J Mater Cycles Waste Manag (2009) 11:2–5
DOI 10.1007/s10163-008-0210-8

SPECIAL FEATURE: ORIGINAL ARTICLE

Chemical Feedstock Recycling & Other Innovative Recycling Techniques 6

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Recycling extruded polystyrene by dissolution with suitable solvents

Received: December 24, 2007 / Accepted: May 8, 2008

Abstract The amount of extruded polystyrene (XPS) waste has increased in recent years due to the increase of its use in the thermal insulation of buildings, transport vehicles, and refrigerators, among others. Dissolution with suitable solvents to achieve a volume reduction of more than 100 times without degradation of polymer chains is one of the cheapest and most efficient methods of recycling XPS. Several environmentally friendly solvents have been tested as dissolution agents for XPS volume reduction; the action of these solvents does not produce any degradation of polymer chains. The solubility of the polymer in such solvents at different temperatures was investigated. The solvent can be easily recycled by distillation, obtaining a high-quality recycled polymer.

Key words Polystyrene · Recycling · Solubility parameters

Introduction

Large and increasing volumes of extruded polystyrene (XPS) are produced each year, and, after use, XPS is considered a residue. The management of this residue involves serious difficulties due to its low density. The transport of these large-volume residues and their low biodegradability make landfill disposal mostly unfeasible.

The two main alternatives for handling polymer wastes are energy recycling, where wastes are incinerated, and mechanical recycling.[1] The incineration of polymer waste meets with strong societal opposition[2] and releases greenhouse gases; there is the Kyoto Protocol to consider, and EU countries are moving toward domestic goals of reducing carbon dioxide emissions by between 10% and 20% by 2010. Mechanical recycling (the conversion of "scrap" polymer into new products) 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 that of the original. Unfortunately, the process of classification and further recovery of these wastes makes them often more expensive than virgin plastic.[3,4]

Dissolution and shrinking is one of the cheapest and most efficient methods of recycling XPS. If it were done in house by the waste producers, the separation of plastics would be easy and effective and the transport costs would be eliminated. The selection of an appropriate solvent is most important for the success of XPS recycling using this method.

It is well known that some pure organic liquids such as toluene, benzene, and other aromatic compounds are good solvents of XPS.[5] These organic solvents, however, are not environmentally friendly and would prevent the further application of recycled XPS in food packaging. Thus, the use of a "green" solvent would avoid those difficulties. The employment of a natural solvent for the treatment of XPS wastes could transform the dissolution of PS wastes in an environmentally friendly technology.

The treatment of XPS with D-limonene has been reported as an attractive alternative for XPS solubilization.[6] This compound does not produce molecular weight degradation during the recycling process. In total, 98% (by weight) of commercially available D-limonene is made up of an essential oil obtained from orange or lemon peel. It is produced from a renewable source, citrus oil, as a byproduct of orange juice manufacture. Chemically, D-limonene is a hydrocarbon classed as a terpene. These compounds are an enormous class of natural products spanning well over 30 000 substance. They have been used throughout history for a broad variety of purposes including perfume, medicine, and flavoring.

In this work, the suitability of several constituents of essential oils from natural sources for use as solvents in the recycling of XPS was investigated. The degree of polymer chain degradation of the recovered XPS is one of the more important factors taken into account to evaluate the differ-

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ent solvents. The degree of polymer chain degradation was estimated by the analysis of the polydispersity and the decomposition temperature.

Experimental

Materials

The constituents of the essential oils used in this work were supplied by Panreac (Madrid, Spain) and are show in Table 1. XPS was supplied by Tecnove Fiberglass (Herencia, Spain). The composition of the XPS is shown in Table 2; it had a polydispersity of 1.7 and a decomposition temperature is 421°C.

Solubility determination

Glass tubes were used to prepare saturated solutions of XPS foams with excess solid solute in solvents. The tubes were stoppered to prevent evaporation of solvents and then the tubes were placed in a constant-temperature thermostatic bath and were allowed to settle for about 5–8 h to ensure equilibrium. For each tube, two samples were withdrawn from the clear saturated solution using glass syringes. These syringes were weighed and the solvent ratio in the sample was determined by thermal gravimetric analysis (TGA). The solubility was expressed as the mass of XPS and the solvent volume ratio was expressed in milliliters.

Determination of polydispersity index

Gel-permeation chromatography was used to determine the polydispersity index (PDI). The PDI 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, Rydalmere, Australia) 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. The polymer was dissolved in THF and filtered through a 0.45-µm filter before analysis. The system was calibrated with narrow disperse polystyrene standards and molecular weights are reported as polystyrene equivalents.

Table 1. Solvent characteristics

Solvent	CAS[a] number	Structure	
Linalool	78–70–6	$C_{10}H_{18}O$	Noncyclic
Geraniol	106–24–1	$C_{10}H_{18}O$	Noncyclic
Limonene	5989–54–8	$C_{10}H_{16}$	Monocyclic
Terpinene	99–85–4	$C_{10}H_{16}$	Monocyclic
Cymene	99–87–6	$C_{10}H_{14}$	Monocyclic
Phellandrene	99–83–2	$C_{10}H_{16}$	Monocyclic
Menthol	89–78–1	$C_{10}H_{20}O$	Monocyclic
Terpineol	98–55–5	$C_{10}H_{18}O$	Monocyclic
Cinnamaldehyde	104–55–2	C_9H_8O	Monocyclic
Eucalyptol	470–82–6	$C_{10}H_{18}O$	Bicyclic

[a] Chemical Abstracts Service

Table 2. Composition of the extruded polystyrene

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

XPS, extruded polystyrene; HBCD, HexaBromo CycloDodecane

Thermal gravimetric analysis (TGA)

The solvent/polymer ratio in the clear saturated solution and the decomposition temperature were determined by thermogravimetric analysis (TA-DSC Q 100, TA instruments, Madrid, Spain), where the weight losses due to the volatilization of solvents and the degradation products were monitored as a function of temperature. The sample weight varied from 10 to 15 mg and samples were heated from room temperature to 500°C at a heating rate of 15°C/min.

Results and discussion

A good green solvent for recycling extruded polystyrene should be made from natural sources, have a high polystyrene dissolution ability, and produce minimum chain degradation. To select the most suitable solvent, several experiments were carried out to study the effect of solvent and temperature on both solubility and degree of polymer chain degradation.

The accuracy and reproducibility of the experimental procedure was determined by comparing the results from three independent runs carried out under identical conditions, i.e., with D-limonene as the solvent at a temperature of 25°C. In these experiments, the solubilities were similar (0.26, 0.25, and 0.26 g/ml), indicating that the repeatability of the experimental procedure was good. Nevertheless, to minimize experimental errors, each run was done twice.

Solubility determination: effect of solvent

The capacities of the solvents shown in Table 1 to dissolve XPS were measured at 25°C. The solubility values are shown in Table 3. As was expected, XPS was not soluble in all the solvents, and the solubility varied in those in which XPS was soluble. To explain these results, one has to keep in mind that polymers have a tendency to be soluble in solvents which have similar properties to themselves. As a result, nonpolar polymers are most soluble in nonpolar solvents and polar polymers are most soluble in polar solvents. Polymers that can form intermolecular hydrogen bridges are most soluble in solvents with the same ability. Polystyrene is a nonpolar and non-hydrogen-bonding polymer and is thus soluble in solvents such as limonene, terpinene, cymene,

Table 3. Experimental solubility of XPS in solvents at 25°C

Solvent	Solubility (g/ml)
Linalool	Not soluble
Geraniol	Not soluble
Limonene	0.26
Terpinene	0.25
Cymene	0.31
Phellandrene	0.28
Menthol	Not soluble
Terpineol	Not soluble
Cinnamaldehyde	0.17
Eucalyptol	0.10

Table 4. Polydispersity and decomposition temperature of XPS in solvents

Solvent	Polydispersity	Decomposition temperature (°C)
Nontreated XPS	1.70	421
Limonene	1.76	419
Terpinene	1.75	415
Cymene	1.80	415
Phellandrene	1.70	417
Cinnamaldehyde	1.73	417
Eucalyptol	1.72	415

and phellandrene (nonpolar solvents with no hydrogen-bonding capacity), while it is not soluble in linalool, geraniol, menthol, and terpineol (more or less polar solvents with hydrogen-bonding capacity).

In addition, cinnamaldehyde and eucalyptol exhibited a lower solubility potential than limonene, terpinene, cymene, and phellandrene. These results can also be explained with regard to the solvent polarities. Cinnamaldehyde and eucalyptol have higher polarities than limonene, terpinene, cymene, and phellandrene do and, therefore, the solubility of XPS in them is lower. Thus, limonene, terpinene, cymene, and phellandrene can be considered as the best solvents for recycling XPS, and these were selected for the following part of the study.

The degradation of polymer chains during the recycling process is associated with reductions in the molecular weight of the polymer and in the decomposition temperature. These changes can give an idea of the level of degradation that the chemical treatment exacts on polymer.

Table 4 shows the polydispersity and decomposition temperature of XPS treated with the different solvents. It can be observed that in all cases the polydispersity remains almost unchanged after the treatment with the assayed solvents; the same is true for the decomposition temperature. Therefore, considering the results obtained, it is possible to affirm that appreciable polymer degradation does not occur during the dissolution process.

Effect of temperature on solubility

A second group of experiments was carried out to determine the temperature at which polymer dissolution should be performed. The temperatures studied were 25°, 40°, and 60°C. Higher temperatures were not tested to prevent polymer chain degradation.

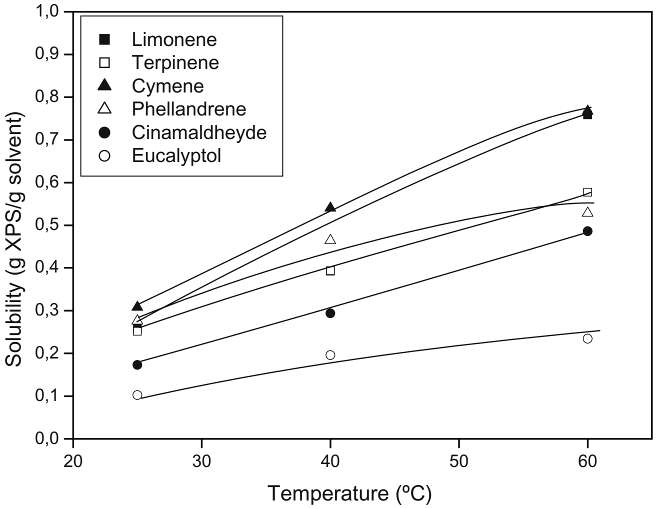

Fig. 1. Effect of temperature on solubility. *XPS*, extruded polystyrene

The results obtained are shown in Fig. 1. It can be observed that for all solvents the solubility increase with increasing temperature. These results can be explained on a thermodynamics basis, which established that the dissolution will take place if the Gibbs free energy is negative. According to the Flory–Huggins theory[7,8] that describes the thermodynamic equilibrium at constant pressure for polymer–solvent mixtures, the free energy change per unit volume of solution can be calculated as:

$$\left[\frac{\Delta G_m}{R \cdot T}\right] = \left(\frac{\phi_1}{V_1}\ln\phi_1 + \frac{\phi_2}{V_2}\ln\phi_2 + \chi_{12}\phi_1\phi_2\right) \tag{1}$$

where T is the temperature expressed in Kelvin, R is the ideal gas constant, ϕ is the volume fraction of each component in the mixture, V is the molar volume of the two components, χ is the Flory–Huggins interaction parameter expressing the interaction enthalpy between two different molecules.

The first two terms on the right side of this equation denote the entropy of mixing, which quantitatively is negative,[9] since in solution the molecules display a more chaotic arrangement than in the solid state. On the other hand, enthalpy of mixing (ΔH_m) at constant pressure for polymer–solvent mixtures can be calculated as:

$$\Delta H_m = \chi_{12}\phi_1\phi_2 \tag{2}$$

where the χ_{12} parameter expresses the interaction enthalpy between two different molecules. This parameter is always positive, opposing the negative entropy effect of mixing.[10] Thus the lower this value is, the greater is the solubility. There is a linear relationship between χ_{12} and the inverse of temperature.[11] Accordingly, when the temperature increases, the value of χ_{12} decreases, and, therefore, as the temperature increases, the dissolution process is favored. A moderate increase in temperature produces an increase of ΔS_m and a

Table 5. Effect of dissolution temperature (T) on polydispersity

Solvent	Polydispersity		
	$T = 25°C$	$T = 40°C$	$T = 60°C$
Limonene	1.76	1.82	1.81
Terpinene	1.75	1.75	1.75
Cymene	1.80	1.90	1.95
Phellandrene	1.70	1.72	1.84
Cinnamaldehyde	1.73	1.76	1.84
Eucalyptol	1.72	1.71	1.77

Table 6. Effect of dissolution temperature on decomposition temperature

Solvent	Decomposition temperature (°C)		
	$T = 25°C$	$T = 40°C$	$T = 60°C$
Limonene	419	418	419
Terpinene	415	417	417
Cymene	415	415	416
Phellandrene	414	414	420
Cinnamaldehyde	417	421	420
Eucalyptol	415	414	416

decrease of the value of ΔH_m, favoring the dissolution process and increasing the solubility.

As a consequence of the gentle heating, incipient polymer thermal degradation occurred. This fact means that the decomposition of the recycled polymer occurs at much lower temperatures than those at which it takes place in the original polymer. Tables 5 and 6 show the results of polydispersity and decomposition temperature for XPS prepared at different dissolution temperatures. It can be observed that although the decomposition temperature did not vary significantly, the polydispersity slightly increased, probably due to the initiation of chain degradation. Considering these results, it may be stated that it is not convenient to carry out the dissolution process at a temperature higher than 60°C because, although solubility is higher at higher temperatures, a certain degree of degradation is produced at higher temperatures.

Conclusions

Several natural solvents were tested as dissolution agents for XPS. The solubility of the polymer in these solvents is affected by solvent polarity; the polymer dissolves better in the nonpolar solvents of the terpenoid family, which are chemically and physically similar to XPS. The solubility of XPS in the solvents increased as the temperature increased, but at the higher temperature assayed in this study (60°C), a slight degradation of the polymer chains occurred.

Acknowledgments Financial support from Consejeria de Educacion y Ciencia (PBI06-0139) Junta de Comunidades de Castilla-La Mancha, Spain and Tecnove-Fiberglass is gratefully acknowledged.

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