



## Preparation and characterization of polystyrene foams from limonene solutions



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### ABSTRACT

The foaming process has been traditionally performed at high temperature because the CO<sub>2</sub> and the polymer should behave as a homogeneous solution. The addition of a solvent could avoid the high working temperature while the homogeneity is ensured. Among the terpene oils, limonene outlines as a good candidate to carry out the dissolution of polystyrene because it respects the green chemistry principle, it is highly soluble in CO<sub>2</sub> and very compatible with the polymer.

The sorption of CO<sub>2</sub> is the first step of the foaming process. The presence of the terpene oil enhances the solubility of the gas which is solubilized in the Polystyrene as well as in the limonene. During the foaming process, many parameters can be tuned to customize the foams. In this work, a fractional factorial design of experiment was proposed to determine the effect of pressure, temperature, concentration of the solution, contact time and vent time over the diameter of cells, its standard deviation and the cells density. The proposed foaming process can be simply performed at mild pressure and temperature thanks to the presence of the solvent. The results showed that the most suitable conditions to foam polystyrene from limonene solutions are 90 bar, 30 °C, 0.1 gPS/ml Lim, 240 min contacting and 30 min venting. Finally, the samples were characterized to determine the amount of residual solvent, their glass transition and degradation temperature checking that the foams presented around 5% of solvent traces but did not show any evidence of degradation.

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### 1. Introduction

Microcellular foams are defined as foams with average cell sizes of less than 10 μm and cell densities greater than 10<sup>9</sup> cells/cm<sup>3</sup>. They are the target products since they typically exhibit high impact strength, toughness and thermal stability, as well as low dielectric constant and thermal conductivity [1]. The use of supercritical fluids (SCFs) as physical blowing agents has been developed for the production of polymer foams because they can create highly functional materials with new features and dramatically improve conventional manufacturing methods, especially from an environmental point of view. Currently, the focus is on carbon dioxide due to its relative ease of handling and more favourable interaction with polymers compared to other inert gas candidates like nitrogen [2].

Several authors have demonstrated that CO<sub>2</sub> can be used to foam amorphous materials such as poly(methylmethacrylate), polystyrene, polycarbonate, and poly(ethyleneterephthalate).

Table 1 shows a good sample of the available literature data [1,3–20] for the foaming of polymers or polymer blends using supercritical CO<sub>2</sub> and the working conditions used to carry out the process: pressure, temperature, contact time and depressurization rate ranges. Generally high pressure and temperature are required to foam the polymers but also there are other parameters playing an important role during the process. By this reason, polymeric foams can be customized and many polymers are screened for their foamability and resulting foam structure, which determines to a great extent the properties of the foam [19].

The process to prepare foams using CO<sub>2</sub> as foaming agent can be divided into three steps: (1) sorption of CO<sub>2</sub> until saturation in the plastic; (2) nucleation of foam bubbles, it is need induce a phase separation by a thermodynamic instability (either a temperature increase or a pressure decrease); and (3) growth of foam's cells. The main steps are schematically depicted in Fig. 1.

As shown in Fig. 1, the foaming process starts by melting the polymer and adding CO<sub>2</sub>. The type of polymer, together with the applied pressure and temperature determine to a large extent the amount of CO<sub>2</sub> that can be dissolved into. During the sorption step, the gas is dissolved inside the polymer inducing swelling, increasing its free volume and segment mobility, causing its

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**Table 1**

Literature review of foamed polymers. Range of pressure, temperature, contact time and depressurization used.

Polymer	Pressure range (bar)	Temperature range (°C)	Contact time range	Depressurization rate or time	Refs
Poly(ethylene terephthalate)	80–160	280	30–50 min	180–190 MPa/s	[3]
Poly(ethylene terephthalate)	90–160	180–260	~60 min		[4]
Isotactic polypropylene	300	200	20–25 min		[5]
Polystyrene	69–210.7	60–180	24 h	0.91–1.17 MPa/s	[6]
Polystyrene	100–200	50–110	240 min	100–400 MPa/s	[1]
Polystyrene	150–200	100	0–60 min	80–400 MPa/s	[7]
Polystyrene	86–140	60–110	240 min	1 MPa/s	[8]
Polystyrene and poly(D,L-lactic acid)	180–380	35–55	240 min	0.1–1.6 MPa/s	[9]
Polystyrene and cellulose acetate	80–230	55–125	60–240 min	20 seg	[10]
Poly(L-lactic acid)	140–610	60–180	300 min		[11]
Poly(lactic acid-co-glycolic acid)	100–250	35–85		0.05–0.20 MPa/s	[12]
Poly(D-lactide) and poly(D-lactide-co-glycolide)	103–276	35–100	20 min	0.3–0.4 MPa/s	[13]
Poly(D,L-lactide) and poly(D,L-lactide-co-glycolide)	230	90	1–40 min	0.006–0.013 MPa/s	[14]
Poly( <i>e</i> -caprolactone-co-lactide)	70–280	60–80	120 min	3–120 seg	[15]
Poly( <i>e</i> -caprolactone)	78–200	40–50	120 min	0.03–1 MPa/s	[16]
Poly( <i>p</i> -dioxanone)	250–450	80–100	60–120 min		[17]
Poly(heteroarylenes)	120–350	40–100			[18]
Polypropylene, polystyrene and poly(styrene-butadiene-styrene)	150–190	160–190	600 min		[19]
Polystyrene, polymethylmethacrylate, poly(styrene-co-butadiene-co-methylmethacrylate) and poly(methylmethacrylate-co-butylacrylate-co-methylmethacrylate)	300	25–80		0.01 MPa/s	[20]

plasticization which involves the modification of the mechanical and physical properties of the polymers. The absorbed gas behaves like a “lubricant” of the polymeric chains which are easier slid and consequently, the glass transition temperature ( $T_g$ ), melting temperature ( $T_m$ ), viscosity ( $\mu$ ) and surface tension ( $\gamma$ ) are decreased. The nucleation stage occurs instantaneously at lower  $T_g$  when the polymer matrix becomes less rigid. Cell growth will stop once the polymer matrix returns to the glassy state, either due to a decrease in temperature or a decrease in the  $\text{CO}_2$  concentration in the polymer and the polymer is no longer plasticized [21].

During the depressurization stage, run at constant temperature, the pressure is reduced, the  $\text{CO}_2$  phase changes from supercritical to gas and nucleation and growth of gas bubbles occurs in the rubbery polymer generating pores. However not only depressurization rate should be control, but also the cooling rate, because it affects the polymer viscosity (Fig. 1) [14].

Important efforts have been carried out to determine the real influence of the experimental parameters on the final foam structure and as a consequence on their properties. In general, increasing

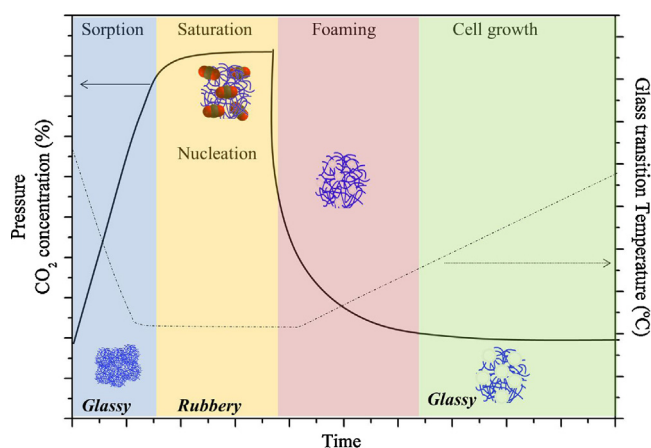
pressure, the pore diameter and the bulk density decreases, while the cell density increases. At higher pressure, more fluid is dissolved into the polymer matrix causing a more pronounced plasticization and viscosity reduction. Nevertheless, the pore cell increases while the bulk foam density and cell population decreases when temperature is increased [9].

In this work, we propose the use of a solvent to decrease the working temperature during the foaming process. The main purposes were the preparation, characterization and optimization of the foams to obtain high cells density and low pore cells by mean of a process which required low energy consumption and does not affect the polymeric chain structure because of the low operation temperature. Limonene was the terpene solvent selected because polystyrene is highly soluble [22,23] it is fully miscible in  $\text{scCO}_2$  [24–26] and the foaming process is feasible at mild working conditions [27]. Furthermore the use of binary fluid mixtures of carbon dioxide and an organic solvent provide flexibilities towards control of pore sizes and connectivity in forming porous matrices [11].  $\text{CO}_2$  is behaved as nonsolvent of the polymer and the mass transfer in the systems occurs in two ways, the limonene is solubilised from the bulk polymeric phase at the same time as  $\text{CO}_2$  is absorbed in the liquid phase. The mass transfer during the foaming is mainly governed by the diffusion of the  $\text{CO}_2$  into the polymeric rich phase and it has been checked that is enhanced because of the presence of the solvent which promotes the relaxation of the polymeric chains.

## 2. Experimental

### 2.1. Materials

Generally, the average molecular weight of commercial PS is between 150,000 and 400,000 g/mol [28]. In this work, the effect of molecular weight on the foaming of the polymer was not studied because it was concluded by Stafford et al. [29] that it did not significantly affect the foams. By this reason, the average weight molecular weight of the selected PS was 280,000 g/mol. Atactic PS was used because other authors checked that polymer syndiotacticity could limit the growth of the cell which can grow only in the amorphous region [10]. PS was supplied in pellets by Sigma-Aldrich (Spain).



**Fig. 1.** Schematic diagram of the steps during a typical foaming process: sorption, saturation, foaming and cell growth. The sorption of  $\text{CO}_2$  into the polymer (continuous line, left axis) is the responsible of the decrease of the glass transition temperature (dashed line, right axis).

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