

## Methods of Recycling Expanded Polystyrene Waste: Synthesis and Characterization

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This work reports the recycling of waste polystyrene that was expanded by homogeneous sulfonation reactions using different methods. The obtained sulfonates polystyrenes (PSS) were identified using various techniques such as FTIR spectrometry, Thermogravimetric Analysis (TGA), and X-ray diffraction (XRD). The FTIR spectrometry showed the appearance of the S-O band at  $1050\text{ cm}^{-1}$  and S=O at  $1180\text{ cm}^{-1}$  of the sulfur trioxide, which confirmed the polystyrene's modification. It is important to note that great thermal stability happened for the material which was modified at  $T = 445\text{ }^{\circ}\text{C}$ , compared with the starting one at  $T = 400\text{ }^{\circ}\text{C}$ . In addition, the average macromolecular masses (Mv) were obtained by viscosity. The polymer exhibited polyelectrolyte behavior. The results showed an increase up to 69% in the degree of sulfonation due to the essentially higher time, besides a positive correlation between the degree and the color during synthesis. This outcome ultimately indicated a high percentage of changing benzene rings and the results were confirmed by the potentiometric dosage method.

**Keywords:** Recycling, Sulfonation, FTIR spectroscopy, Thermal stability, Degree of sulfonation

### INTRODUCTION

Expandable polystyrene (EPS) is a durable material. It contains a better thermal insulation effect and light insulation which can be used in Photoactivity [1]. However, it is characterized by low fire resistance and low bending strength. EPS is applied in many construction projects for thermal insulation and especially for the soundproofing of new buildings, modernization or renovation works, and the insulation of walls, roofs, floors, and ceilings [2].

The large annual production of this material causes a large waste problem that cannot be solved through landfilling or incineration, as appropriate and secure stockpiling is not affordable, particularly in developing regions of the world [3]. In addition, burning produces greenhouse effects such as NO<sub>x</sub> and CO<sub>x</sub> causing environmental changes [3]. Various researchers [4] have employed chemical recycling of WPS to their corresponding monomers or hydrocarbons. The

procedure is not effective due to the lower price of virgin hydrocarbons and monomers in comparison to those extracted from recycling; therefore, it is necessary to develop functional techniques to recycle WPS.

Polystyrene recycling is well-established in many countries, however, the use of recycled polystyrene in applications for foodstuffs is restricted [5,6].

Direct recycling involves the creation of specific products for WPS such as pyrolysis [7] to produce oil [8] or as ethanolsis to produce liquid fuel [9] and catalytic breaking to create fuels and volatile gases [10,11], styrene monomers and exchange ion resins [10]. Whereas indirect recycling implies the alteration of SPW to produce new compounds such as synthetic dyes, paints [12,13], hydrocarbon oils, and gases [14].

The modification of the polymer chain with acidic sulfonic groups (-SO<sub>3</sub>H) results in a polyelectrolyte called sulfonated polystyrene (PSS), which can be used in a wide range of applications [15], such as biocompatible electrodes [16,17], material for the absorption of drugs and heavy metals

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[18-20], moisture humidity material [21], photovoltaic system components [22,23], exchange membranes ion [24-27], flocculation materials for water treatment [28-30], Photocatalytic Activity [31] and bioanalytical [32].

The modification of the materials concludes changes in the polymer properties, usually solubility and thermal stability are the most studied [33]. Polymers dissolve, disperse, or swell when in contact with water, changing the properties of water systems. Generally, they contain hydrophilic groups in their structure, they can be non-ionic, anionic, cationic, or amphoteric. The purpose of this type of polymer is to increase the viscosity of aqueous solutions [33], allowing a wide range of industrial applications. The temperature has a great effect on the stability of water-soluble polymers, and heating causes physical and chemical changes in the properties of polymers [33].

This work reports the recycling of waste polystyrene that was expanded by homogeneous sulfonation reactions using different methods. The obtained sulfonates polystyrenes (PSS) were identified using various techniques such as FTIR spectrometry, Thermogravimetric Analysis (TGA), and X-ray diffraction (XRD). Eventually, the viscometric average macromolecular masses of copolymers were determined.

## EXPERIMENTAL

### Materials

Expanded polystyrene waste recovered from household appliance packaging (WPS). Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 97%, Fluka, Germany), acetic anhydride ((CH<sub>3</sub>CO)<sub>2</sub>O, 98%, Sigma-Aldrich, USA and silver sulfate Ag<sub>2</sub>SO<sub>4</sub>, 99%, Biochem, USA) to obtain reaction sulfonating agent, Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>, 99%, Biochem, USA) and distilled water as a solvent.

## METHODS

### 1<sup>st</sup> Method

The modification was performed in a flask at solvent boiling temperature when WPS (5 g) was dissolved in dichloromethane. The mixture was stirred for 15 min, then sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) (3 ml) was added as a sulfonating agent [34] (Fig. 1). The reaction occurred at different temperatures (Table 1). Then, the obtained copolymer was precipitated and

washed in distilled water. The product was dried under a vacuum at 60 °C and stored in a desiccator.

### 2<sup>nd</sup> Method

The sulfonation procedure is compatible with the description of Holbook *et al.* [35]. As it is schematically shown in Fig. 1. The description briefly goes as follows: in an Erlenmeyer flask, a quantity of 5 g of expanded polystyrene was dissolved in 20 ml of sulfuric acid and then 0.02 g of silver sulfate was added as a catalyst. The solution was heated to 90 °C at different times, then precipitated in dilute sulfuric acid, washed with distilled water, and dried in the oven.

### 3<sup>rd</sup> Method

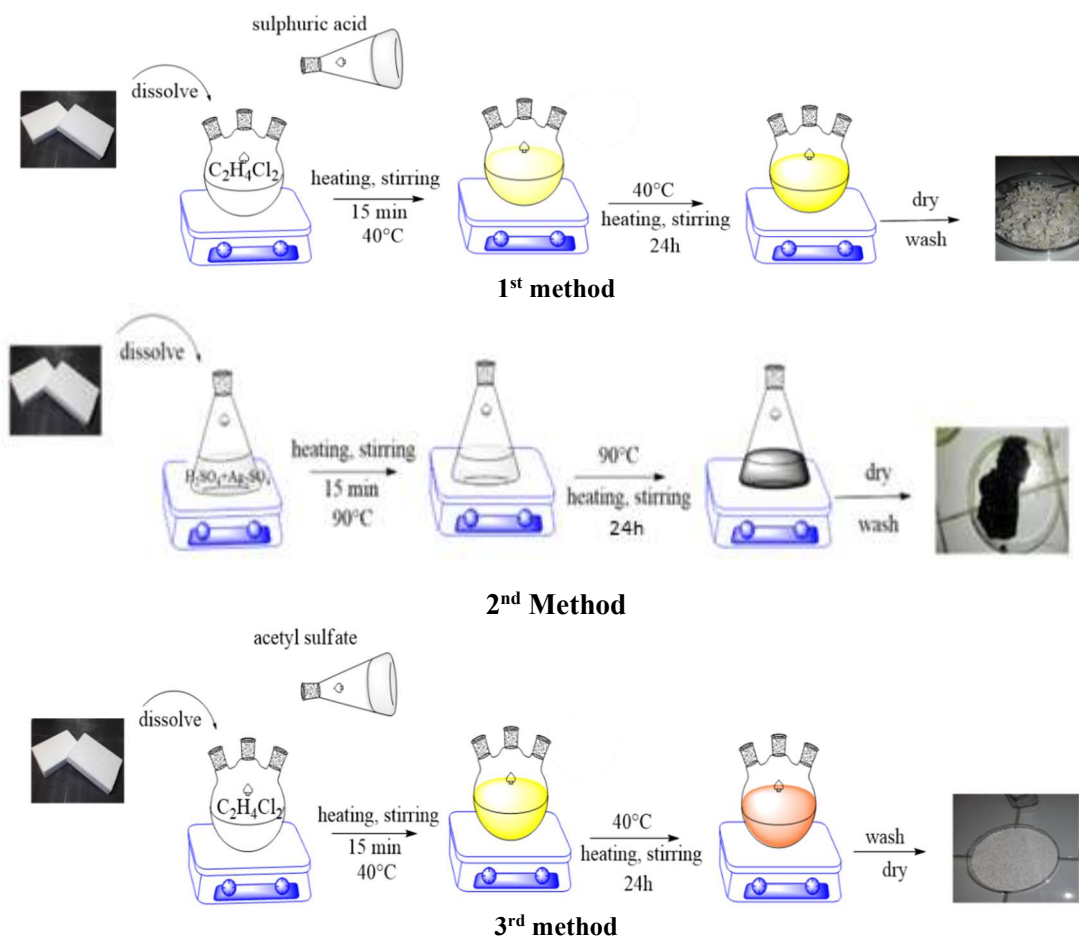
The WPS (5 g) was melted into the dichloromethane in a volumetric flask with magnetic stirring. The solution of acetyl sulfate (A mixture that contains acetic anhydride and dichloromethane and is put in an ice bath (4 °C) [36] with H<sub>2</sub>SO<sub>4</sub> (3 ml) slowly added to the solution.) was stirred for 10 minutes and then added slowly, drop by drop. The whole mixture was then heated in a thermostat bath to the solvent reflux temperature (around 40 °C) (Fig. 1). After the specified time in Table 1, the process was stopped.

In this article, the copolymers are noted [PSS/method number/h] knowing that PSS is polystyrene sulfonated, method number between 01 and 03, and for an hour between 2 and 24 h. The sulfonation degree (DS) was identified as the molar proportion of sulfonated styrene units. The DS was determined by titration: 0.4 g of sulfonated polystyrene which was dissolved in one of two solvents (water or dichloromethane). The change in the degree of sulfonation for PSS results from a change in a solvent. The mixture has been titrated by the phenolphthalein endpoint using sodium hydroxide.

The following law is applied [37]:

$$DS = \frac{[0.104M(\text{NaOH}) \times V(\text{NaOH})]}{[W - 0.081M(\text{NaOH}) \times V(\text{NaOH})]} * 100 \quad (1)$$

Where M and V: are the molarity and the added volume of NaOH respectively; W: is the mass of the sample; 104: repetition of molar mass of the PS unit and 81: molar mass of the sulfonic group.



**Fig. 1.** Schematic of the preparations.

**Table 1.** Presents the Solubility and the Degree of Sulfonation of the Samples (X: Soluble in Solvent)

Methods	Samples	Reaction time (h)	DS (%)	Conversion rate (%)	Solubility		
					Water	Dichloromethane	Hydrochloric acid
01	PSS/01/2h	2	5	42		X	X
	PSS/01/4h	4	7	46		X	X
	PSS/01/6h	6	16	50		X	X
	PSS/01/12h	12	21	42		X	X
	PSS/01/24h	24	25	49		X	X
02	PSS/02/2h	2	40	71	X		
	PSS/02/4h	4	42	70	X		
	PSS/02/6h	6	53	76	X		
	PSS/02/12h	12	59	76	X		
	PSS/02/24h	24	66	77	X		
03	PSS/03/2h	2	10	45		X	X
	PSS/03/4h	4	13	46		X	X
	PSS/03/6h	6	20	51		X	X
	PSS/03/12h	12	46	53	X		
	PSS/03/24h	24	69	53	X		

The solubility study was made using 0.1 g PSS in 5 ml of different solvents such as dichloromethane, acid, and distilled water. When the PSS was added, this mixture was stirred magnetically for 25 min.

### Characterization of Sulfonated Polystyrene

The viscometric molar mass was obtained with the Ubbelohde-Schott Gerate AVS400 (Mainz, Germany). Measurements were made at 25 °C in a thermostatic bath in water using the equation of Mark-Howink:

$$[\eta] = KM_v^\alpha \quad (2)$$

Where  $\alpha = 0.741$  and  $k = 41,6 \times 10^{-4} \text{ ml g}^{-1}$  are Mark-Howink parameters [38]

The FTIR spectra were registered using an Agilent Technologies FTIR spectrometer Cary 600 Series. PS and PSS samples were measured in powder form. FTIR analysis was applied to provide qualitative information on the Sulfur trioxide groups.

The thermal stability of the samples was examined by thermogravimetry TA-Q600 (DSC/ATG). Thermal analyzer from 50 °C to 650 °C (heating rate of 10 °C min<sup>-1</sup>) in air and under a pressure of 1 bar with approximately 7 mg of sample.

X-ray diffraction analysis were performed utilizing a Rikagu ultima IV (BD64000266-01) and Pb CBO selections list. The diffractometer was operated at 40 mA and 40 kV with a 2 $\theta$  sweep between 5° and 70° and a speed of 10° min<sup>-1</sup>.

## RESULTS AND DISCUSSION

### Change Rate and Solubility

The solubility of the sulfonated polymer was used to assess if the products of the reaction had various degrees of sulfonation, and from the results obtained, it is noticed that all the samples of the 1<sup>st</sup> method are soluble in dichloromethane and acids and not soluble in water, in opposition to the second method (all the products are soluble in water and insoluble in dichloromethane and acid). The solubility in the 3<sup>rd</sup> method is different. In the first 3 cases, the products are soluble in dichloromethane and acid and insoluble in water. The last 2 cases show the opposite (insoluble in dichloromethane and acid and soluble in water).

From there, it is deduced that the degree of sulfonation is different in the samples and Table 1 confirms this result. The increase in the rate of modification results in a fast solubility in the water thanks to the charges carrying this polymer and this result is also granted by Andrade *et al.* [7].

Figure 2 represents the time of each test and its degree of sulfonation. It is observed that the degree of sulfonation increases with time and consequently the color of the reaction becomes very dark (Fig. 1). The maximum value obtained is 25% for the 1<sup>st</sup> method, 66% for the 2<sup>nd</sup>, and 69% for the 3<sup>rd</sup> method. As the process proceeds, sulfonic groups are inserted into the polystyrene. Figure 3a represents the reaction mechanism of the modification with H<sub>2</sub>SO<sub>4</sub> alone in the first method, with the presence of silver sulfate in the 2<sup>nd</sup> method and acetyl sulfate in the 3<sup>rd</sup> method. However, these reagents (Ag<sub>2</sub>SO<sub>4</sub> and (CH<sub>3</sub>CO)<sub>2</sub>O) promote the insertion of sulfonate groups into the polystyrene chain until the majority of the aromatic rings are modified, and to avoid the appearance of S-S bonds that block the modification (Fig. 3b), as was the case in the 1<sup>st</sup> method which gave us a low rate of modification for PSS/01/24h.

### Viscometric Mass

From the Mark-Howink Eq. (2) the viscometric average macromolecular mass was determined (Table 2) using salt in reduced viscosity variation. We observe a linear variation of the latter as a function of the concentration because, in the

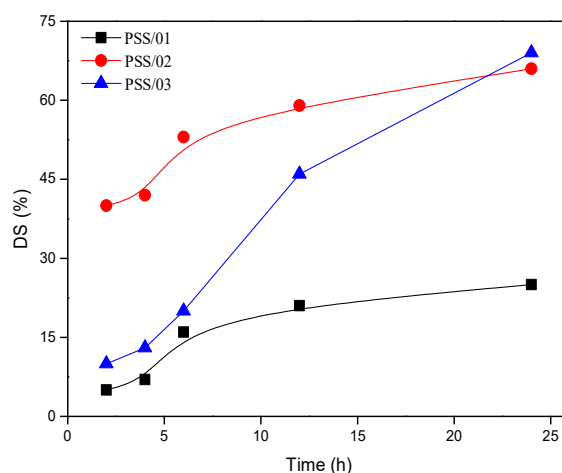
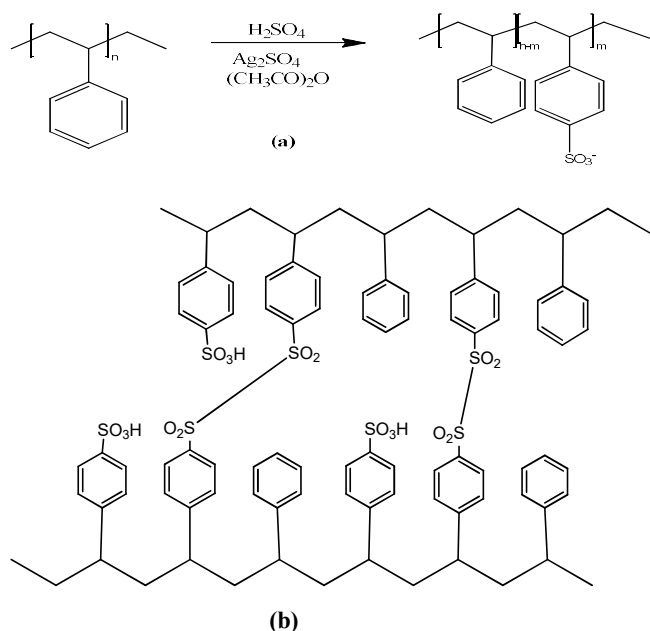


Fig. 2. Variation of sulfonation rate *versus* time.



**Fig. 3.** (a) Mechanism of reaction and (b) Structure of PSS/01/24h.

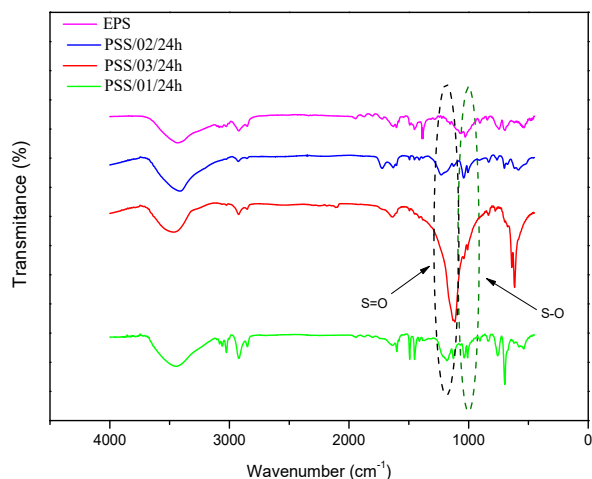
**Table 2.** Presents the Viscometric Mass of the Samples

Samples viscometric mass	
PSS/03/24h	153690 g mol <sup>-1</sup>
PSS/02/24h	319692 g mol <sup>-1</sup>
PSS/03/12h	134525 g mol <sup>-1</sup>
PSS/02/12h	251473 g mol <sup>-1</sup>

absence of salt, it increases with the decrease in the polymer concentration. After all, the electrostatic repulsion makes this polymer chain very extended [39]. In addition, this polymer exhibits polyelectrolyte behavior.

### FT-IR Characterization

All three methods were successfully sulfonated. FTIR examination of the PSS (Fig. 4) indicated the appearance of bands for S-O which were not found in the spectra of the polystyrene waste. The presence of an S-O band of stretching vibration symmetric at 1050 cm<sup>-1</sup> and stretching vibration antisymmetric S=O at 1180 cm<sup>-1</sup> [34] suggests the existence of bound Sulfur trioxide groups in each sample. The band linked to benzene para-substituted (840 cm<sup>-1</sup>) confirms the



**Fig. 4.** Infrared spectra of EPS, PSS/01/24, PSS/02/24h and PSS/03/24h.

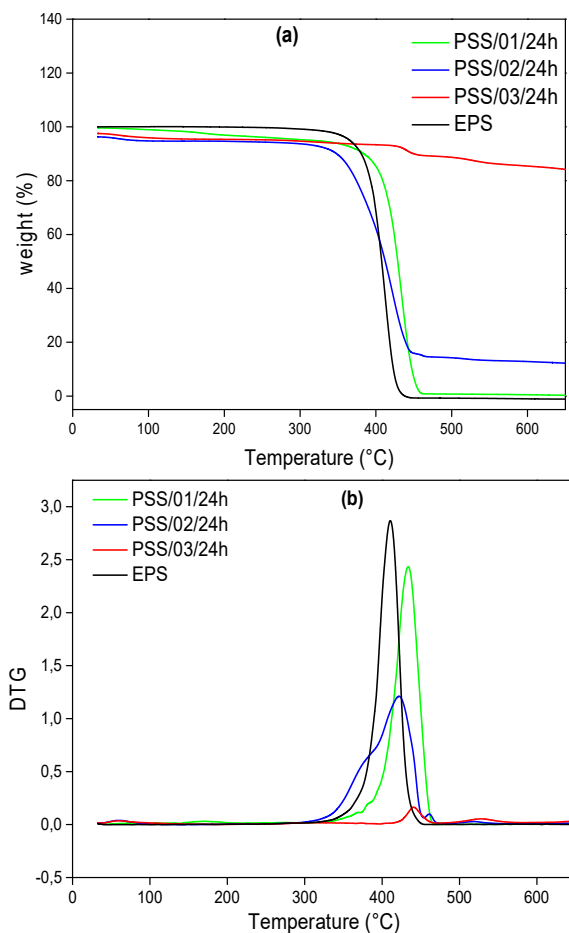
substitution of the aromatic cycle.

### Thermal Properties

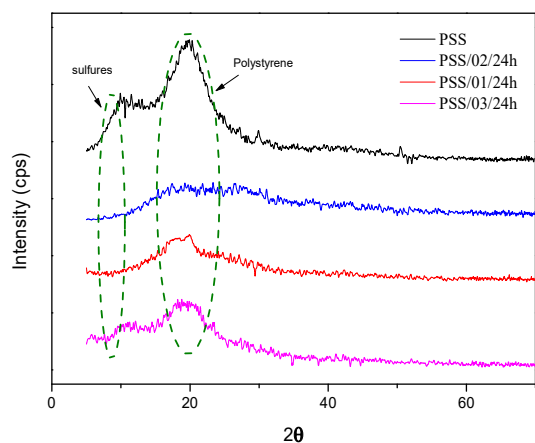
All samples were examined for thermal stability by TGA. This study indicates that an increase in thermal stability is observed for sulfonated polystyrenes depending on the concentration of sulfonic groups, in comparison to WPS (Fig. 5a), with the onset of weight loss at 400 °C. The PS shows a process of weight loss with its onset at around 350 °C. In Fig. 5b, the one-step degradation process for PS-SO<sub>3</sub>H, with degradation temperature is better visualized in the range of 400, 433, 422, and 444 °C for WPS, PSS/01/24h, PSS/02/24h, and PSS/03/24h successively.

### XDR Characterization

Figure 6 represents the results obtained by X-ray diffraction for different samples, showing that WPS and PSS are essentially amorphous. The XDR pattern of PS shows some wide bands between the characteristic peaks of polystyrene, 2θ = 15-20.44°. On the other hand, PSS X-ray diffraction analysis shows a small peak between 2θ = 8-15° which is associated with the existence of sulfurs. This crystallinity degree was observed in the PSS pattern because of the diffraction from the association of sulfonated polystyrene chains [40].



**Fig. 5.** (a) Thermogravimetric and (b) DTG curves of samples WPS, PSS/01/24h, PSS/02/24h, PSS/03/24h.



**Fig. 6.** X-ray diffraction patterns of EPS, PSS/01/24h, PSS/02/24h, PSS/03/24h.

## CONCLUSION

The sulfonation of waste-expanded polystyrene by three methods and different degrees of sulfonation were studied. The structure and composition of obtained copolymers PSS/01, PSS/02, and PSS/03, were characterized by FTIR spectrometry, Thermogravimetric Analysis (TGA), and X-ray diffraction (XRD). The FTIR spectrometry shows the characteristic bands of sulfur trioxide, which confirms the modification. The thermogravimetry result indicates the high thermal stability of obtained copolymers compared to the starting material. The molecular weights were obtained by viscosity, and a polyelectrolyte behavior was observed.

Furthermore, the calculated high degree of sulfonation of our copolymers was found equal to 25%, 66%, and 69% respectively due to the different modifying reagents added. The time of reaction was also the parameter that affected the final quantity of sulfonate groups which were effectively bound to the polystyrene chain. In addition, other properties like solubility and thermal stability were observed (the main goal of this work).

## Abbreviations

PS: Polystyrene  
 EPS: Expandable polystyrene  
 DTG: Differential thermogravimetric  
 XRD: X-ray diffraction  
 WPS: Expanded polystyrene waste  
 DS: Sulfonation degree  
 PSS: Sulfonate polystyrene  
 Mv: Viscometric molar mass  
 FTIR: Fourier transform infrared spectroscopy  
 DSC: Differential scanning calorimetry  
 TGA: Thermogravimetric Analysis  
 SO<sub>3</sub>H: Sulfur trioxide group

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