



Improving the Properties of Waste Polystyrene Foam via Heterogeneous Sulfonation: A Sustainable Method for Oil/Water Separation Applications

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Keywords:

Sulfonated Polystyrene.
Environmental Sustainability.
Sulfonation Reactions.
Oil/water Separation.
Plastic Waste.

ABSTRACT

The heterogeneous sulfonation process was used to modify waste polystyrene foam by introducing sulfonate groups to the benzene ring to enhance its hydrophilicity and thermal stability. This process was carried out using concentrated sulfuric acid at different temperatures. The sulfonation of PS was confirmed using FTIR spectrophotometry. The degree of sulfonation (DS) and cation-exchange capacity (CEC) were quantitatively assessed, and the result shows that sulfonated polystyrene PSS synthesized at 40°C exhibited the highest DS and CEC of 20.11%. 0.43 meq/g, respectively. Sulfonated polystyrene (PSS) samples were also analyzed by contact angle measurement and thermogravimetric analysis (TGA). The results indicate that sulfonated polystyrene (PSS) has increased wettability, surface polarity, and higher thermal stability compared to pure polystyrene (PS). The use of sulfonated polystyrene (PSS) in applying oil/water separation as membranes shows promising results, exhibiting high separation efficiency and water flux. These results highlight the importance of transforming plastic waste through sulfonation as an effective and sustainable approach to reducing waste and converting waste into valuable materials.

تحسين خصائص مخلفات رغوة البوليسترين المهدمة عبر السلفنة غير المتجانسة: طريقة مستدامة لتطبيقات فصل الزيت عن الماء

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الكلمات المفتاحية:

البوليسترين المُسلفن.
الاستدامة البيئية.
تفاعلات السلفنة.
فصل الزيت عن الماء.
نفايات البلاستيك.

الملخص

استُخدمت عملية السلفنة غير المتجانسة لتحويل مخلفات رغوة البوليسترين المهدمة، وذلك بإضافة مجموعات سلفونات إلى حلقة البيزن لتعزيز قابليتها للماء واستقرارها الحراري. أُجريت هذه العملية باستخدام حمض الكبريتيك المُركز عند درجات حرارة مختلفة. وتم تأكيد سلفنة البوليسترين باستخدام مطيافية الأشعة تحت الحمراء فورييه (FTIR). وُقيمت درجة السلفنة (DS) وسعة تبادل الكاتيوني (CEC)، وأظهرت النتيجة أن البوليسترين المُصنّع عند درجة حرارة 40 درجة مئوية أظهر أعلى درجة سلفنة وسعة تبادل كاتيون بنسبة 20.11 % على التوالي. كما حُللت عينات البوليسترين المُسلفن (PSS) باستخدام قياس زاوية التلامس والتحليل الوزني الحراري (TGA). وتشير النتائج إلى أن البوليسترين المُسلفن (PSS) يتميز بقابلية بلل أعلى، وقطبية سطحية أعلى، واستقرار حراري أعلى مقارنةً بالبوليسترين النقي (PS). يُظهر استخدام

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البوليسترين المُسلفن (PSS) في فصل الزيت عن الماء كأغشية نتائج واعدة، إذ يتميز بكفاءة فصل عالية وتدفق

مائي ممتاز. تُبرز هذه النتائج أهمية تحويل النفايات البلاستيكية عبر السلفنة كنجز فعال ومستدام للحد من

النفايات وتحويلها إلى مواد قيمة.

1. Introduction

Global plastic production and disposal have reached unprecedented levels, with more than 400 million tons of plastic produced annually, much of which ends up in landfills or is incinerated, contributing to serious environmental pollution. [1]. Among these plastics, polystyrene is widely used in packaging, food containers, and insulation. However, its non-biodegradable nature and resistance to photodegradation [2, 3]. Accumulation of polystyrene waste in landfills or burning it poses significant environmental and health risks. [4, 5].

One promising approach to dealing with polystyrene waste is the chemical modification of polystyrene through sulfonation, a process of introducing sulfonate groups (-SO₃H) into the polystyrene chain. Sulfonated polystyrene exhibits unique properties, such as increased hydrophilicity, ion exchange capacity, and thermal stability, making it suitable for a wide range of applications, including water treatment, catalysis, and proton exchange membranes [6]. It has been shown that using concentrated sulfuric acid (98%) with a reaction time of 10 minutes at 80°C effectively sulfonates polystyrene, achieving a calcium removal efficiency of 94.5% and a heavy metal removal efficiency of more than 95% for Zn²⁺, Cd²⁺ and Cu²⁺ [7].

The potential applications of PSS were explored, particularly in

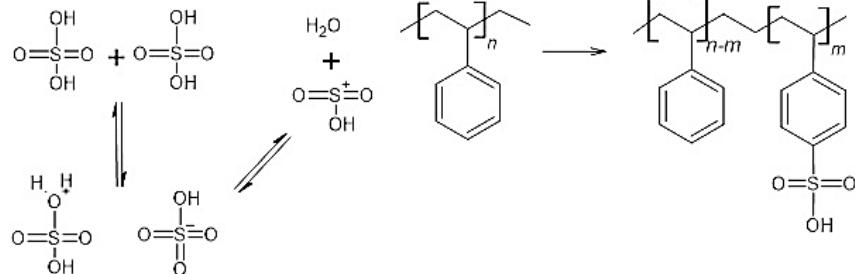


Fig. 1: PS sulfonation reaction using a heterogeneous method. [12]

This study focuses on the synthesis, characterization, and application of PSS derived from waste foam packaging. The results of this study highlight the potential of sulfonation as a sustainable and efficient method for transforming polystyrene waste into higher-value products, contributing to the circular economy and reducing the environmental impact of plastic pollution.

2. Materials and Methods

2.1 Materials

Polystyrene foam waste from packaging boxes, with a molecular weight of 3.4×10^4 g/mol, was calculated by measuring viscosity. Acetic anhydride from Eurosar Scientific Ltd. Sulfuric acid from Riedel-deHaen. 1,2-dichloroethane from Eurosar Scientific Ltd. Ethylenediaminetetraacetic acid (EDTA) from BDH Chemicals. Ammonium chloride (NH₄Cl) from Riedel-de Haen.

2.2 Synthesis of PS Sulfonate

Waste PS foam was crushed into small pieces, washed with distilled water, and dried at 60°C. PSS was synthesized through the heterogeneous method, using concentrated sulfuric acid at varying temperatures (room temperature, 40°C, and 60°C) for 24 hours. A grounded 0.5 g of polystyrene foam waste was mixed with 60 ml of concentrated sulfuric acid in a 250 ml round-bottom flask containing a stirring bar. The flask was immersed in a silicon oil bath; the reaction took place at three different temperatures. The polymer was separated by filtration and washed with distilled water several times to remove the remaining sulfuric acid, then the polymer was dried in an oven at 60 °C.

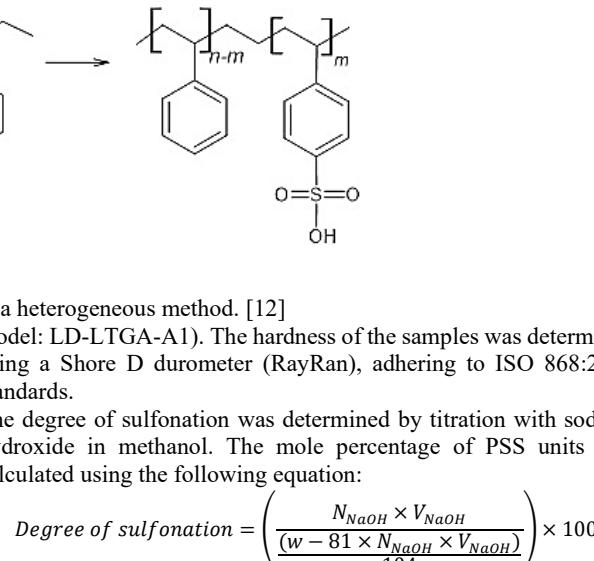
2.3 Instruments and Characterization

Fourier-transform infrared spectroscopy (FTIR) was conducted using a Tensor II Bruker FTIR spectrometer. Contact angle measurements were performed at ambient conditions using a Ramé-Hart instrument (model 200-F4). Thermogravimetric analyses (TGA) were carried out with an Automatic Thermo Gravimetric Analyzer (Labodam

water treatment, where it demonstrated effective removal of calcium and magnesium ions, as well as methylene blue dye [8-10]. Additionally, the material showed promise in oil/water separation, highlighting its versatility in addressing environmental challenges [11]. The sulfonation process not only transforms polystyrene waste into a valuable material but also contributes to the development of sustainable and eco-friendly products.

Polystyrene modification is conducted using two methods homogenous and heterogeneous reactions. While both homogeneous and heterogeneous sulfonation methods modify polystyrene effectively, homogeneous sulfonation produces uniquely crosslinked polymers, complicating characterization due to the interwoven structural and chemical changes. [6]

The sulfonation reaction follows an electrophilic aromatic substitution mechanism, replacing hydrogen atoms with sulfonate-SO₃H groups, as shown in Fig. 1. For the heterogeneous method, due to steric hindrance, sulfonation predominantly occurs at the para position [12]. The resulting PSS is expected to exhibit enhanced solubility and processability.



model: LD-LTGA-A1). The hardness of the samples was determined using a Shore D durometer (RayRan), adhering to ISO 868:2003 standards.

The degree of sulfonation was determined by titration with sodium hydroxide in methanol. The mole percentage of PSS units was calculated using the following equation:

$$\text{Degree of sulfonation} = \left(\frac{N_{NaOH} \times V_{NaOH}}{(w - 81 \times N_{NaOH} \times V_{NaOH})} \right) \times 100$$

Where N is the concentration of NaOH, V is the titration volume, and W is the weight of the PSS sample, 104 repetition of molar mass of the PS unit and 81 molar mass of the sulfonic group [1].

The Cation-Exchange Capacity (CEC) of PSS were measured by conducting an ion-exchange experiment. A known weight of the PSS resin (0.3 g) was added to 100 mL of a 0.2 M NaCl solution. The mixture was stirred for 48 hours for complete equilibration and release (H⁺) into the solution. Then, 25 mL of the solution was withdrawn for titration by using 0.01 M NaOH solution and phenolphthalein as an indicator. where the volume of NaOH used to reach the endpoint provided a measure of the H⁺ ions released into the solution. The initial concentration of sodium ions (C₀) was calculated based on the known concentration of the NaCl solution, while the equilibrium concentration (C_e) was derived from the titration results. The CEC was then computed using the following formula:

$$\text{Cation - exchange capacity} \left(\frac{\text{meq}}{\text{g}} \right) = \frac{(C_0 - C_e) \times V_e}{m_p}$$

m_p is the weight of dry resin, and V_e is the volume of NaOH at equivalence. [13]

2.4 Applications in Oil/Water Separation

The effectiveness of using PSS in oil/water separation was evaluated through the fabrication of a membrane from the PSS on nylon membrane mesh using a non-solvent-induced phase separation

technique [11]. A solution of 0.017 g of PSS in 2 mL of carbon tetrachloride (CCl_4) was prepared. Nylon membrane mesh was submerged in this solution and subjected to ultrasonication for 5 minutes, followed by immersion in an anhydrous ethanol bath for 10 minutes. This process facilitated the precipitation of the PSS onto the mesh, creating a microporous structure. Upon immersion in PSS/ CCl_4 solution, the amide groups of nylon reacted with the $-SO_3H$ groups to permanently fix them on the nylon fibres [14].

To evaluate the separation efficiency of the PS- SO_3H /nylon mesh, it was wetted with water and positioned between two vertical plastic tubes. A mixture of 5 mL of corn oil and 15 mL of deionized water was introduced into the upper tube. Under the influence of gravity, the water was allowed to pass through the mesh while the oil was retained above. The volumes of water used before (V_0) and collected water after (V_1) separation were recorded, along with the water passing time (Δt). The separation efficiency was calculated using the formula:

$$\text{Separation efficiency} = P = 100\% \times \frac{V_1}{V_0}$$

Additionally, the water flux through the membrane was determined with the equation:

$$\text{Water flux} = f = \frac{V}{(S\Delta t)}$$

Where S represents the effective area of the mesh, and V is the volume of water collected after separation.

3. Results and discussions

3.1 Characterization of SSP

3.1.1 Infrared spectroscopy

Infrared spectroscopy was employed to confirm the sulfonation reaction of PS waste. The sulfonation of PS was confirmed using FTIR spectrophotometry, as shown in Fig. 2, which revealed distinct spectral changes indicative of successful functionalization. The spectrum before sulfonation displayed characteristic peaks, including CH sp^3 stretching vibrations at 3022 cm^{-1} , CH_2 symmetrical stretching at 2924 cm^{-1} , and $C=C$ vibrations in the aromatic skeleton at 1600 cm^{-1} .

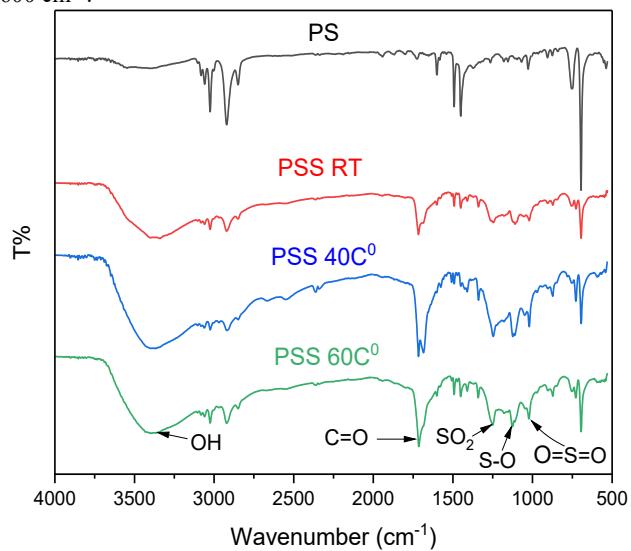


Fig. 2: FTIR spectra of the PS waste and PSS synthesized at different temperatures.

The appearance of new absorption bands at 1040 cm^{-1} ($-SO_3$ symmetric stretching) and 1180 cm^{-1} ($-SO_3$ antisymmetric stretching) confirmed the incorporation of sulfonate groups. Additional bands at 840 cm^{-1} validated aromatic ring substitution, while the presence of a strong 3420 cm^{-1} band indicated hydrogen bonding with water molecules. Other significant peaks corresponding to $C-H$, $C=C$, and aliphatic ring vibrations further supported the structural modification of PS. These findings similar to other research groups [14-16] which, demonstrate the effectiveness of the sulfonation process in introducing hydrophilic functional groups, enhancing the polymer's chemical properties for potential applications in ion exchange and adsorption.

3.1.2 Cation-Exchange Capacity

Fig. 3 illustrates the (CEC) of the produced polymer as a function of sulfonation temperature. The Fig. shows that the CEC values increase

with sulfonation temperature, peaking at 40°C start to decrease. PSS synthesized at 40°C exhibited the highest DS of 20.11% and CEC of 0.43 meq/g. While lower sulfonation temperatures (25°C) yield a lower CEC of around 0.30 meq/g, thus lower DS of 13.19%, indicating less effective sulfonation. At 60°C , the CEC is about 0.37 meq/g (DS = 18.13%), suggesting that although higher temperatures enhance sulfonation, excessive heat may lead to degradation or reduced efficiency [13]. These results underscore the impact of reaction conditions on sulfonation efficiency and ion exchange capabilities, indicating that elevated temperatures favourably influence the sulfonation process.

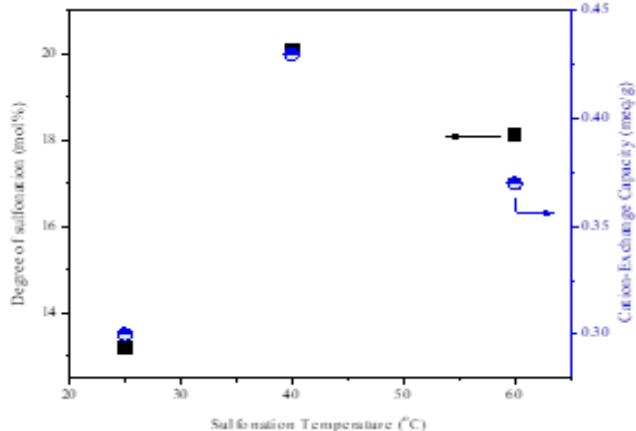


Fig. 3: Degree of sulfonation and the ion-exchange capacity of sulfonation polystyrene at PSS-RT, PSS-40 and PSS-60.

3.1.3 Contact Angle

Contact angle measurements provide insight into the hydrophilicity of PSS surfaces. The results of contact angle measurements indicate that as the concentration of sulfonate groups on the polymer chains increases, the contact angle decreases. A contact angle below 90° indicates hydrophilicity, while angles above 90° indicate hydrophobicity. Fig. 4 shows the water droplet images on PSS samples. The contact angle of PS is measured at 92.0° , classifying it as a hydrophobic material. In contrast, sulfonated PS synthesized at 40°C exhibited the lowest contact angle (57.2°), confirming its increased polarity due to sulfonation.

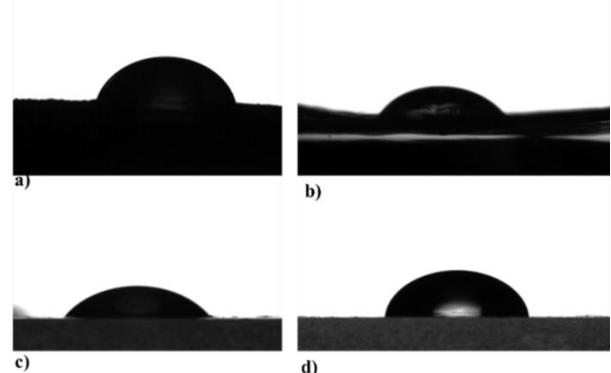


Fig. 4: Water Contact Angle Measurements of PS and PSS: (a) PSS-RT, (b) PSS-40°C, (c) PSS-60°C, and (d) PS.

Fig. 5 shows the contact angle measurements of PS and sulfonated PS synthesized at different temperatures. The Figure depicted the effect of sulfonation on the contact angle and thus hydrophilicity. The contact angle of polystyrene is significantly high (with an average θ of 92.0°), indicating its hydrophobic nature. In contrast, the sulfonated samples exhibit a low contact angle (the average θ is 67.3°), reflecting the increased wettability and hydrophilicity due to the introduction of sulfonate groups. For PSS-40, the contact angles decrease (average θ is 57.2°) and then increase slightly for PSS-60. These results are attributed to structural changes that affect the concentration of sulfonate groups on polymer chains. This is consistent with research showing that increasing the degree of sulfonation leads to a significant decrease in water contact angles, which then enhances the hydrophilic properties [17, 18].

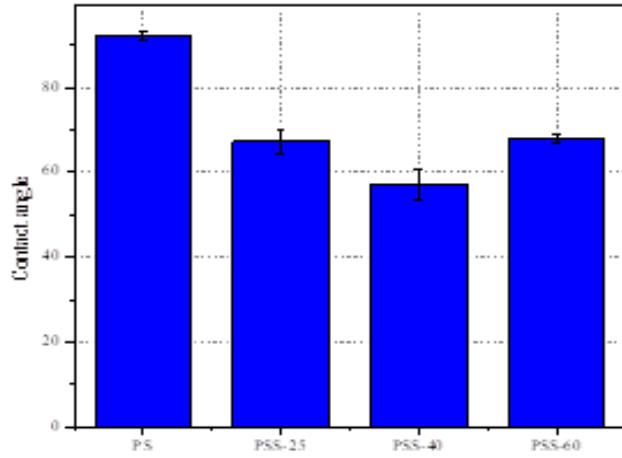


Fig. 5: Contact angle and standard deviation (STDV) of polystyrene, PSS-RT, PSS-40, and PSS-60. 3.1.4 Thermogravimetric Analysis The thermal stability of sulfonated polystyrene (PSS) is a critical factor in its application, particularly in membrane technologies. Thermogravimetric analysis (TGA) was conducted to assess the thermal stability of PSS. Fig. 6 reveals that pure PS begins to degrade at approximately 114°C, with weight loss occurring up to 245°C due to moisture release and the degradation of short chains.

In contrast, the sulfonated samples exhibit initial weight loss at lower temperatures (78°C for PSS-RT, 91°C for PSS-40, and 110°C for PSS-60), indicating the release of water molecules facilitated by the presence of sulfonate groups. Gong et al. [19] demonstrated that sulfonated virgin PS exhibits significant weight loss starting around 200°C, accompanied by the release of volatiles like sulfur dioxide from sulfonic acid groups during sulfonation.

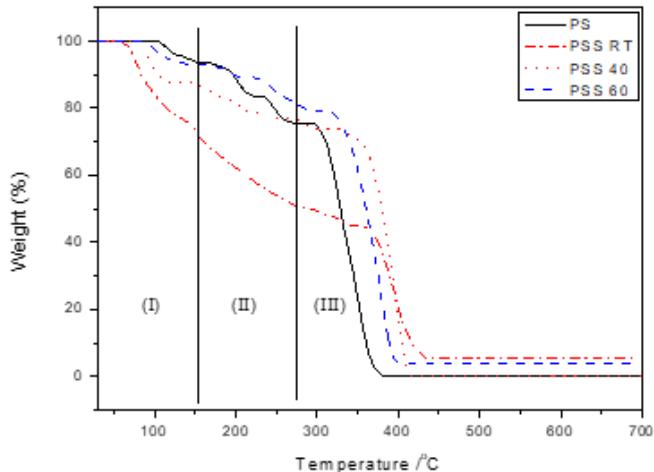


Fig. 6: Thermogravimetric analysis of PS and PSS PSSRT, PSS40°C, PSS60°C.

Notably, PSS retains structural integrity up to 393°C, demonstrating enhanced thermal stability compared to PS which is similar to the result obtained by other research [16]. This improved thermal performance, attributed to the cleavage of C-S bonds and the evolution of sulfur dioxide, underscores the significance of sulfonation in optimizing PS's thermal properties, making it suitable for applications requiring high thermal resistance. In general, the TGA results show initial water loss (78–114°C) which is in the material due to the hydrophilic characteristic induced by the sulfonate groups [15] sulfonate group cleavage (150–300°C) [20], and backbone degradation (393°C). PSS exhibited improved thermal stability compared to pristine PS.[21]

3.1.5 Hardness tests

Hardness tests of PSS are a key property that can be characteristic of its mechanical properties. The results of this study show that the sulfonation process significantly increased the surface hardness of PS, as measured by Shore D hardness Table 1. PSS-60 exhibited the highest hardness (56.2), followed by PSS-40 (42.5) and PSS-RT (40.5), indicating increased cross-linking and polymer chain

rearrangement. Higher degrees of sulfonation lead to increased ionic interactions, which can enhance the material's hardness and mechanical properties [22].

Table 1: Hardness values and standard deviation (STDV) of shore hardness (D) of polystyrene, PSSRT, PSS40°C, and PSS60°C.

Sample	average hardness	STDV
PS	11.13	1.1
PSS RT	40.5	2.6
PSS 40°C	42.5	2.0
PSS 60°C	56.2	2.6

3.2 Applications of PSS in oil/water separation

Membranes are often created by grafting polymerization of styrene onto a polymer, followed by sulfonation to introduce sulfonic acid groups, which enhances ionic conductivity and separation efficiency. These membranes are used in various industrial applications, such as fuel cells and wastewater treatment.

Membrane separation is one of the most effective techniques for oil-water separation. PSS was used to change the nylon mesh into a hydrophilic/hydrophobic membrane. The hydrophilic/hydrophobic compositions of the PSS membrane allow the oil-water mixture to separate under gravity, as shown in Fig. 7. In Fig. 7a, the water/oil mixture is seen at the top of the tube, and the water droplet emerges from the membrane at the bottom of the tube. Fig. 7b shows the separation process after 24 hours. The oil layer remains at the top of the membrane, while the water emerges through the membrane. Fig. 7c and Fig. 7d show the water and oil after separation, indicating that the presence of (-SO₃H) significantly affected the separation process.

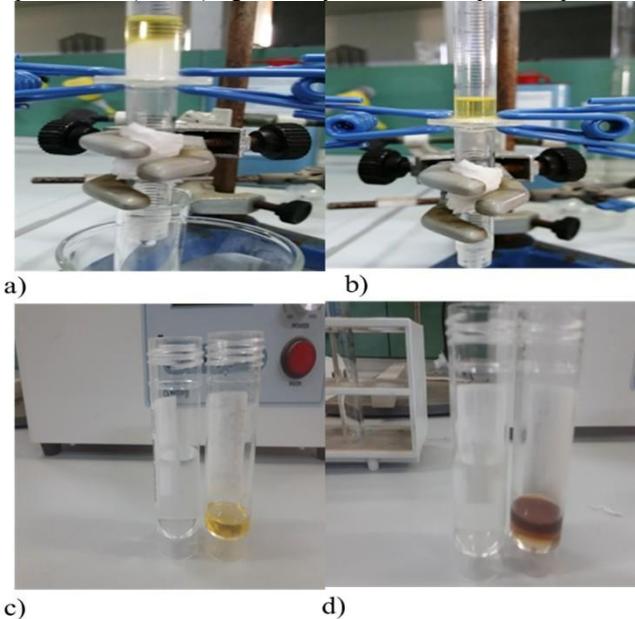


Fig. 7: Oil/water separation techniques, a) mixture of oil/water, b) after 24h of the process, c and d) the water and oil after separation. The separation efficiency and water flux results are shown in Table 2, the water flux, which is the volume of water that passes through a certain area in one hour. Membrane PSS-RT shows water flux of 6.98 L/m²h, membrane PSS-40 shows water flux of 6.68 L/m²h, and membrane PSS-60 shows water flux of 6.55 L/m²h. The separation efficiency of the membranes obtained was as follows: PSS-RT 96%, PSS-40 86%, and PSS-60 100%.

Table 2: Water flux and separation efficiency of sulfonated polystyrene PSS-RT, PSS-40°C, and PSS-60°C for Oil/water separation.

Sample	Water flux (f) (L/m ² h)	Separation efficiency (p) %
PSS RT	6.98	96
PSS 40°C	6.68	86
PSS 60°C	6.55	100

4. Conclusions

Sulfonation of waste PS foam was successfully performed using a heterogeneous reaction method. Concentrated sulphuric acid was used at different temperatures: room temperature, 40 °C, and 60 °C for 24 hours. FTIR results confirmed the successful synthesis of PSS

Improving the Properties of Waste Polystyrene Foam via Heterogeneous Sulfonation: A Sustainable Method for Oil/Water Swaei et al. under different conditions. The presence of the S–O absorption band at 1180 cm⁻¹ and SO₂ at 1040 cm⁻¹ provided evidence that a sulfonation reaction had occurred. The degree of sulfonation (DS) and cation-exchange capacity (CEC) were measured. The results showed that PSS had a higher CEC compared with pure polystyrene (PS), and that the extent of sulfonation directly affected the material properties, with PSS synthesised at 40 °C exhibiting a higher DS of 20.11%. Contact-angle measurements revealed that sulfonated polystyrene (PSS) exhibits much lower contact angles than pure polystyrene (PS), indicating increased hydrophilicity due to the introduction of sulfonate groups. Thermogravimetric analysis (TGA) results indicated that sulfonated polystyrene (PSS) has improved thermal stability compared with pure polystyrene (PS). Hardness tests showed that PSS samples exhibited improved mechanical properties compared with PS. One of the most promising applications of this polymer is its use in separating a mixture of water and oil. The separation process demonstrated that the polymer's ability to separate the mixture is remarkable. Overall, the results show that sulfonated polymer, with different degrees of sulfonation, has a remarkable ability to separate oil from water. Therefore, the sulfonation process is considered an effective and promising method for utilising polystyrene waste and converting it into products of technical and economic value.

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