

Recycling of Polystyrene Wastes by Supercritical CO₂ Technology

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Dissolution with suitable solvents to achieve a volume reduction of more than 100 times without degradation of polymer chains is an attractive alternative to incineration or mechanical recycling for the recycling of polystyrene (PS) foam wastes.

The volume reduction of expanded (EPS) or extruded (XPS) polystyrene wastes by solvent collapse of the foam structure and further thermal treatment to recover the solvent owns several disadvantages. The solvent removal by atmospheric distillation or even by vacuum distillation produces a certain degree of polymer chain degradation, involving also important energy consumption for solvent recovery and lets a certain level of solvent residues in the recovered plastic. In this way, CO₂ supercritical technology appears as an interesting alternative for the elimination of solvent because of low operating temperatures, leaving no solvent residues in the recovered PS and a product without structural modification.

INTRODUCTION

In the last years, disposal of the non-biodegradable plastic wastes has been recognized as a serious environmental problem. Recycling these wastes has great interest in order to prevent the environmental pollution and to preserve natural sources [1, 2, 3].

The two main alternatives for handling polymer wastes are energy recycling, where wastes are incinerated, and mechanical recycling. The incineration of polymer waste meets with strong societal opposition [4] and releases greenhouse gases. Besides, mechanical recycling is a popular recovery path for manufacturers and is carried out on single-polymer waste streams. A market for recycled products can only be found if the quality is close to, or even better than the original [5]. Unfortunately the process of recovery of these wastes are often more expensive than virgin plastics [6, 7]. Furthermore, these recycling processes have other economic problems related to the transportation cost, because the low density of Polystyrene (PS) waste and therefore, the transport of the big volume residues make economically unfeasible this process.

Reducing the cost of the two recycling processes mentioned before, it could be accomplished by dissolution with suitable solvents to get a volume reduction without degradation of polymer chains, since, if dissolution is developed in the source of residue production, the transportation would be more efficient than in conventional recycling methods [8].

It is well known that some aromatic compounds such as toluene or benzene are good solvents of PS foams [9], but they are not environmentally friendly and would prevent the further application of recycled PS, for example, in food packaging. Thus, the use of a “green” solvent would avoid those difficulties. The employment of a natural solvent for the treatment of PS wastes could transform the dissolution of PS wastes in an environmentally friendly technology.

The treatment of PS with terpene oil has been reported as an attractive alternative for PS solubilization [10]. However, solvent removal process by atmospheric or vacuum distillation presents several disadvantages as the formation of undesirable by-products as a consequence of thermal degradation of polymer chains, as well as important energy consumption and a worst plastic quality, due to certain level of solvent residues [8, 11].

To avoid all of these disadvantages, elimination of the solvent with liquid or supercritical CO₂ can be considered as an attractive alternative process, because of low operating temperatures and the fact of leaving no solvents residues in the recovered PS. Also, the use of CO₂ is very attractive for the polymer solvent separation since is capable of swelling the polymer making accessible the internal part of the polymer bulk to the CO₂, by this way it is easier the removal of organic solvent and enabling that polymeric chains remain intact; and finally, when the pressure is reduced, the total elimination of the solvent with the carbon dioxide [12].

The main advantages that present this process are due to the high affinity of supercritical fluids with organic solvents, also their high diffusivity along with the moderate solubility in polymer is combined with plasticization, and this feature provides a suitable environment for guest materials to migrate into the polymer matrix. Another important advantage is decreasing the viscosity of polymer solutions, so melts facilitates their processing. Finally it is important to stand out the low toxicity and environmental acceptability of this technology [13].

This work proposes a global process to polystyrene recycling in two steps: a polystyrene dissolution with suitable solvents followed by solvent elimination by supercritical fluids. In order to develop a “green process” the constituents of essential oils, d-limonene, were selected as the most appropriate solvents.

MATERIAL AND PROCEDURES

The constituents of essential oils used in this work were supplied by Panreac.

Liquid CO₂ (purity 99.5%) was supplied by Carbueros Metalicos S.A. (Madrid, Spain).

PS was supplied by Tecnove Fiberglass. PS composition is shown in Table 1. The PS has a polydispersity of 1.7 and its decomposition temperature is 421 °C.

Table 1. Extruded Polystyrene Waste

Composition	% w/w
XPS	90-93
Flame retardant (HBCD)	2-3
Nucleating agent (Talc)	0-1
Ethanol	2
Pigments	0.2-0.3

Figure 1 shows the schematics of experimental set-up. The set-up consists of a stainless-steel high pressure vessel with an internal volume of 1200 ml (supplied by Burghof). The vessel is made of SS316 and can be operated up to 200 bar and 300°C.

A pressure indicator having a range from 0 to 250 bar and accuracy of ± 10 bar is used for the pressure measurements. The temperature is measured using a with an accuracy of $\pm 0,1$ K. A rupture disc is also provided on the vessel for safety.

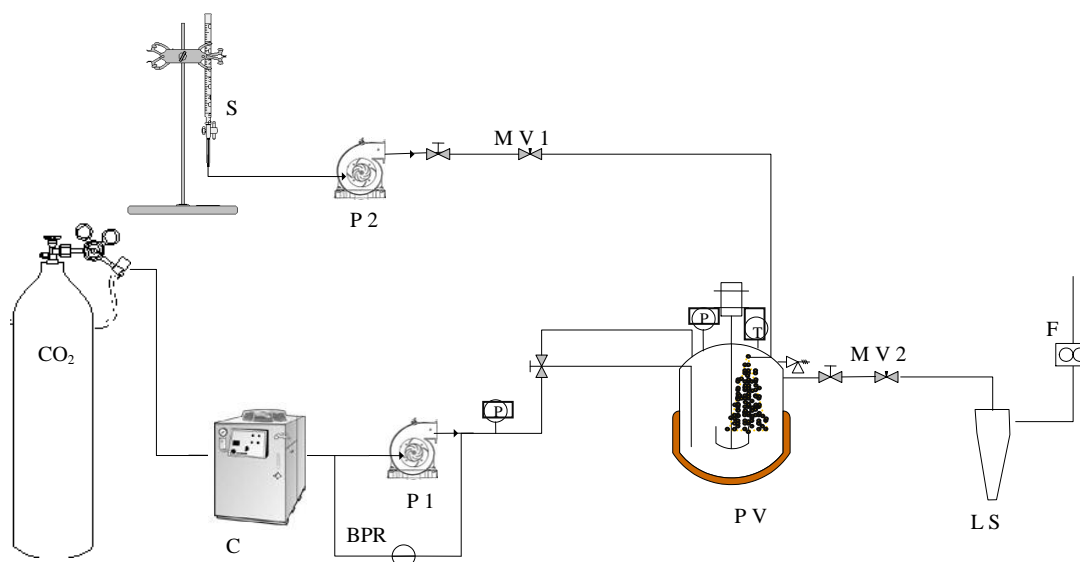


Figure 1. Simplified scheme of SAS apparatus. BPR, back pressure regulator; C, CO₂ cooler; F, flowmeter; LS, liquid solvent recovery vessel; MV1 and MV2, micrometering valve; P1 and P2, pumps; PV, pressure vessel.

The experimental procedure used to remove Limonene by CO₂ from a polystyrene/Limonene solution consists of cooling CO₂ from the cylinder in the ice bath to avoid cavitation problems in the pump, where it was compressed until the desired working pressure was reached. This pressure was controlled by the back pressure regulator.

The solution containing polystyrene from the burette was compressed in a second pump. When the solution had reached the desired working pressure, it was injected into the precipitation vessel through a stainless steel nozzle (1/16") located at the top of this vessel but separate from the CO₂ inlet.

Following contact of the two streams, polystyrene was precipitated and retained inside vessel. The gaseous phase was allowed to leave vessel through and outlet point at the bottom and expanded into the liquid solvent recovery vessel. This expansion and the flow were regulated by a micrometering valve.

Determination of Polydispersity index

Gel permeation chromatography was used to determine the polydispersity index. The PDI calculated is the weight average molecular weight divided by the number average molecular weight. Analysis was performed on a Waters Associates Liquid Chromatography system (Waters 717, Rydalmer) equipped with a differential refractometer and two μ -Styragel

columns (HR1 and HR4). The mobile phase was tetrahydrofuran (THF) at a flow rate of 1 ml/min. Polymer was dissolved in THF and filtered through 0.45 μm filter before analysis. The system was calibrated with narrow disperse polystyrene standards and molecular weights are reported as polystyrene equivalents.

Thermal Gravimetric analysis (TGA)

The solvents ratio in the clear saturated solution and the decomposition temperature was determined by thermogravimetric analysis (TA-DSC Q 100), where the weight loss due to the volatilization of solvents and the degradation products is monitored as a function of temperature. The sample weight varies from 10 to 15 mg. Samples are heated from the room temperature to 600 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}/\text{min}$.

RESULTS

Dense carbon dioxide has been tested to dissolve Limonene from the solvent-polymer systems by Supercritical Antisolvent Extraction. This technique is the one that can allow the effective fractionation of liquid solutions containing solid solutes. CO_2 soluble compounds at process conditions remain in the fluid phase; whereas, insoluble compounds precipitate and a very effective fractionation can be obtained.

The first one, it has been analyzed the solubility of Limonene in CO_2 , which has been examined in great depth in the literature [14-23].

According to these authors, Limonene is fully miscible with CO_2 and the solubility increases in temperature lead to lower solubility rates [21] because Limonene is a monoterpene hydrocarbons with low molecular weight, high vapour pressure and low polarity, factors that favour solubility in dense gases, especially in supercritical CO_2 [24].

Sato and col. (1995) [19] have studied extraction with supercritical CO_2 in order to obtain terpeneless citrus oil. The operating temperature and pressure were in the range 313K-333K and 8,8-11,8 MPa, respectively. The CO_2 flow rate ranged from 0,091 to 0,512 g/s. When the column was at 333 K and 8,8 MPa, Limonene was extracted selectively and in this conditions, the solubility of pure Limonene were reported to be 5,2 mg/g [20, 26, 28, 29].

Therefore, CO_2 is a very good solvent for Limonene, exhibits relatively high solubility, and the results show that at 100 bar and 30 $^{\circ}\text{C}$ Limonene is completely soluble in CO_2 .

On the other hand, solubility of PS in CO_2 has also been studied by several authors such as O'Neill and col. (1998), Kirby, C. and McHugh, M.A. (1999), Rindfleisch and col. (1999) and Xu, D. and col. (2005) [34, 35, 36, 37]. Rindfleisch and col. (1996) and Kirby and McHugh, (1999) noted that CO_2 can dissolve PS if the molecular weight of the polymer is less than 1000 g/mol. However, the experiments performed to determine PS solubility were only operated to pressure and temperatures sufficiently far from operation conditions. The poor solubility of PS in CO_2 was checked by O'Neill and col. (1998) [34] and by Rindfleisch and col. (1999) [36] at 225 $^{\circ}\text{C}$ and 2100 bar who concluded that only very low molecular weight PS was slightly soluble in CO_2 , and PS with 500 g/mol was insignificantly soluble

(<<0,1%), while the higher molecular weight (1850 g/mol) was completely insoluble in CO₂ [34, 35, 36].

According to bibliography that have been mentioned, in this preliminary study we performed experiments at low temperature and pressure, since according the of essential oil solubility, temperatures between 40 and 50°C and extraction pressures lower than 10 MPa are usually sufficient to obtain the well-soluble volatile essential oils and at these conditions, the solubility of PS in CO₂ was found insignificant and it was ensured that only Limonene was dissolved and removed with flowing CO₂ [17].

The first experiment was carried out to ensure that polystyrene-limonene mixture dragging did not occur during the extraction runs. In these experiments the extractor was loaded with 10 g of mixture and using CO₂ with a density of 250 Kg/m³ (P = 7.7 MPa, T = 313 K) and Q = 2 L/min. Figure 2 show the limonene concentrations in CO₂ measured in the ternary system Limonene-Polystyrene-CO₂. The horizontal line indicates the solubility of pure limonene in CO₂, $y = 0.00216$ [17].

Figure 2 shows that limonene concentration increases with increasing limonene amount in the mixture. This tendency stands constants when maximum solubility of Limonene in PS+CO₂+Limonene is reached.

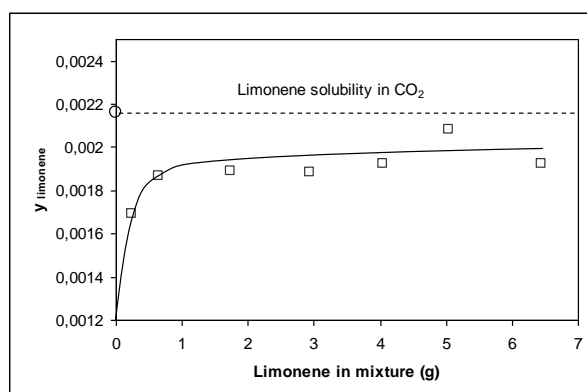


Figure 2. Limonene concentration (mole fraction) in the CO₂ exit stream on the amount of limonene in the mixture polystyrene+limonene at 313 K and 7.7 MPa.

It is important to note that Limonene solubility in ternary system (PS+CO₂+Limonene) is less than in binary one (CO₂+Limonene) and that there is not dragging of liquid phase. Therefore, this method and operation conditions were selected for subsequent experiment.

The second experiment was carried out at the conditions tested, in order to determine yields, it means, Limonene exhaustion and the evolution with time of extraction composition. Figure 3 shows that 7 hours are sufficient to obtain a 80% yield, because no significant yield increase was obtained after this time.

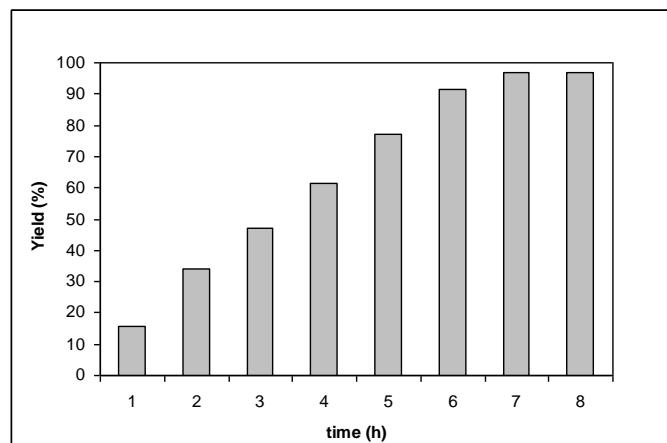


Figure 3. Evolution with time of extraction yields. Q=2 L/min Conditions: P=7.7 MPa; T= 313 K; L= 10 g ; Q=2 L/min.

In order to determine the quality of PS recovered after Supercritical Antisolvent Extraction, it was analyzed by thermogravimetric analysis (TGA) to establish Limonene amount in polymer and by GPC to determine a possible structural modification.

Results from TGA showed an only weight loss around 421°C, which belongs with polymer degradation, as any weight loss is observed at Limonene boiling temperature (176 °C), it is possible to conclude that PS is almost free of solvent. On the other hand, GPC analysis determines that there is not any variation in polydispersity values. These results are summarized in table 2.

Table 2. Polydispersity and Decomposition temperature of Polystyrene recovered

	PS untreated	PS recovered
Polydispersity	1.70	1.74
T _D (°C)	421	417

According to results, it is concluded that polymer degradation does not occur during the Supercritical Antisolvent Extraction with supercritical CO₂.

CONCLUSIONS

This work presents a new recycling process to polystyrene recycling with almost no molecular weight degradation and barely solvent. It is possible to carry out in two stages, in the first one polystyrene dissolution and in the second one elimination of Limonene by supercritical CO₂.

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