₂ versus 5% with the CO₂). Finally, blending Itraconazole with EC 20cps at 10 or 40%wt by this process [45] increased the initial wetting and the drug release rate.

Nikitine et al. [20] worked with the Eudragit, a pharmaceutical grade polymer. Foams were obtained, with porosity range between 65 and 90%. Here, higher temperature enhances the growth phenomenon, consequently, the expansion rate and the average diameter increase.

This polymer was implemented with Carvedilol (CAR), an API used to prevent heart failures [22,46]. Indeed, an amorphous solid dispersion of CAR in Eudragit E100 is preferable for a rapid dissolu-

Table 2

The processing conditions used for the extrusion assisted by sc-CO₂ for the scaffolds fabrication.

Matrix	Fillers	Extrusion			sc-N ₂ (%)	Ref.
		Screw type	Temperature	Speed		
PCL	Chitosan	Twin-screw	90–100 °C	100 rpm	0.5	[49]

tion. It was found that the process improved the dissolution rate of the drug. With a flow rate of 0.25 cm³/min of supercritical CO₂ with a CAR mass content of 20% in Eudragit E100, 100% was dissolved in less than 5 min against only 18% of dissolution in the same time lapse for the unprocessed crystalline CAR [22].

Lyons et al. used also polyethylene oxide (PEO) blend at different ratios with Eudragit and CAR [46]. The dissolution analysis still showed a faster dissolution of the CAR for the sample made with CO₂ in comparison with the samples without CO₂.

More recently, Eudragit was used with another poorly water-soluble crystalline active pharmaceutical ingredient: spirinolactone [19]. Like for Verreck et al. [44], it was observed that the extrusion assisted by sc-CO₂ process could lower the degree of API decomposition because the supercritical fluid enables to decrease the process temperature. Moreover, the complete dissolution of the drug for the foamed sample was achieved in less than 10 min, whereas only 20% of dissolution was obtained for the unprocessed microcrystalline spirinolactone.

4.1.2. Scaffolds for regeneration of human body tissues

The main purpose of tissue engineering is to overcome the lack of tissue donors and the immune repulsion between receptors and donors. In the process of tissue engineering, cells are cultured on a scaffold to form a nature-like tissue, which is then implanted in the defective part in the patient body. A successful tissue engineering implant largely depends on the role played by three-dimensional porous scaffolds. The ideal scaffolds should be biodegradable and bioabsorbable to support the replacement of new tissues. In addition, the scaffolds must be biocompatible without inflammation or immune reactions and possess proper mechanical properties to support the growth of new tissues [47,48]. Extrusion assisted by sc-CO₂ allows creating such porous structures.

Recently, Jing et al. [49] studied a new method for scaffold production. The purpose of this study was to evaluate the feasibility of a preparation method combining extrusion foaming and particulate leaching for the preparation of highly interconnected three-dimensional polymeric scaffolds with controlled pore sizes. In this work, the poly(ϵ -caprolactone) (PCL), a biocompatible and biodegradable polymer, was used as the matrix material. It was blended with poly(ethylene oxide) (PEO) as a sacrificial polymer because of its water solubility and a melting temperature similar to that of PCL. Sodium chloride (NaCl) was used as the particles. Here, the blowing agent used was supercritical nitrogen (sc-N₂) because of its low solubility in most polymers compared to CO₂ but yielding to a finer porous structure in the foaming process. Chitosan nanofibres (CSNF) were also used in this study to create a nanofibrous structure in the porous PCL scaffolds and to further improve the biocompatibility of the scaffolds. They were introduced into the micropores of the scaffolds by freeze-drying (also known as thermally induced phase separation). Different blends were made with PCL/PEO ratio of 70/30, 60/40 and 50/50. These blends were mixed with 10%wt of NaCl. The extrusion foaming was made in a twin-screw extruder with 0.5%wt of gas, the operating parameters are given in Table 2. After the foaming operation, the samples were transferred in deionized water to leach out the PEO and NaCl. The scaffolds were then soaked in a chitosan solution to introduce chitosan nanofibres in the porous PCL scaffolds. The last step was the lyophilisation of the scaffolds. After extrusion

foaming, they observed that the number of larger pores increased as PEO increased in the blends. Porous channels could be seen throughout the blends; however, the channels became longer with an increase of PEO in the blends. The authors found that NaCl particles improve the porosity and pore interconnectivity. The chitosan fibres enhanced slightly the compressive modulus and increased the water uptake rate.

Another method, which includes a screw and sc-CO₂ for the manufacturing of scaffolds is the microcellular injection moulding process (commercially known as the MuCell® Process). This process is capable of mass-producing plastics parts with complex geometries, relatively low porosity and excellent dimensional stability. For example, Mi et al. [50] had produced PLA/TPU (thermoplastic polyurethane) scaffolds with this process. They found that the PLA (3001D, NatureWorks) and the TPU (Elastollan 1185A, BASF) are immiscible but, in light of the biocompatibility, tuneable mechanical properties, and porous microstructure, the scaffolds manufactured via this process have the potential to be used for multiple tissue types in a variety of medical and tissue engineering applications. They also investigated the injection foaming of TPU with different blowing agents (water, CO₂ and water+CO₂) [51]. They observed that for the foaming with water+CO₂, the water molecules not only plasticized the TPU molecules but also grew cells initially nucleated by CO₂ at the advancing melt front which, combined with fountain flow behaviour (material from the centre of the part flows outward to the mould surface at the advancing melt front), led to the elimination of the solid skin layer. Zhao et al. [52] chose to work on a blend of PLA and PHBV (Polyhydroxybutyrate-Valerate) with this method. The blends made with different weight ratios (100:0, 85:15, 70:30, 55:45, and 0:100) were produced using both conventional and microcellular injection moulding process. The increase of PHBV content significantly decreased the cell size and increased the cell density in the microcellular specimens. Moreover, adding PHBV slightly decreased the tensile strength for both specimens.

4.2. Biodegradable or biobased polymers for packaging and other consumer plastics applications

The biodegradable and biobased polymers can be used in the field of packaging or consumer plastics to address environmental concerns. The main rationale for foaming this type of materials is to decrease their weight. Applications with biodegradable or biobased polymers are reviewed in this part and operating parameters are listed in Table 3.

4.2.1. Structure and porosity of PLA foams

The poly (lactic acid) or polylactide (PLA) is one of the most promising biodegradable, biobased and biocompatible polymer. It is manufactured by polymerisation of lactic acid (LA), which is mostly produced by fermentation of glucose or maltose obtained by enzymatic hydrolysis of starch cereal grains. The PLA degrades primarily by hydrolysis, after several months of exposure to moisture [53].

Nofar and Park [1] recently published a review on the fundamental properties, foaming mechanisms, and processing technologies for PLA foams. Their investigations of PLA foaming showed that enhanced crystallization kinetics significantly increases the expan-

Table 3The processing conditions used for the extrusion assisted by sc-CO₂ for the foaming of several biodegradable or bio-based polymers.

Polymers	Additives	Extrusion			sc-CO ₂ (%)	Ref.
		Screw type	Temperature	Speed		
PLA 2002D	Modified clay Cloisite 30B	Single-screw	150–210 °C	80 rpm	5	[11]
PLA 8302D			140–180 °C			
PLA 2002D	Pine flour Talc	Single-screw	150–170 °C	80 rpm	5	[12]
PLA 3001D			130–160 °C			
PLA 3001D	PP-g-AM Talc	Single screw	130–160 °C	N/A	4	[13]
PLA 3001D	Chain-extender Talc	Single-screw	130–150 °C	N/A	4	[14]
Ecovio (PLA/PBAT) PBAT Ecoflex + PLA 3001D PHBV	Modified clay (Cloisite 30B)	Single-screw	120–160 °C	30–55 rpm	1.5–4	[15]
PLA 2002D + suspension starch –glycerol–water	PLA-g-MA	Co-rotating twin-screw	N/A	150 rpm	7–10	[16]
PLA 4032D	–	Co-rotating twin-screw	N/A	150 rpm	5–9	[17]
PLA 2002D	Chain-extender	Co-rotating twin-screw	110–190 °C	150 rpm	5–9	[18]
PLA 8302D			130–190 °C			
PLA 4032D	Chain-extender	Tandem line	130–210 °C	N/A	5–9	[24]
PLA 2002D			115–210 °C			
PLA 8051D	Modified clay (Cloisite 30B)	Tandem line	100–140 °C	100–120 rpm	2–8	[57]
PLA 2002D			110–190 °C			
PLA 8302D	Talc	Counter-rotating twin-screw	100 °C	100–120 rpm	1.8–9.4	[55]
PLA 6300D	–	Tandem line	110–140 °C		5	[56]
PLA 2002D	Chain-extender	Co-rotating twin-screw	115–190 °C	100 rpm	2–7	[59]
PLA 3251D			120–190 °C			
PLA 8052D	Treated clay Nanocor I30P	Co-rotating twin-screw	110–190 °C	100 rpm	N/A	[60]
PLA 2002D			140–170 °C			
PLA 2002D	Modified clay (Cloisite 30B)	Single-screw	N/A	N/A	N/A	[61]
PLA 3001D	Oleamide (foaming agent) Hydrotalcite	N/A	130–200 °C	100 rpm	N/A	[62]
Pregelatinized wheat starch + sodium hydroxide	Ultraviolet absorber Crosslinking reagent (EPI)	Co-rotating twin-screw	70 °C	120 rpm	1	[63]
Native wheat starch + sodium hydroxide	Crosslinking reagent (EPI) + Acetylation reagent (Ac)	Co-rotating twin-screw	60–70 °C	120 rpm	1	[64]
Corn starch						
PVOH	Microfibrillated cellulose	Tandem line	70–195 °C	100 rpm	5–9	[64]

sion ratio and the cell density of foamed samples. The crystal nuclei that are induced during foam processing can increase PLA inherently low melt strength through the crystal-to-crystal network. Adding nanoparticles improved the PLA foams expansion and cell nucleation behaviour by increasing its melt strength and enhancing its heterogeneous cell nucleation power.

A patent filed in 2005 [54] describes extruded polylactide foams blown with carbon dioxide. The invention relates to a process that comprises forming a pressurized, molten mixture of a melt-processable PLA resin containing 5–15% by weight of carbon dioxide. This molten mixture is then extruded through a die to a region of reduced pressure. At this point, the carbon dioxide expands and the PLA resin cools to form stable foam having at least 70% closed cells. During this process, the carbon dioxide is introduced and maintained under supercritical conditions from the time of blending into the molten resin until it reaches the extrusion die. Very high quality extruded foams are prepared in these process. Densities as low as 16–32 kg/m³ can be obtained with good cell structure, good appearance and consistent quality. The optimal range of CO₂ content is 7–11% in weight.

The first work about the foaming of poly(lactic acid) with CO₂ near supercritical conditions was reported by Reigner et al. [55]. In this work, the authors have achieved PLA foams in density range of 20–25 kg/m³. They observed a very narrow processing window. A CO₂ content below 7%wt led to a poor expansion ratio whereas a content of CO₂ above 8.3%wt led to shrinkage upon ageing. Mihai et al. [16] found similar results by blending PLA with thermoplastic starch, with the help of a compatibilizer agent (PLA-g-AM). The CO₂ incorporation into the blends led to very poorly expanded foams until they reached a critical CO₂ content around 7%wt at which point the foams were highly expanded and with a significant reduction of the density. The density found by the authors was about 25 kg/m³ between 7 and 10%wt of CO₂. The foam morphology for the pure PLA and the blend was characterized by fine cells and open-cell structure. A significant crystallinity was developed during the foaming process. They also worked on the behaviour of different grades of PLA with supercritical carbon dioxide [17]. Again, in this study, the CO₂ content has to be higher than 7%wt to obtain highly porous structure (density around 35 kg/m³). For 5% CO₂, the foam morphology was coarse and the foam densities ranged from 400 to 1000 kg/m³ whereas with 7%wt, densities ranged between 32 and

315 kg/m³. The PLA with the smallest D-lactic acid content produced foam with the lowest density. The crystallinity of PLA foams increased with CO₂ concentration and L-lactic acid content. Lee et al. [56] studied the effect of extrusion foaming on PLA with both a PBA (CO₂) and a CBA (azodicarbonamide). It was found that the foam densities were lower with CO₂ (<0.10 g/cm³ with 5%wt CO₂) than with the CBA (0.5 g/cm³ for the lowest density with 0.8%wt CBA).

Adding a chain extender to the polymer can improve the melt strength of PLA. Mihai et al. [18] added between 0 and 2%wt of a chain-extender (CE), an epoxy-styrene-acrylic oligomer (CesaExtend OMAN698493 from Clariant Additive Masterbatches), to different PLA, an amorphous (PLA8302D) and a semi-crystalline grade (PLA4032D). They managed to obtain low-density foams with the semi-crystalline PLA with only 5%wt of CO₂ whereas 9%wt of CO₂ was necessary to obtain such a low-density foam with the amorphous PLA. This was in agreement with their previous study [16,17]. At 5%wt CO₂ for the semi-crystalline PLA, the density decreased from 65 to 30 kg/m³ with 2%wt of CE, showing in this case the benefit of the higher melt strength. At higher blowing agent concentration, however, low-density foams were obtained regardless of the CE concentration. Similar results were found by Wang et al. [24], who have observed an increased melt strength and elasticity by branching the PLA with 0.35 and 0.7%wt CE. These improvements led to an increase of the cell densities, which ranged from 20 to 40 kg/m³ (depending on the PLA grade) with 9% CO₂. They observed a close relationship between cell morphology and expansion ratio. Following cell walls ruptures, an open-cell structure is induced and resistance for the blowing agent to diffuse into the atmosphere is significantly reduced, leading to a low foam expansion ratio. If a close-cell structure is induced, gas will diffuse into adjacent cells and bulk expansion ratio will increase. As pointed by Nofar and Park [1], an enhanced crystallization kinetics can significantly increase the expansion ratio and the cell density of foamed PLA samples. Wang et al. [24], observed that by varying the length of the die reservoir, the crystallization of the PLA with 0.7%wt of CE can be controlled. A die with a longer isothermal residence time induced higher crystallinity and higher expansion ratio over a much wider temperature window in comparison with a die with no reservoir. For Pilla et al. [13], the optimum chain extender percentage was 1%wt, the cell density decreasing above this CE content. Unlike these studies, for Larsen and Neldin [57], the addition of the chain extender (2%wt) did not lead to a decrease of the foam density. Adding CE is found to introduce inhomogeneities at different length scales. The foam density ranged between 20 and 30 kg/m³ with 8% of CO₂ and die temperature as low as 110 °C.

To obtain finer cell structure and higher cell density, a nucleating agent can be added to favour heterogeneous nucleation. For Reigner et al. [55], by adding 0.5%wt of talc in PLA below 7% CO₂, the cell population density increased a 100-fold while the average cell size dropped from a few hundreds micrometres down to less than 60 μm. Similar results were observed by Pilla et al. [13]. In addition, coupling talc with a chain extender led to a denser and more uniform cell structure. Some authors [16] did not observe change in the foam structure and cell sizes. They explained this phenomenon by their high blowing agent concentrations (8%), and the fact that the heterogeneous nucleation induced by talc was surpassed by the heterogeneous nucleation induced by the CO₂ concentration fluctuation.

4.2.2. Nanocomposites made of PLA and silicate layered materials

One effective way to improve the PLA mechanical properties, and particularly its brittleness, is to add multilayer silicate materials like clay for the creation of nanocomposites. Moreover, clay addition can have an improving effect on barrier properties of a

polymer matrix, due to creation of tortuous path that contributes to delay water vapour molecules permeation [58], which can be advantageous for packaging applications.

The use of extrusion assisted by sc-CO₂ for the preparation of polymer/clay nanocomposites is widening because of the expansion effect on the interlayer distance of clay by the CO₂. For Matuana and Diaz [11], an increase in the heterogeneous nucleation with 5%wt clays (montmorillonite Cloisite 30B) was observed at 5%wt sc-CO₂. This addition allowed both homogeneous and heterogeneous nucleation stages to occur during the foaming process. Finally, they obtained microcellular plastics with an order of 10⁹ cells/cm³ and an average cell size of less than 10 μm. Jiang et al. [59] observed an increase in the interlayer spacing between PLA and 2.5%wt clays with the help of CO₂ because of the intercalation of PLA chains into the gallery spaces. This indicated that the addition of sc-CO₂ was helpful in the clay layer expansion, owing to its gas diffusion and plasticizing ability during compounding of nanocomposites. Compared with pure PLA, the elongation at break and tensile strength for nanocomposites compounded with 5 wt% CO₂ were improved by 166% and 25%, respectively. The nucleation effect was also observed by Keshkter et al. [25] with blends having a clay content of 0.5, 1, 2 and 5%wt at 5 or 9%wt CO₂. An increased cell density, expansion ratio and melt strength were observed due to the nanoclay role as a cell nucleation agent. Moreover, with the presence of dissolved CO₂, clay nanoparticles, and shear action, the PLA crystallization kinetics was significantly enhanced.

In the case of Zhao et al. [60], they chose to pre-foam a blend of PLA/nanoclay before using this materials in the MuCell® Process. Indeed, in the microcellular injection moulding process, it is challenging to obtain homogeneous dispersion of nanofillers because of the short cycle time. The first step was to prepare pellets of nanocomposite loaded at 4%wt clay in extrusion. Then, the pellets were pre-foamed with a single-screw extruder coupled with a high-precision syringe pump. Finally, the foams are pelletized and used in microcellular injection moulding with CO₂ or N₂ as physical blowing agents. The pellets of nanocomposite were also used in microcellular injection moulding without pre-foaming. The authors have observed in WAXD analysis a better clay intercalation and exfoliation in the PLA matrix with the pre-foaming. The pre-foaming also led to smaller cell size and cells better distributed than those of the samples without pre-foaming. This pre-foaming step increased the cell densities, the tensile strength and strain-at-break. TGA analyses showed that pre-foaming did not cause the macromolecular weight of PLA to decrease or change significantly.

4.2.3. Blending of PLA with other biopolymers

The foaming of the PLA with another biodegradable polymer, the PBAT (poly(butylene adipate-co-terephthalate)), was also studied in the literature. Pilla et al. [14] tested two different blends at 45/55 ratio: a commercially available compatibilized PLA/PBAT blend (Ecovio, BASF) and a non-compatibilized PLA/PBAT blend with the PLA 3001D and the PBAT Ecoflex. They added 0.5% talc as nucleating agent. The compatibilization led to a reduction of the average cell size and the volume expansion ratio but increased the cell density. The die temperature had no effect on the volume expansion ratio between 130 and 150 °C, except for the pure PLA and non-compatibilized blend PLA/PBAT. For these materials, the volume expansion ratio increased at lower die temperature (between 1.6 and 1.8 at 130 °C vs. between 1.4 and 1.6 at 150 °C). The results showed that the addition of talc in both blends decreased the average cell size and volume expansion ratio and increased the cell density but had varying effect on the open cell content of the foamed samples. This addition had also an effect on the crystallinity, which increases.

In another approach, Matuana and Diaz [12] had studied the influence of wood-flour particles in the foaming behaviour of the

Table 4The processing conditions used for the extrusion assisted by CO₂ for the biobased polymers in the food area.

Materials	Extrusion			Q(CO ₂) or CO ₂ (%)	Ref.
	Screw type	Temperature	Speed		
Corn flour + tomato powder	Co-rotating intermeshing twin-screw	30–130 °C	250 rpm	N/A	[65]
Corn flour + ginseng powder					
Corn flour + green tea	Co-rotating intermeshing twin-screw	95–120 °C	150 rpm	1%	[66]
Cornmeal + alkalinized cocoa powder		95–135 °C	150 rpm	500 mL/min	[67]
Corn starch	Co-rotating intermeshing twin-screw	90–120 °C	150 rpm	200 mL/min	[68]
Corn grits + corn fibre		40–130 °C	150–200 rpm	500 mL/min	[69]
Wheat	Co-rotating intermeshing twin-screw	30–130 °C	250 rpm	N/A	[70]
Corn flour + hull-less barley					

PLA. Particles had an effect on the melt rheology, which plays an important role during cell growth and stabilization. In this study, they added between 0 and 30%wt of wood-flour (pine flour) and 0.5%wt of talc (to promote heterogeneous nucleation) in a PLA matrix. The CO₂ content was approximately 5%wt. They observed that melt index of PLA decreased as the wood-flour content increased in the matrix. However, the authors found a way to counteract this aspect by incorporating various concentrations of a rheology modifier into the composite. The rheology modifier is a low molecular weight maleic anhydride-modified polypropylene (Epole E-43 from Eastman Chemical). At the end, they produced microcellular foamed PLA/wood-flour composites with uniform and homogeneous cellular structures similar to those achieved in neat PLA foams. By adding the wood-flour, the average cell size increased from 7.4 to 11.3 μm and the cell population density decreased from 1.46×10^9 to 0.26×10^9 cells/cm³.

4.2.4. Other applications

Kuo et al. [61] worked on a different problematic. They managed to create PLA foams with high reflectivity. In this work, they compounded PLA 3001, a foaming agent promoter (oleamide), a nucleating agent (hydrotalcite LDH-40) and an ultraviolet absorber (Tinuvin 320) with a twin-screw extruder and pelletized it. The results showed that the extrusion assisted by sc-CO₂ exhibit faster manufacturing speed and better capability of mass-production than batch supercritical CO₂ foaming processes. The density, average cell size, foaming ratio, and reflectivity of PLA foam made by supercritical fluid extrusion (SCFX) can reach 0.04 g/cm³, 5 mm, 20, and 99%, respectively. They managed to obtain LED lamp with maximum luminance, viewing angle, and reflectivity of 15,200 cd/m², 123°, and 99%, respectively.

Following a study about the foaming of crosslinked starch [62] in which Ayoub and Rizvi managed to obtain uniform foam, they used the same process to produce moisture resistant starch-based foams [63]. In these studies, they finally obtained microcellular foam having a non-porous skin and a high degree of uniformity in their cell size. The addition of crosslinking agent has been found to enhance the foam uniformity. They observed that adding the acetylation agent to the crosslinking imparted significant water resistance to the extruded samples. The second study has also demonstrated that modification sequence has a significant impact on the structures and properties of dual-modified starches. Reaction conditions employed in modification process determine the distribution and location of modifying groups, which in turn determine the properties of the modified starch. In addition, this kind of material could be controlled to produce particles with morphology and properties useful for green plastics industry.

The poly(vinyl alcohol) (PVOH) is a water soluble and biodegradable polymer which is compatible with many organic and inorganic materials. It can be used in many fields (drug delivery, packaging, heavy metal ions adsorption, and in acoustic noise reduction). Zhao et al. [64] have mixed PVOH with microfibrillated cellulose (MFC) which is a biodegradable nanofiller with high aspect ratio, stiffness

and strength. They chose to work with two physical blowing agents (PBA): sc-CO₂ and water. The foaming experiments were made on a tandem line with 22.5%wt water in the pure PVOH (Mowiol 23–88 of Kuaray Company) and 12.5%wt water in the composite PVOH/MFC. The content of MFC (KY100 G by Daicel FineChem) was 0, 0.05 or 0.1%wt. When water was used alone as blowing agent, the nucleation during the PVOH extrusion foaming was greatly weakened. When the sc-CO₂ and the water were coupled, the water facilitated the CO₂ processing and improved the extrusion foaming process. This is explain by the fact that water plasticizes the PVOH and thereby increases the low solubility of CO₂ while sc-CO₂ promotes cell density that cannot be achieved by using water alone. The MFC in the PVOH affected the melt strength and crystallinity. During the foaming, it served as cell nucleating agent and influenced cell nucleation and cell growth behaviour through crystallization. Like in many others publications, the cell density was increased with increased CO₂ content and decreased die temperatures.

In the same optic as Keshktar et al. [25], Le Moigne et al. [15], studied the use of SCFX to improve the clay (Cloisite 30B) dispersion in the poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) polymer. In this publication, they observed that the prior preparation of a masterbatch was a necessary step to obtained good clay dispersion and limited PHBV degradation during the extrusion foaming process. To prepare this masterbatch, they used the method of melt intercalation by using a co-rotating twin-screw extruder with 10 or 20%wt of Cloisite 30B. The masterbatch was then diluted at 2.5%wt of clay before SCFX. Here the sc-CO₂ content had a great importance. They found a narrow window of sc-CO₂ mass fraction in which the good clay dispersion appeared to favour homogeneous nucleation while limiting the coalescence of the pores. It allowed obtaining nanobiocomposite foams with better homogeneity and porosity up to 50%. Nevertheless, the crystallization of the PHBV upon the foaming process should hamper the diffusion of the sc-CO₂ within the matrix and hence the nucleation and growth of the pores which, in turn, limit the homogeneity and ultimate porosity of the foams.

4.3. Biobased polymers used in the food area

Due to the ubiquitous presence of water in food, the steam extrusion is used in this domain with starchy or proteinaceous materials. In this method, the water acts as plasticizer and blowing agent but involves high temperature (130–170 °C), shear and low moisture content (13–20%). These conditions prevent the use of heat sensitive ingredients. To avoid the drawbacks of this technique, the injection of CO₂ can be used. Some studies from Ryu et al. [65–70] are dedicated to the injection of pressurized CO₂ in the barrel of an extruder (between 1 to 5 MPa). With the injection of pressurized CO₂, the extrusion temperature is decreased (below 100 °C) and prevents the degradation of the nutrients. The products made can be used in the food industry, especially in snack foods with

Table 5The processing conditions used for the extrusion assisted by sc-CO₂ for the biobased polymer in the food area.

Materials	Extrusion			Q(sc-CO ₂) or sc-CO ₂ (%)	Ref.
	Screw type	Temperature	Speed		
Flour, sugar, whey protein concentrate, salt. . .	Co-rotating twin-screw	36–38 °C	N/A	N/A	[74]
Wheat flour, water, salt, sugar, dry skim milk, vital wheat gluten. . .	Co-rotating twin-screw	31–37 °C	39 rpm	N/A	[75]
Waxy rice flour, rice bran, soy protein concentrate	Co-rotating twin-screw	80 °C	120 rpm	7.6 × 10 ⁻⁵ kg/s	[77]
Whey protein concentrate, pregelatinized corn starch, prebiotic fibre. . .	Co-rotating twin-screw	70–80 °C	120 rpm	7.6 × 10 ⁻⁵ kg/s	[78]
Waxy rice flour, soy protein concentrate, toasted defatted soy flour. . .	Co-rotating twin-screw	80 °C	120 rpm	7.6 × 10 ⁻⁵ kg/s	[79]
Milk protein concentrate, apple pomace, grape pomace, pre-gelatinized starch. . .	Co-rotating twin-screw	86–94 °C	135–180 rpm	7.6 × 10 ⁻⁵ kg/s	[80]
Whey protein concentrate, masa flour, pre-gelatinized starch, oat fibre, vegetable shortening	Co-rotating twin-screw	40–75 °C	130 rpm	0.3–0.7%	[81]
Whey protein concentrate, pre-gelatinized corn starch. . .	Co-rotating twin-screw	25–90 °C	180 rpm	1%	[82]
Whey protein concentrate, pre-gelatinized corn starch. . .	Co-rotating twin-screw	25–90 °C	180 rpm	1%	[83]
Whey protein concentrate, pre-gelatinized corn starch. . .	Co-rotating twin-screw	90 °C	180 rpm	2%	[84]
Whey protein concentrate, corn oil, unsalted cream butter (for anhydrous butter oil preparation)	Co-rotating twin-screw	90 °C	180 rpm	1%	[85]

nutritional or antioxidant properties. The materials used and the processing conditions are shown in Table 4.

Not only the pressurized CO₂ allows a decrease of the operating temperature, but also the injection of sc-CO₂ is preferable for a better expansion rate and viscosity reduction. Sauceau et al. [10] reviewed recently the used of sc-CO₂ extrusion in the field of food area. The main recent applications concerned by the SCFX in the food area have been detailed here and the processing conditions are listed in Table 5.

4.3.1. Starchy products

In 1992, Rizvi and Mulvaney [71] patented a novel extrusion technology for producing highly expanded starch with sc-CO₂ used as an expansion agent and plasticizer. This patent was extended to other applications like cereals and flour products [5,72,73] with a porous structure differing from the one obtained by steam extrusion. The new porous structure was generally closed, with a fine and regular porosity, and sometimes a smoother surface state (non porous skin). This was explained by a higher nucleation rate associated with more rapid nucleation limiting gas diffusion.

For example, Hicsamaz et al. [74] showed that SCFX technology could be used to continuously produce yeast-free dough using CO₂ as a swelling gas. The SCFX-leavened dough was found to have rheological properties comparable to the commercial dough and without ethanol released. The leavened dough could be produced by SCFX process in about 2 min, eliminating the need for proofing and holding time. Ruttarattamongkol et al. [75] continued this previous work but the objective was to obtain breads with similar density to the one of conventional yeast-leavened and commercial bread products. The dough was made of wheat flour, water, salt, sugar, dry skim milk, vital wheat gluten and others ingredients based on a preliminary study [76]. The bread obtained had a density between 0.19 and 0.45 g/cm³. It had similar qualities to commercial products. This process reduces the time and space required to produce bread and other expanded baked goods.

4.3.2. Fibrous and proteinaceous products

Another application of SCFX process is the expansion and production of fortified crisps. Paraman et al. [77] evaluated this process

of SCFX for rice-based expanded products. They observed that the addition of rice bran, soy protein concentrate, distilled monoglyceride, salt and micronutrient premix in the rice flour can produce protein, fibre and micronutrients fortified puffed rice with balance nutritional profile. The addition of 22.5% of soy protein improved the protein amount in the final product from 5.8 to 21.5%. The presence of vitamin A and C is maintained due to lower temperature and shear. The final product had a density of 0.31 g/cm³ and was very crispy with good textural characteristics. They also used this method to produce whey protein crisps that contained a high amount of proteins and prebiotic fibres [78]. A formulation containing 60% whey protein concentrates (WPC-80) and 8% prebiotic soluble fibres resulted in protein crisps with good expansion characteristics and crispiness. In the case of Sharif et al. [79], the crisps were made with rice-soy and were fortified with soy protein concentrate and toasted defatted soy flour. They observed an increase of the protein content and an improvement of the amino acid balance in the food, providing a more nutritious product. More recently, Sun et al. [80] investigated the potential of incorporating fruit pomace (fruit residues) and concentrated whey in high protein products. They found that the addition of pomace and whey did not affect the overall textural quality of final extrudates. Moreover, the fruit pomace addition improved the dietary fibre content of the final products. They managed to obtain protein extrudate piece density ranging between 0.24 and 0.31 g/cm³. Cho and Rizvi [81] developed an effective process for expanded SCFX chips with high nutrient concentration. They managed to produce with this process healthy snack chips containing up to 60%wt protein content without any chemical modification. They obtained uniformly expanded cellular structure when expansion operation was performed below whey protein denaturation temperature. The textural properties of baked and fried products were comparable to commercial extruded or fried chip products. The sc-CO₂ content was the critical parameter to control the expansion and texture of the final product.

4.3.3. Texturized products

Whey proteins (WP) are used in many food applications because they have the ability to gel upon heating and to provide desirable food texture. The most common technique used to texturize WPs

is thermoplastic extrusion. In general, functionality of WPs can be altered by heating, adding salts, adjusting the pH, and shearing. Heat-induced gelation of WPs has been extensively studied and used to add texture to food products. In 2008, Manoi and Rizvi [82] investigated the modification of whey protein concentrates (WPC) by using the extrusion assisted by supercritical CO₂. It was hypothesized that reactive SCFX process in highly alkaline or acidic environment combined with controlled shear and heat in the presence of mineral salts (CaCl₂ and NaCl) and sc-CO₂ would favourably alter the gelling and functional properties of WPC. The results obtained by Manoi and Rizvi confirmed this hypothesis as they generated new WP ingredients with unique gelling and functional properties, which may open up a new avenue for utilisation of WP as a thickening or gelling agent in food formulations. Texturized proteins (tWPC) samples produced under acidic (pH = 2.89) and alkaline (pH = 8.16) conditions with sc-CO₂ exhibited high stability of rheological properties over a wide temperature range (25–85 °C). The water holding capacity of pH-treated WPC samples was increased with sc-CO₂. In 2009, the same authors [83] investigated the mechanisms of interactions of WPC in the same acidic (pH = 2.89) and alkaline (8.16) conditions to elucidate their influences on the selected physicochemical properties of the final tWPC products. They found that the mechanism of interactions in WP during the process is highly depending on pH. Approximately 30% and 80% of proteins in the tWPC produced at pH 2.89 and 8.16, respectively, became insoluble in the standard buffer. In a study of 2012 following the work on whey proteins, Mustapha et al. [84] studied the texturization effect of the extrusion assisted by supercritical CO₂ on the surface hydrophobicity of the whey protein concentrate. They found that this process could form cold-set protein gels and emulsion gels that can be used as gelling and emulsifying ingredient for use in many food applications. Ruttarattanamongkol et al. [85] had then studied the effect of the incorporation of tWPC in an emulsion containing liquid oil (corn oil or butter oil) by SCFX process. They observed that this incorporation in an aqueous phase retarded the droplet coalescence. They produced freshly prepared emulsions with monomodal and narrow droplet size distribution. Emulsions with higher elastic modulus were obtained by increasing the oil concentration due to the droplets repulsion and deformation. The storage temperatures and oil contents markedly affected the stability and rheological behaviours of emulsions containing crystallisable butter oil.

5. Conclusion

This overview enlightens the growing use of extrusion assisted by supercritical fluid with different kinds of biopolymer. Temperature appears to be the first and most important parameter to master the manufacture of highly porous material. With a decrease in the melt temperature, an increase in the overall porosity is observed. A higher CO₂ content allows to decrease the operating temperature. In addition, a lot of parameters do influence the properties of the foams made with bio-based or bio-degradable polymers. With PLA, for example, the addition of clay or chain-extenders will change the porosity.

For biocompatible polymers used in pharmaceutical products, this technique allows the use of sensitive molecules because of the plasticizing effect of the CO₂ and the correlative decrease of operating temperature, pressure, viscosity and shear stresses. Due to the fine porous structure induced at the die exit, this process opens new application areas. The manufacture of scaffolds could benefit from this technique too.

In the food area, the SCFX helps to create expanded food with improved nutritional properties and allows operating at lower temperature in comparison with the more classic steam extrusion.

There are obviously still several challenges to be overcome, as for instance the need to move away from fabricating microcellular to nanocellular foams to reach superior properties (thermal, mechanical, electrical, etc.) [86]. But the extrusion assisted by supercritical fluid has already proven to be a very promising method to create biopolymer foams with a broad spectrum of application in many fields.

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References

- [1] M. Nofar, C.B. Park, Poly (lactic acid) foaming, *Prog. Polym. Sci.* 39 (2014) 1721–1741.
- [2] S.-T. Lee, Introduction, in: S.-T. Lee, C.B. Park (Eds.), *Foam Extrusion: Principles and Practice*, Second edition, CRC Press, 2014, pp. 1–18.
- [3] J. Zhang, G.M. Rizvi, C.B. Park, M.M. Hasan, Study on cell nucleation behavior of HDPE-wood composites/supercritical CO₂ solution based on rheological properties, *J. Mater. Sci.* 46 (2011) 3777–3784.
- [4] M. Lee, C. Tzoganakis, C.B. Park, Extrusion of PE/PS blends with supercritical carbon dioxide, *Polym. Eng. Sci.* 38 (1998) 1112–1120.
- [5] S.S.H. Rizvi, S.J. Mulvaney, A.S. Sokhey, The combined application of supercritical fluid and extrusion technology, *Trends Food Sci. Technol.* 6 (1995) 232–240.
- [6] C.B. Park, A.H. Behraves, R.D. Venter, Low density microcellular foam processing in extrusion using CO₂, *Polym. Eng. Sci.* 38 (1998) 1812–1823.
- [7] B. Jeon, H.K. Kim, S.W. Cha, S.J. Lee, M.-S. Han, K.S. Lee, Microcellular foam processing of biodegradable polymers—review, *Int. J. Precis. Eng. Manuf.* 14 (2013) 679–690.
- [8] D.L. Tomasko, H.B. Li, D.H. Liu, X.M. Han, M.J. Wingert, L.J. Lee, K.W. Koelling, A review of CO₂ applications in the processing of polymers, *Ind. Eng. Chem. Res.* 42 (2003) 6431–6456.
- [9] S.P. Nalawade, F. Picchioni, L.P.B.M. Janssen, Supercritical carbon dioxide as a green solvent for processing polymer melts: processing aspects and applications, *Prog. Polym. Sci.* 31 (2006) 19–43.
- [10] M. Saucéau, J. Fages, A. Common, C. Nikitine, E. Rodier, New challenges in polymer foaming: a review of extrusion processes assisted by supercritical carbon dioxide, *Prog. Polym. Sci.* 36 (2011) 749–766.
- [11] L.M. Matuana, C.A. Diaz, Study of cell nucleation in microcellular poly(lactic acid) foamed with supercritical CO₂ through a continuous-extrusion process, *Ind. Eng. Chem. Res.* 49 (2010) 2186–2193.
- [12] L.M. Matuana, C.A. Diaz, Strategy to produce microcellular foamed poly(lactic acid)/wood-flour composites in a continuous extrusion process, *Ind. Eng. Chem. Res.* 52 (2013) 12032–12040.
- [13] S. Pilla, S.G. Kim, G.K. Auer, S. Gong, C.B. Park, Microcellular extrusion-foaming of polylactide with chain-extender, *Polym. Eng. Sci.* 49 (2009) 1653–1660.
- [14] S. Pilla, S.G. Kim, G.K. Auer, S. Gong, C.B. Park, Microcellular extrusion foaming of poly(lactide)/poly(butylene adipate-co-terephthalate) blends, *Mater. Sci. Eng. C* 30 (2010) 255–262.
- [15] N. Le Moigne, M. Saucéau, M. Benyakhlef, R. Jemai, J.-C. Benezet, E. Rodier, J.-M. Lopez-Cuesta, J. Fages, Foaming of poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/organo-clays nano-biocomposites by a continuous supercritical CO₂ assisted extrusion process, *Eur. Polym. J.* 61 (2014) 157–171.
- [16] M. Mihai, M.A. Huneault, B.D. Favis, H. Li, Extrusion foaming of semi-crystalline PLA and PLA/thermoplastic starch blends, *Macromol. Biosci.* 7 (2007) 907–920.
- [17] M. Mihai, M.A. Huneault, B.D. Favis, Crystallinity development in cellular poly(lactic acid) in the presence of supercritical carbon dioxide, *J. Appl. Polym. Sci.* 113 (2009) 2920–2932.
- [18] M. Mihai, M.A. Huneault, B.D. Favis, Rheology and extrusion foaming of chain-branched poly(lactic acid), *Polym. Eng. Sci.* 50 (2010) 629–642.
- [19] T. Vigh, M. Saucéau, J. Fages, E. Rodier, I. Wagner, P.L. Sôti, G. Marosi, Z.K. Nagy, Effect of supercritical CO₂ plasticization on the degradation and residual crystallinity of melt-extruded spirinolactone, *Polym. Adv. Technol.* 25 (2014) 1135–1144.
- [20] C. Nikitine, E. Rodier, M. Saucéau, J. Letourneau, J. Fages, Controlling the structure of a porous polymer by coupling supercritical CO₂ and single screw extrusion process, *J. Appl. Polym. Sci.* 115 (2010) 981–990.
- [21] C. Nikitine, E. Rodier, M. Saucéau, J. Fages, Residence time distribution of a pharmaceutical grade polymer melt in a single screw extrusion process, *Chem. Eng. Res. Des.* 87 (2009) 809–816.
- [22] Z.K. Nagy, M. Saucéau, K. Nyúl, E. Rodier, B. Vajna, G. Marosi, J. Fages, Use of supercritical CO₂-aided and conventional melt extrusion for enhancing the dissolution rate of an active pharmaceutical ingredient, *Polym. Adv. Technol.* 23 (2012) 909–918.
- [23] A. Common, E. Rodier, M. Saucéau, J. Fages, Flow and mixing efficiency characterisation in a CO₂-assisted single-screw extrusion process by

- residence time distribution using Raman spectroscopy, *Chem. Eng. Res. Des.* 92 (2014) 1210–1218.
- [24] J. Wang, W. Zhu, H. Zhang, C.B. Park, Continuous processing of low-density, microcellular poly(lactic acid) foams with controlled cell morphology and crystallinity, *Chem. Eng. Sci.* 75 (2012) 390–399.
- [25] M. Keshkar, M. Nofar, C.B. Park, P.J. Carreau, Extruded PLA/clay nanocomposite foams blown with supercritical CO₂, *Polymer* 55 (2014) 4077–4090.
- [26] J.W.S. Lee, K. Wang, C.B. Park, Challenge to extrusion of low-density microcellular polycarbonate foams using supercritical carbon dioxide, *Ind. Eng. Chem. Res.* 44 (2005) 92–99.
- [27] C.B. Park, D.F. Baldwin, N.P. Suh, Effect of the pressure drop rate on cell nucleation in continuous processing of microcellular polymers, *Polym. Eng. Sci.* 35 (1995) 432–440.
- [28] X. Xu, C.B. Park, D. Xu, R. Pop-Iliev, Effects of die geometry on cell nucleation of PS foams blown with CO₂, *Polym. Eng. Sci.* 43 (2003) 1378–1390.
- [29] S. Alavi, S.S.H. Rizvi, Strategies for enhancing expansion in starch-based microcellular foams produced by supercritical fluid extrusion, *Int. J. Food Prop.* 8 (2005) 23–34.
- [30] A. Behravesch, C. Park, M. Pan, R. Venter, Effective suppression of cell coalescence during chapping in the extrusion of microcellular HIPS foams, 212th National ACS Meeting, *Polym. Prepr.* 37 (1996) 767–768.
- [31] H.E. Naguib, C.B. Park, N. Reichelt, Fundamental foaming mechanisms governing the volume expansion of extruded polypropylene foams, *J. Appl. Polym. Sci.* 91 (2004) 2661–2668.
- [32] C.B. Park, V. Padareva, P.C. Lee, H.E. Naguib, Extruded open-celled LDPE-based foams using non-homogeneous melt structure, *J. Polym. Eng. Sci.* 25 (2005) 239–260.
- [33] Q. Huang, B. Seibig, D. Paul, Polycarbonate hollow fiber membranes by melt extrusion, *J. Membr. Sci.* 161 (1999) 287–291.
- [34] *Plastics—The Facts 2014/2015* www.plastics-europe.org.
- [35] European Bioplastics, Institute for Bioplastics and Biocomposites, nova-Institute (2014) www.bio-based.eu/markets/.
- [36] R. Chandra, R. Rustgi, Biodegradable polymers, *Prog. Polym. Sci.* 23 (1998) 1273–1335.
- [37] T.A. Hottle, M.M. Bilec, A.E. Landis, Sustainability assessments of bio-based polymers, *Polym. Degrad. Stab.* 98 (2013) 1898–1907.
- [38] C.J. Weber, V. Haugaard, R. Festersen, G. Bertelsen, Production and applications of biobased packaging materials for the food industry, *Food Addit. Contam.* 19 (2002) 172–177.
- [39] J. Black, Biocompatibility: definitions and issues, in: J. Black (Ed.), *Biological Performance of Materials: Fundamentals of Biocompatibility*, Fourth edition, CRC Press, 2005, pp. 3–15.
- [40] D.F. Williams, On the mechanisms of biocompatibility, *Biomaterials* 29 (2008) 2941–2953.
- [41] A. Soroudi, I. Jakubowicz, Recycling of bioplastics, their blends and biocomposites: a review, *Eur. Polym. J.* 49 (2013) 2839–2858.
- [42] G. Verreck, A. Decorte, H. Li, D. Tomasko, A. Arien, J. Peeters, P. Rombaut, G. Van den Mooter, M.E. Brewster, The effect of pressurized carbon dioxide as a plasticizer and foaming agent on the hot melt extrusion process and extrudate properties of pharmaceutical polymers, *J. Supercrit. Fluids* 38 (2006) 383–391.
- [43] G. Verreck, A. Decorte, K. Heymans, J. Adriaensen, D. Cleeren, A. Jacobs, D. Liu, D. Tomasko, A. Arien, J. Peeters, et al., The effect of pressurized carbon dioxide as a temporary plasticizer and foaming agent on the hot stage extrusion process and extrudate properties of solid dispersions of itraconazole with PVP-VA 64, *Eur. J. Pharm. Sci.* 26 (2005) 349–358.
- [44] G. Verreck, A. Decorte, K. Heymans, J. Adriaensen, D. Liu, D. Tomasko, A. Arien, J. Peeters, G. Van den Mooter, M.E. Brewster, Hot stage extrusion of p-amino salicylic acid with EC using CO₂ as a temporary plasticizer, *Int. J. Pharm.* 327 (2006) 45–50.
- [45] G. Verreck, A. Decorte, K. Heymans, J. Adriaensen, D. Liu, D.L. Tomasko, A. Arien, J. Peeters, P. Rombaut, G. Van den Mooter, et al., The effect of supercritical CO₂ as a reversible plasticizer and foaming agent on the hot stage extrusion of itraconazole with EC 20cps, *J. Supercrit. Fluids* 40 (2007) 153–162.
- [46] J.G. Lyons, M. Hallinan, J.E. Kennedy, D.M. Devine, L.M. Geever, P. Blackie, C.L. Higginbotham, Preparation of monolithic matrices for oral drug delivery using a supercritical fluid assisted hot melt extrusion process, *Int. J. Pharm.* 329 (2007) 62–71.
- [47] H. Tian, Z. Tang, X. Zhuang, X. Chen, X. Jing, Biodegradable synthetic polymers: preparation functionalization and biomedical application, *Prog. Polym. Sci.* 37 (2012) 237–280.
- [48] A. Salerno, C. Domingo Pascual, Bio-based polymers, supercritical fluids and tissue engineering, *Process Biochem.* 50 (2015) 826–838.
- [49] X. Jing, H. Mi, T. Cordie, M. Salick, X. Peng, L. Turng, Fabrication of porous poly(ϵ -caprolactone) scaffolds containing chitosan nanofibers by combining extrusion foaming, leaching, and freeze-drying methods, *Ind. Eng. Chem. Res.* 53 (2015) 17909–17918.
- [50] H.-Y. Mi, M.R. Salick, X. Jing, B.R. Jacques, W.C. Crone, X.-F. Peng, L.-S. Turng, Characterization of thermoplastic polyurethane/poly(lactic acid) (TPU/PLA) tissue engineering scaffolds fabricated by microcellular injection molding, *Mater. Sci. Eng. C* 33 (2013) 4767–4776.
- [51] H.-Y. Mi, X. Jing, M.R. Salick, P. Xiang-Fang, L.-S. Turng, A novel thermoplastic polyurethane scaffold fabrication method based on injection foaming with water and supercritical carbon dioxide as cblowing agents, *Polym. Eng. Sci.* 54 (2014) 2947–2957.
- [52] H. Zhao, Z. Cui, X. Sun, L.-S. Turng, X. Peng, Morphology and properties of injection molded solid and microcellular poly(lactic acid)/poly(hydroxybutyrate-valerate) (PLA/PHBV) blends, *Ind. Eng. Chem. Res.* 52 (2013) 2569–2581.
- [53] R. Auras, B. Harte, S. Selke, An overview of polylactides as packaging materials, *Macromol. Biosci.* 4 (2004) 835–864.
- [54] K. Cink, J.C. Smith, J. Nangeroni, J.R. Randall, Extruded polylactide foams blown with carbon dioxide, *WO Patent App. PCT/US2005/009892*, 2005.
- [55] J. Reigner, R. Gendron, M.F. Champagne, Extrusion foaming of poly(lactic acid) blown with CO₂: toward 100% green material, *Cell. Polym.* 26 (2007) 83–115.
- [56] S.T. Lee, L. Kareko, J. Jun, Study of thermoplastic PLA foam extrusion, *J. Cell. Plast.* 44 (2008) 293–305.
- [57] Å. Larsen, C. Neldin, Physical extruder foaming of poly(lactic acid)-processing and foam properties, *Polym. Eng. Sci.* 53 (2013) 941–949.
- [58] S. Ahmadzadeh, A. Nasirpour, J. Keramat, N. Hamdami, T. Behzad, S. Desobry, Nanoporous cellulose nanocomposite foams as high insulated food packaging materials, *Colloids Surf. A: Physicochem. Eng. Aspects* 468 (2015) 201–210.
- [59] G. Jiang, H.-X. Huang, Z.-K. Chen, Microstructure and thermal behavior of polylactide/clay nanocomposites melt compounded under supercritical CO₂, *Adv. Polym. Technol.* 30 (2011) 174–182.
- [60] H. Zhao, G. Zhao, L.-S. Turng, X. Peng, Enhancing nanofiller dispersion through prefoaming and its effect on the microstructure of microcellular injection molded polylactide acid/clay nanocomposites, *Ind. Eng. Chem. Res.* 54 (2015) 7122–7130.
- [61] C.-C. Kuo, L.-C. Liu, W.-C. Liang, H.-C. Liu, C.-M. Chen, Preparation of polylactide acid (PLA) foams with supercritical carbon dioxide and their applications for reflectors of white light-emitting diode (LED) lamps, *Mater. Res. Bull.* 67 (2015) 170–175.
- [62] A. Ayoub, S.S.H. Rizvi, Properties of supercritical fluid extrusion-based crosslinked starch extrudates, *J. Appl. Polym. Sci.* 107 (2008) 3663–3671.
- [63] A. Ayoub, S.S.H. Rizvi, Reactive supercritical fluid extrusion for development of moisture resistant starch-based foams, *J. Appl. Polym. Sci.* 120 (2011) 2242–2250.
- [64] N. Zhao, L.H. Mark, C. Zhu, C.B. Park, Q. Li, R. Glenn, T.R. Thompson, Foaming poly(vinyl alcohol)/microfibrillated cellulose composites with CO₂ and water as Co-blowing agents, *Ind. Eng. Chem. Res.* 53 (2014) 11962–11972.
- [65] M.T. Masatcioglu, E. Yalcin, M. Kim, G.-H. Ryu, S. Celik, H. Köksel, Physical and chemical properties of tomato, green tea, and ginseng-supplemented corn extrudates produced by conventional extrusion and CO₂ injection process, *Eur. Food Res. Technol.* 237 (2013) 801–809.
- [66] S.E. Ondo, S. Singkhornart, G.-H. Ryu, Effects of die temperature, alkalinized cocoa powder content and CO₂ gas injection on physical properties of extruded cornmeal, *J. Food Eng.* 117 (2013) 173–182.
- [67] L. Myat, G.-H. Ryu, Effect of carbon dioxide injection on physicochemical properties and saccharification of extruded corn starch for fermentation substrate preparation, *J. Microb. Biochem. Technol.* 05 (2013) 18–24.
- [68] Y.-Y. Wang, G.-H. Ryu, Physicochemical and antioxidant properties of extruded corn grits with corn fiber by CO₂ injection extrusion process, *J. Cereal Sci.* 58 (2013) 110–116.
- [69] S. Singkhornart, S. Edou-ondo, G.-H. Ryu, Influence of germination and extrusion with CO₂ injection on physicochemical properties of wheat extrudates, *Food Chem.* 143 (2014) 122–131.
- [70] M. Tugrul Masatcioglu, E. Yalcin, P.J. Hwan, G.-H. Ryu, S. Celik, H. Köksel, Hull-less barley flour supplemented corn extrudates produced by conventional extrusion and CO₂ injection process, *Innov. Food Sci. Emerg. Technol.* 26 (2014) 302–309.
- [71] S.S.H. Rizvi, S.J. Mulvaney, Extrusion processing with supercritical fluids, *US Patent 5120559*, 1992.
- [72] S.J. Mulvaney, S.S.H. Rizvi, Extrusion processing with supercritical fluids, *Food Technol.* 47 (1993) 74–82.
- [73] S.S.H. Rizvi, S.J. Mulvaney, Supercritical fluid extrusion process and apparatus, *US Patent 5417992*, 1995.
- [74] Z. Hicsamaz, E. Dogan, C. Chu, S.S.H. Rizvi, Leavened dough processing by supercritical fluid extrusion (SCFX), *J. Agric. Food Chem.* 51 (2003) 6191–6197.
- [75] K. Ruttarattanamongkol, M.E. Wagner, S.S.H. Rizvi, Properties of yeast free bread produced by supercritical fluid extrusion (SCFX) and vacuum baking, *Innov. Food Sci. Emerg. Technol.* 12 (2011) 542–550.
- [76] M. Kasih, Innovative Application of Supercritical Fluid Extrusion (SCFX) in Yeast Free Bread Production, Doctoral Thesis, Cornell University, 2009.
- [77] I. Paraman, M.E. Wagner, S.S.H. Rizvi, Micronutrient and protein-fortified whole grain puffed rice made by supercritical fluid extrusion, *J. Agric. Food Chem.* 60 (2012) 11188–11194.
- [78] I. Paraman, S. Supriyadi, M.E. Wagner, S.S.H. Rizvi, Prebiotic fibre-incorporated whey protein crisps processed by supercritical fluid extrusion, *Int. J. Food Sci. Technol.* 48 (2013) 2193–2199.
- [79] M.K. Sharif, S.S.H. Rizvi, I. Paraman, Characterization of supercritical fluid extrusion processed rice-soy crisps fortified with micronutrients and soy protein, *LWT—Food Sci. Technol.* 56 (2014) 414–420.
- [80] V.Z. Sun, I. Paraman, S.S.H. Rizvi, Supercritical fluid extrusion of protein puff made with fruit pomace and liquid whey, *Food Bioprocess Technol.* 8 (2015) 1707–1715.
- [81] K.Y. Cho, S.S.H. Rizvi, New generation of healthy snack food by supercritical fluid extrusion, *J. Food Process. Preserv.* 34 (2010) 192–218.
- [82] K. Manoi, S.S.H. Rizvi, Rheological characterizations of texturized whey protein concentrate-based powders produced by reactive supercritical fluid extrusion, *Food Res. Int.* 41 (2008) 786–796.

- [83] K. Manoi, S.S.H. Rizvi, Physicochemical changes in whey protein concentrate texturized by reactive supercritical fluid extrusion, *J. Food Eng.* 95 (2009) 627–635.
- [84] N.A. Mustapha, K. Ruttarattanamongkol, S.S.H. Rizvi, The effects of supercritical fluid extrusion process on surface hydrophobicity of whey protein concentrate and its relation to storage and heat stability of concentrated emulsions, *Food Res. Int.* 48 (2012) 470–477.
- [85] K. Ruttarattanamongkol, M. Nor Afizah, S.S.H. Rizvi, Stability and rheological properties of corn oil and butter oil emulsions stabilized with texturized whey proteins by supercritical fluid extrusion, *J. Food Eng.* 166 (2015) 139–147.
- [86] C. Okolieocha, D. Raps, K. Subramaniam, V. Altstädt, Microcellular to nanocellular polymer foams: progress (2004–2015) and future directions—a review, *Eur. Polym. J.* 73 (2015) 500–519.