EXPANDED POLYSTYRENE (EPS) RECYCLING: AN ENVIRONMENTALLY FRIENDLY PROCESS TO RECOVER DISSOLVED POLYSTYRENE (PS) USING WASTE COOKING SOYBEAN OIL


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ABSTRACT
The current work presents a simple method for recycling waste expanded polystyrene (EPS), using waste cooking soybean oil (WCSO). The process of polystyrene recovery combines dissolving of EPS in D-limonene with further separation and mixture with WCSO. The chemical, thermal, and morphological properties of the obtained material were characterized by the techniques; Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), X Ray diffraction (XRD), and Scanning Electron Microscopy (SEM). The characteristics of the recovered polystyrene presented high similarity with standard polystyrene (PS), which suggests low contamination by other materials. The great advantage of this recycling method is that it allows the obtention of PS in a solid state at room temperature, without the need for heat, in contrast to other reported EPS recycling methods. The results are promising and point to a viable and simple process of recycling EPS, which offers several environmental benefits.

KEYWORDS: Polymer waste valorization, Waste Management, Polystyrene.

RECICLAGEM DE POLIESTIRENO EXPANDIDO (EPS) RECYCLING: UM PROCESSO AMBIENTALMENTE FAVORÁVEL PARA A RECUPERAÇÃO DO POLIESTIRENO (PS) USANDO ÓLEO DE SOJA RESIDUAL

RESUMO
O presente trabalho apresenta um método simples para a reciclagem de resíduos de poliestireno expandido (EPS), utilizando óleo de soja residual (WCSO). O processo de recuperação de poliestireno combina a dissolução de EPS em D-limoneno com sua posterior separação e mistura com WCSO. As propriedades químicas, térmicas e morfológicas do material obtido foram caracterizadas pelas técnicas de Espectroscopia de Infravermelho com Transformada de Fourier (FTIR), Análise Termogravimétrica (TGA), Difração de Raios X (DRX) e Microscopia Eletrônica de Varredura (MEV). As características do poliestireno recuperado apresentaram alta similaridade com o poliestireno padrão (PS), o que sugere baixa contaminação por outros materiais. A grande vantagem deste método de reciclagem é que nos permite obter PS em estado sólido à temperatura ambiente, sem necessidade de aquecimento, ao contrário de outros métodos de reciclagem de EPS relatados. Os resultados são promissores e apontam para um processo viável e simples de reciclagem de EPS, oferecendo diversos benefícios ambientais.

Palavras chave: Valorização de resíduos poliméricos, Gestão de Resíduos, Poliestireno.
1 INTRODUCTION

Expanded polystyrene (EPS) is a polymer used worldwide, however, its extensive use has led to a disposal problem due to the high volume occupied and the time that it takes to decompose naturally. Based on this, recycling is always a viable alternative for correct management of waste produced by modern society (Lima et al., 2021). In fact, managing EPS waste involves certain difficulties; the low mass/volume ratio of EPS waste leads to a high cost of transport and storage, which discourages interest in recycling it. Landfill and incineration of EPS are the two most common methods to dispose of this waste material (Pol, 2010). However, landfills are high cost, and the incineration process has high-energy consumption and releases potentially toxic gases. Faced with this, alternative methods for recycling EPS waste are needed.

Several techniques to recycle EPS waste have already been proposed. For example, depolymerization, named chemical recycling, is based on EPS chemical decomposition to produce low molecular weight products (Manrich and Santos, 2009). This method can reduce the volume of plastic that ends up in landfills and produce high-quality raw materials, decreasing the demand for fossil fuels and other natural resources. Unfortunately, the chemical recycling process can produce large emission of greenhouse gases, which poses a climate risk (Brandrup, 2006). In mechanical recycling, polymer waste is mechanically crushed into granules that can be used to make new products. This method maintains the molecular structure, and is less energy intensive than chemical recycling, without using toxic chemicals. The main disadvantage of this method is that plastics are not infinitely recyclable mechanically (Brandrup, 2006). Energy recycling is when polymer waste is incinerated to produce heat, which is useful in various ways, such as in producing electricity. However, installing an incineration plant is an expensive process and the smoke produced during polymer incineration includes acid gases, carcinogenic dioxins, particulates, heavy metals, and nitrogen oxide (Brandrup, 2006). Additionally, EPS waste has commonly been recycled and added to other materials, such as: wood plastic composites made from post-used polystyrene foam (Koay et al., 2018); wood plastic composites made from post-used dissolved polystyrene packing (Agoua et al., 2013); wood plastic composites using recycled expanded polystyrene and wood flour (Poletto, 2011); the development of rice husk–plastic composites for building materials (Choi et al., 2006); composites made from cement dust and polystyrene waste that can be used as building construction materials (Asaad and Tawfik, 2011); crumbled recycled foam polystyrene waste that can be used to produce the filler in concrete (Laukautis et al., 2005); composite material for building of popular houses, based on Styrofoam (polystyrene) and gypsum (Macedo et al., 2011); use of expanded polystyrene waste in the creation of waterproofing paint (Bellon et al., 2019); recovery and incorporation of expanded polystyrene solid waste in lightweight concrete (Espinoza-Merchan et al., 2020); producing multi-strength grade lightweight concrete containing expanded polyethylene beads (Sadrromtazi et al., 2012); and a polystyrene/concrete composite as a structural thermal insulating material (Makhmud and Alexander, 2017). However, none of these materials are widely used, mainly because they are not economically profitable.

In order to make the recycling process more attractive, EPS waste has been dissolved by organic solvents to reduce its volume, saving transport and storage costs. Widely used solvents include: ethanol (Bellon et al., 2019); limonene (Garcia et al., 2009; Gutiérrez et al., 2012; Gutiérrez
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Unfortunately, most of these processes are environmentally harmful because the most commonly used solvents are toxic, such as toluene, acetone, ethyl acetate, benzene, chloroform, and cyclohexane (Yi-Bo Zhao et al., 2018; Bellon et al., 2019). In contrast, dissolution processes using natural and nontoxic solvents are often reported (Garcia et al., 2009; Bellon et al., 2019; Jimenez-Francisco et al., 2020). One of them, D-limonene (hydrocarbon classed as a terpene) has been reported as an attractive natural solvent for waste EPS dissolution (Garcia et al., 2009; Bellon et al., 2019; Jimenez-Francisco et al., 2020). This solvent is an essential oil, obtained from orange or lemon peel as a byproduct of juice manufacture. D-Limonene is generally recognized as a non-toxic substance, and some advantages of its use to dissolve EPS waste include: (i) This process does not produce any degradation of polymeric chains (Gil-Jasso et al., 2019); (ii) After the dissolution process, the polystyrene can be recovered (Gutiérrez et al., 2012; Gutiérrez et al., 2014; Gil-Jasso et al., 2019); and (iii) The solvent can also be recovered and reused to dissolve a new waste EPS batch (Gil-Jasso et al., 2019). Based on these factors, the process of dissolving EPS in D-limonene has been used as a primary step in polymer recycling. The current work is an example of how dissolved EPS and waste cooking soybean oil (WCSO), when combined, give rise to a new material that can be used in several applications. Sarmiento et al. also show that expanded polystyrene and waste cooking oil can be used to produce recycled EPS with potential use as a construction material (Sarmiento et al., 2016).

In particular, soybean oil is an important commercial product, representing approximately 30% of the total vegetable oils produced in the world, and it is currently used for the preparation of food (Gunstone, 2002). In this context, waste cooking soybean oil (WCSO) refers to an oil which has been used for frying and can no longer be used for the same purposes. The incorrect disposal of WCSO can cause several environmental problems (Gunstone, 2002). When WCSO is discharged directly in water tributaries, it can form a superficial layer of oil that reduces oxygen diffusion into the water source, causing damages to aquatic ecosystems. It is well known that only 1 L of oil can contaminate 1000 L of drinking water, and for this reason, applications that include the use of this waste are welcomed to minimize WCSO pollution.

Corroborating with the aforementioned, the current work stems from the idea that the environmental problems caused by the incorrect disposal of EPS and WCSO can be mitigated when both are recycled and combined to recover polystyrene (PS).

2 MATERIALS AND METHODS

In this study, commercial waste from EPS packaging was used. The raw material was crushed into small pellets in order to produce a homogeneous material (the average particle size was approximately 4 mm). The solvent D-limonene, 99% purity, was purchased from a local store, Óleos Essenciais ®, and used without further purification.
For dissolution experiments, 50 ml of D-limonene and 15 g of EPS were placed in a beaker, and then the mixture was shaken (~15 minutes) until its complete dissolution. This proportion (EPS/D-limonene) was determined in preliminary dissolution experiments. All experiments were carried out at room temperature. After the complete dissolution, the mixture was carefully transferred to a separating funnel where the dissolved polystyrene was separated from the D-limonene, after allowing the mixture to precipitate overnight. Thereafter, the lower layer (D-limonene) was drained out, and the paste (upper layer - polystyrene) was combined with waste cooking soybean oil (WCSO) to produce a solid polymeric material.

Waste cooking soybean oil was collected from households and street vendors located in Uberaba City, Brazil. After collection, the WCSO was only filtered through filter paper (Whatman 41 sized 20-25 micron) to remove bits of food residues. The polystyrene was recovered simply by mixing equal volumes of reagents (dissolved polystyrene and WCSO) at room temperature. After agitating for one minute, a solid precipitated. Finally, this solid was squeezed between layers of hand paper towels, to remove the maximum excess oil, and left to dry at room temperature.

The chemical, thermal, and morphological properties of the obtained material, were characterized by the techniques: Fourier Transform Infrared Spectroscopy (FTIR, Cary 660 by Agilent Instruments), Thermogravimetric Analysis (TGA), X-Ray diffraction with Cu Kα radiation with steps of 1 degree (Theta)/min (Shimadzu model 6100), and Scanning Electron Microscopy using the backscattered electron mode (SEM, model LEO 1450VP).

3 RESULTS AND DISCUSSION

![Figure 1: a) Dissolution of EPS at room temperature by D-limonene, b) Layer separation in dissolved polystyrene and D-limonene, after 48 h, c) FTIR spectra of the dissolved polystyrene and, c) FTIR spectra of the D-limonene.](image-url)
As mentioned previously, dissolution assays were carried out in a beaker, where crushed waste EPS was immersed in D-limonene at room temperature, see figure 1(a). Figure 1(b) shows the separation process between dissolved polystyrene (upper layer) and D-limonene (lower layer), after 48h. This procedure allowed the recovery of both D-limonene, which was drained out, and the dissolved polystyrene. All components resulting from the separation were analyzed using FTIR spectroscopy (Fig. 1(c): Polystyrene and Fig. 1(d): D-limonene).

Figure 1(c) shows the infrared absorption spectra of the dissolved polystyrene. There are several absorption peaks within the involved wavenumber range, similar to those previously reported for standard polystyrene (Al-Kadhemy et al., 2016; Vardhan and Shukla, 2018). The peak at 3082 cm\(^{-1}\) corresponds to C–H stretching vibrations of ring hydrogen. The absorption bands around 2800 and 3000 are due to C-H stretch aliphatic vibrations. Specifically, the peak at 2854 cm\(^{-1}\) corresponds to an aromatic C–H. The absorption at 1643 cm\(^{-1}\) is related to C=C stretching. The two peaks at 1492 and 1600 cm\(^{-1}\) are assigned to aromatic C=C stretching. In the region from 1300 to 1380 cm\(^{-1}\), the peak observed at 1376 cm\(^{-1}\) corresponds to aromatic CH\(_2\) bending. In addition, the peaks located around 650 to 1250 cm\(^{-1}\) correspond to C–H deformation.

Figure 1(d) shows the infrared absorption spectra of the recovered D-limonene, which is similar to the spectrum for the raw D-limonene, before the dissolution process. The broad absorption band at approximately 3300 cm\(^{-1}\) is related to hydroxyl group stretching. The intense absorptions that appear around 3000–2850 cm\(^{-1}\) are attributed to the C–H, methylene bond, vibration. The peak at 1645 cm\(^{-1}\) is related to the stretching of the double bonds, C=C, which is present in the endocyclic and exocyclic positions of the D-limonene structure. The peaks between 1480–1350 cm\(^{-1}\) are associated with the deformation of the C–H bond belonging to the alkyl groups. The peak at 1050 cm\(^{-1}\) is attributed to the bending of =C–H bonds, and at 887 cm\(^{-1}\) is attributed to =C–H. In the region between 3200 and 3500 cm\(^{-1}\), the broadening peak is attributed to O–H vibration, probably due to water in the D-limonene solution. It is important to mention that, based on our experiments and previous reports (Gil-Jasso et al., 2019), the recovered D-limonene can be used again in other dissolution processes, with the same efficiency as the raw D-limonene.

When dissolved polystyrene and WCSO are mixed, in equal proportions of volume, a polymer solid is precipitated. The mass agglomerated at the bottom of the beaker was easily removed and cleaned. Figure 2 illustrates the reaction sequence, showing the light amber colored polymer mass and the reaction residue material. Sarmiento and co-workers also used waste cooking oil for recycling EPS. However, in that study, the oil was used as a solvent, with the EPS dissolved at 165°C, and then recovered (Sarmiento et al., 2016). Contrary to this, the current work presents a process carried out at room temperature. In this context, recycling dissolved EPS with WCSO may reduce the energy requirement and is cost-effective.

After the precipitation of PS (Figure 1), it is in the paste form because a small amount of D-limonene continues to dissolve PS agglomerates. When this mixture is placed in contact with WCSO, it is dissolved by the residual D-limonene, releasing the PS, which becomes a solid aggregate. Therefore, the WCSO acts as an antisolvent when it is added to the D-limonene/PS mixture. We observed that the D-limonene exhibits an acceptable solubility in WSCO at moderate working conditions, while solid PS is generally insoluble in WSCO. Thus, the addition of frying soybean oil induces the supersaturation and precipitation of the polymer due to the dissolution of
limonene in WSCO. In fact, its use for polymer phase separation has been extensively reported in the literature, especially using carbon dioxide as a non-solvent, and numerous techniques have been developed in recent years (Campardelli et al., 2014; Gutiérrez et al., 2016). Based on this, WCSO stands out as a potential material to be used as a liquid antisolvent in other polymer production processes.

Figure 2: Schematic representation of the PS recovery, showing the light amber colored polymer mass and the reaction residue or unreacted material.

To confirm the composition of the recycled polymer and the residue, Fourier transform infrared spectroscopy measurements were performed (Fig. 3). The FTIR spectrum for the recovered polymer, figure 3(a), is identical to that shown in Figure 2(c), indicating that the product is polystyrene. An extra peak can be observed at approximately 1745 cm\(^{-1}\) (see the red arrow) which is related to the polymerization residue contamination. Contamination is basically a mixture with a small fraction of dissolved D-limonene. There is approximately 2.0 %w of superficial WCSO+D-limonene in the final material. Contamination can be removed by simply squeezing the material between sheets of paper. These results indicate that the final polymer can be further applied, as there is no significant surface fat content. However, to do so, it is necessary to measure several properties in the final PS, such as mechanical, chemical, and physical properties. As expected, the FTIR spectrum illustrated in Figure 3(b) is quite similar to that reported for the waste cooking soybean oil (WCSO) (Laskar et al., 2018; Rafati et al., 2018). The absorption peaks at 2921, 2854, 1745, and 1155 cm\(^{-1}\) are due to triglycerides, which are basic components in cooking oils (Laskar et al., 2018; Rafati et al., 2018). The absorptions at 2921 and 2854 cm\(^{-1}\) are related to asymmetrical stretching vibrations of C-H and the absorptions at 1745, and 1155 cm\(^{-1}\) are due to C=O bond stretching and -CH\(_2\)-, respectively. As can be seen, this spectrum contains a significant number of peaks, mainly in the region between 1750 and 700 cm\(^{-1}\). For better understanding, the functional groups and modes of vibration associated with the absorptions are illustrated in Fig 3(b) (Laskar et al., 2018; Rafati et al., 2018). In figure 2, it is possible to observe that the soybean oil changed color after the polymer solidification process, which suggests oil oxidation during this process (Komoda et al., 1966).
Focusing on the polymeric material, Figure 4 presents the X-ray diffraction (XRD) for the recovered EPS. The XRD pattern shows a prominent peak observed at 2θ = 19.65°, suggesting that the polystyrene has certain crystallinity (JunFei et al., 2010; Wankasi and Dikio, 2014). The recovered polystyrene has a rough surface, as shown by the SEM image in the inset of Figure 4. This surface morphology could be a feature of non-controlled solidification processes. It is well known that when a polymer solidifies, it may retain an amorphous structure, crystallize completely, or become semi crystalline.

Figure 5 presents the TGA curves of recovered EPS. Recovered EPS shows an inflection close to 163° C (T_i); this temperature corresponds to initial weight loss (volatiles components loss). Furthermore, it shows a decomposition temperature at 50% weight loss ~ 412° C (related to degradation of PS chains). Finally, recovered EPS shows maximum decomposition temperatures (\text{\textit{T}}_{\text{max}}) ~ 576° C (total degradation). The weight loss before T_i is due to the residual decomposition. The incomplete degradation of the solid PS after ~ 450° C suggests the existence of impurities, probably WCSO impurities arising from the frying processes.
The results, shown in this section, demonstrate that it is possible to recover PS from waste EPS, however, further works are necessary to define the properties and applications of the recycled polymer. Additionally, WCSO stands out as a potential material to be used as a liquid antisolvent in other polymer production processes.
4 CONCLUSION

The current work stems from the idea that waste expanded polystyrene can dissolve in D-limonene and recovered using waste cooking soybean oil (WCSO), to produces a new polystyrene-based product. The obtained polymer was soft and malleable, making it a possible candidate as a renewable additive in diverse applications. Additionally, solvent recovery was carried out to make the process more sustainable. The environmentally friendly process, performed entirely at room temperature, opens a new sustainable and green approach toward the recycling and recovery of polystyrene waste. Avoiding any heating step, which can be high cost, this process meets the financial challenges inherent in any industry applications.

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