RECYCLING OF POLYSTYRENE WASTES BY SUPERCRITICAL CO_2 TECHNOLOGY

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Abstract

Polystyrene (PS) is currently used as packaging, insulating and storing material in various industrial or domestic fields. As a result, a large quantity of PS wastes is produced. Plastic wastes are not usually biodegradable, so it is necessary to suggest a technology to recycle them. Landfill and incineration are reasonable cheap methods, but not environmentally acceptable, therefore, alternative methods for polymer recycling are required.

Dissolution and shrinking with natural solvents is a cheap and efficient process for polymer waste management, thus, PS wastes show an important volume reduction of more than 100 times. As it has been studied, PS is dissolved better in the nonpolar solvents of the terpene family, as p-cymene, limonene or α-phellandrene, showing solubility values around 0.3 g/ml. However, polar terpene solvents, with high tendency to form hydrogen bonds, as geraniol or linalool, present solubility values of 0.005 g/ml. For this reason, nonpolar terpene oils were selected to study PS dissolution process.

Finally, solvent can be recovered by means of supercritical technology, in order to obtain a polymer with a reduced volume and without degradation of the polymeric chains.

Keywords: *Polystyrene, terpene oil, supercritical CO_2.*

1. Introduction

In the last years, disposal of the non-biodegradable plastic wastes has been recognized as a serious environmental problem. The recycling of 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. Unfortunately, this last method of recovery are often more expensive than using virgin plastics [4, 5]. An interesting and cost-effective alternative can be the dissolution of the foam wastes with suitable solvents, to get a volume reduction without degradation of polymer chains. Furthermore if the foam shrinking is carried out in house of the residue producer, the transportation would be more efficient than in conventional recycling methods [6].

Aromatic compounds, such as toluene or benzene, are good solvents of PS foams [7], but they are not environmentally friendly and would limit 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. By this reason, terpene oils have been reported as an attractive alternative for PS foam recycling [8]. 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 [6, 9]. To avoid all of these disadvantages, elimination of the solvent with liquid or supercritical CO_2 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 CO_2 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 CO_2 [10].

This work proposes a global process for 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 were selected as the most appropriate solvents.

2. Materials and Methods

Polystyrene pellets with a weight average molecular weight of 280000 g/mol were supplied by Sigma-Aldrich.

The solvents tested in this study were anisole, cinnamaldehyde, p-cymene, eucalyptol, geraniol, limonene, linalool, α-phellandrene, α-pinene, γ-terpinene and α-terpineol; all of them were supplied by Sigma-Aldrich and were used without further purification.

Carbon dioxide (99.8%) was purchased from Carburos Metálicos España S.A. (Madrid, Spain).

Solubility determination was carried out by thermogravimetric analysis (TA-DSC Q 100). Glass tubes were used to prepare saturated solutions of PS pellets with excess solid solute in different terpene oils. The tubes were sealed to prevent evaporation of solvents and placed in a thermostatic bath at a constant temperature; they were allowed to settle about 48 hours to ensure equilibrium. For each tube, two samples were withdrawn and weighted from the clear saturated solution to minimize experimental errors. The solvent ratio in the sample was determined by thermal gravimetric analysis where samples were heated from the room temperature to 600ºC at a heating rate of 10ºC/min. Thermogravimetric analysis showed two weight losses as a function of temperature, the first one belongs to volatilization of solvent and the last one to PS decomposition.

Solvent removal was carried out in an experimental set-up which consists of a stainless-steel high pressure vessel with an internal volume of 350 ml. 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 temperature indicator with an accuracy of ± 0.1 K.

3. Results and Discussion

The first stage consists in the dissolution of polystyrene with suitable solvents. A good solvent for the recycling of extruded polystyrene should have high dissolution ability and high volatility that will allow its removal with minimum temperature to avoid chain degradation. By this reason, a set of experiments was carried out to check which terpenic solvents could be used to dissolve PS [6]. Table 1 shows the values of the solubility of PS in different terpenic solvents at 25ºC.

Table 1. Experimental solubility of PS in terpene oils

Solvent	Solubility (g/ml)
Anisole	0.2578
Cinammaldehyde	0.1957
p-Cymene	0.3529
Eucalyptol	0.2977
Geraniol	0.0029
Limonene	0.2473
Linalool	0.0059
□-Phellandrene	0.2879
□-Pinene	0.2901
□-Terpinene	0.2427
□-Terpineol	0.0063

As expected, the solvents with polar groups in their structure do not dissolve the PS (geraniol and linalool) or exhibit a lower solubility potential. Limonene, γ-terpinene, p-cymene and α-pinene exhibit similar solubility values being good alternatives to carry out the recycling process that is why nonpolar terpene oils were selected to study PS dissolution process.

The second stage for the recycling of PS wastes consists of solvent removal by means of dense CO_2. Thus, it was analyzed the solubility of the selected terpene oils in CO_2, observing that they are fully miscible with dense gas, and the solubility increases in temperature, lead to lower solubility rates [11] because all of them are monoterpene hydrocarbons with low molecular weight, high vapor pressure and low polarity, factors that favor solubility in dense gases, especially in supercritical CO_2 [12].

Sato and col. (1995) [13] have studied the extraction of citrus oil 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. At such conditions, limonene was extracted selectively, showing a solubility value of 5 mg/g confirming that CO_2 is a very good solvent for terpenes and exhibits relatively high solubility in CO_2.

On the other hand, solubility of PS in CO_2 has also been studied by several authors [14,15,16,17]. In all case a poor solubility of the polymer in CO_2 has been observed [14,16]. The general conclusion would be that PS with very low molecular weight is slightly soluble in CO_2, for instance 500 g/mol exhibit a rather small solubility lower than 0.1%, while for higher molecular weights (>1850 g/mol) PS is completely insoluble in CO_2 [14,15,16].

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