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Diffusion of Water through Poly(styrenesulfonate) membranes produced from the sulfonation of wasted PS plastic cups

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Summary

In this work, poly(styrenesulfonate) membranes were produced through the sulfonation of wasted polystyrene plastic cups. The produced membranes presented good workability and ion exchange capacity of 1.3 ± 0.1 meq/g. The sulfonated membranes showed significantly increase in the water sorption, what is relevant in industry since most of the processes of separation deal with the presence of ions which means of transport is the water. The membrane of sulfonated polystyrene plastic cups (PSSwastecups) was compared with the sulfonated membrane of virgin resin (PSSstandard). The viscosimetric molar weight of PSSstandard was higher than PSSwastecups how indicated by difference between intrinsic viscosity. This fact influences the production of the membrane and consequently the transport property. The PSSwastecups absorbs a higher amount of water than the PSSstandard, what is due to the presence of less macromolecule chain coils, producing low-density regions where clusters may be formed. This diminishes the diffusion coefficient and increases the water sorption in the PSSwastecups membrane.

1. Introduction

Polystyrene is a polymer that is used in several applications such as cups and trays in the food industry, as well as wrapping for electronics devices and foams. The high consumption of this polymer increases the discard of material in the landfill, which may be minimized by using this polymer in the production of modified polymers. The polystyrene is easily sulfonated [1]. The properties of the produced material depend on the content of sulphonic groups because the sulfonation of PS may increase the polymer solubility in water and other polar solvents [2]. Depending on the degree of sulfonation, the sulfonated polystyrene can be used in water treatment [3, 4] or in concrete as an admixture [5].

Membranes that are chemically modified by the presence of highly polar groups can act as ion exchange resins. Commercial exchange resins based on PS are prepared using a crosslink agent such as Divinylbenzene (DVB), and in this case, the sulfonated polymer isn't soluble in water. However, the sulfonation process can be controlled in order to avoid the necessity of using DVB in the production of sulfonated polystyrene [6].

The preparation and characterization of ion-exchange membranes have been well developed in the past decades. This kind of membrane can be used in several technological processes such as water purification, desalinization, metal recovering, etc [7]. Another application for the sulfonated membranes is their potential use in fuel cells. Currently, sulfonated membranes of perfluorcarbon are being used for this purpose [8].

Nowadays there is an increasing interest on the development of new materials for separation processes. These materials should be produced in a low cost process and have good mechanical and chemical properties. On this way, the membrane performance depends on the kind of chemical modification and on the chemical and mechanical property resultant during the process.

In most of exchange resin processes, the water transport is extremely important. Membranes such as Nafion® (sulfonated perfluorcarbon) show high water permeability coefficients [9]. The same effect can be observed in films of sulfonated polystyrene fixed on alumina (Al_2O_3), where it was observed an increment on the water vapor after an increment on the water permeability coefficient through the PSS membrane, even though there is a diminishing on the diffusion coefficient with a high increment on the water content [10]. These facts show that previously hydrophobic polymers showed an increment on the water transport parameters when chemically modified by hydrophilic groups such as the sulphonic group.

In this work, films of sulfonated polystyrene were produced using wasted polystyrene plastic cups as raw material. This polymer was chosen based on two essential aspects: i) due to the high discard of this material it is interesting to find viable ways of reusing it and ii) due to the ease on the reaction of sulfonation of the polystyrene [1]. The quality control of the sulfonating agent, time and reaction temperature allows choosing the membrane degree of sulfonation and then, controlling its water solubility [2]. In this paper, sulfonated membranes of polystyrene were characterized through infrared spectroscopy, ion exchange capacity and water sorption.

2. Experimental

2.1. Synthesis and characterization of the poly(styrenesulfonate)

Zanata® wasted polystyrene plastic cups, as well as commercial virgin polystyrene, were used in order to prepare poly(styrenesulfonate). The commercial virgin polystyrene was used as a standard material.

In the preparation of poly(styrenesulfonate), 3.0 g of polystyrene were dissolved in 30 mL of dichloromethane (CH_2Cl_2). 4.2 mL of acetic anhydride and 2.7 mL of H_2SO_4 97% were slowly added to this solution under constant stirring. Subsequently, the stirring was kept for 20 min, and then became occasional during the synthesis period. The reaction system was kept at 25ºC for 90 minutes. Next, the sulfonated polymer was precipitated with distilled water up to pH 5. The polymer was dried at room temperature and ground until a powder was obtained.

2.2. Production of membranes

The sulfonated polymers (PSSwastecups and PSSstandard) were dissolved in THF to obtain 10% and 8.3% w/w solutions, respectively. Then, the solutions were cast on glass plates to a uniform wet thickness of 200 µm. the solvent was evaporated at 25ºC and the membrane was removed using an water bath.

2.3. Characterization of the materials

2.3.1. Ion Exchange Capacity

The parameter that measures the quantity of ionizable groups in the membrane is the ion exchange capacity (IEC), expressed in quantity of exchanging groups per unit of mass of the membrane. For this purpose, the sulfonated membrane (0.100 g) were added to 20.0 mL of a 0.05 mol/L NaCl solution. The system was kept under stirring for 24 hours. Afterwards, the solution was titrated with a 0.0500 mol.L^{-1} solution of NaOH. The ion exchange capacity was calculated from the number of H^{+} mols changed on the membrane structure.

2.3.2. Determination of Intrinsic Viscosity

The intrinsic viscosity of the sulfonated polymer solutions was obtained through the flow measures of the solvent and solutions in an Ostwald viscometer. The viscometer was kept in a thermostatted bath at 25ºC. 5 mL of tetrahydrofuran was added to the viscometer and the level of the solvent was raised up to the superior viscometer mark using a pipette filler bulb, and then the solvent flow time was measured. The same procedure was followed using the solutions of the sulfonated polymers.

2.3.3.Sorption Measurements

The water absorption as a function of time was measured in tests of sorption kinetics. The membranes of the sulfonated materials were put into a test tube, hanging on a piece of wire and in direct contact with the water. This set was put into a thermostatted bath at 25ºC. Membranes were periodically weighed until the saturation condition was attained.

3. Results and Discuss

The sulfonated polystyrene obtained through the sulfonation of wasted plastic cups is a dark brown material, little soluble in water, but soluble in THF. The sulfonation of the polystyrene may be verified through the analysis of the functional groups using the infrared spectrometry technique. The infrared spectra of the PS plastic cup and of the PSS in membrane form are presented in figure 1.

The observed changes between the two spectra are produced by the presence of the sulfonic group in the sulfonated material, and may be observed mainly in the region from 3700 to 3000 cm^{-1}, where a intense band related to the acid character of the sulfonic group and water sorption appears; and in the region from 1200 to 1150 cm^{-1}, where there is an intense band in approximately 1170 cm^{-1}, which is attributed to the symmetric stretching of the SO_2 group. The same behavior is observed for the virgin material that was used as standard.

The sulfonation of the polystyrene completely changes its characteristics, turning the material into an ion exchanger. This was evaluated from the results of exchange capacity determination. Table I presents the results obtained for the sulfonated polystyrene of waste cups (PSSwastcups), standard sulfonated polystyrene (PSSstandard) and for the commercial ion exchange resin, Amberlite IR120Na.

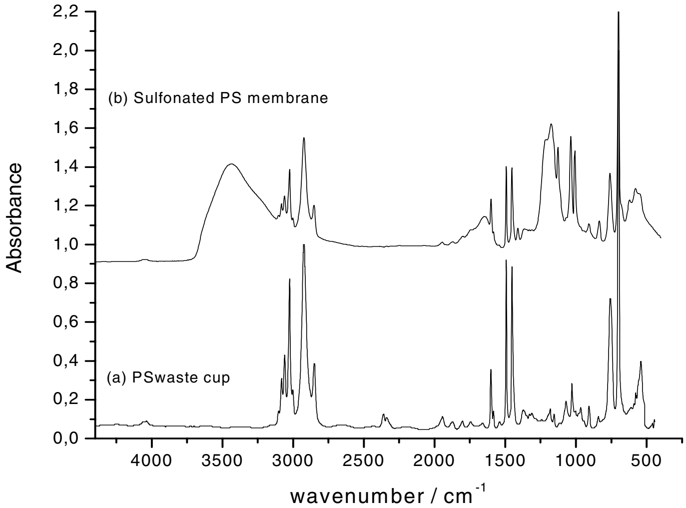


Figure 1. FTIR spectra of waste PS plastic cups (a) and sulfonated PS membrane (b)

According to the results presented in table 1, the sulfonated membranes present approximately the same ion exchange capacity, showing that the sulfonation methodology allows the production of practically identical materials when concerning the ion exchange capacity despite the differences regarding the source of the polymers. In relation to the commercial ion exchange resin, the ion exchange capacity of the membranes is about 38 % inferior. It is possible to increase the sulfonation percentage of the resin since the little solubility of the material is guaranteed due to the use of a cross-link agent, divinylbenzene (DVB). This may be explained since the exchange capacity of the materials is directly related to the amount of sulfonic groups added to the polystyrene. Regarding the PSS membranes, with the rise of the time or the amount of sulfonating agent there is a drastic increase in the level of sulfonation although the material that is produced in this condition is soluble in water and other polar solvents.

Table 1. IEC values for $PSS_{standard}$ and $PSS_{wastecups}$ membranes

Samples	IEC (meq/g)
$PSS_{Standard}$ membrane	1.3
$PSS_{wastecups}$ membrane	1.2
Exchange resin – Amberlite IR120Na*	1.9

Although the membrane’s exchange capacity is inferior to those of the ion exchange resin, the presence of sulfonic groups is an improvement guarantee of the transport processes selectivity, being relevant that waste material was used while a toxic and expensive reagent such as DVB wasn’t.

Besides the exchange capacity, crystallinity and molar weight are significant properties when discussing the water transport through these membranes. Both the original and the sulfonated materials, independently on their origin, are amorphous. Since the materials are produced from different sources, the molar weight may be their main difference. In order to evaluate indirectly the molar weight effect, the intrinsic viscosities of the polymer solutions were determined. The results are presented in table 2.

Table 2. Intrinsic Viscosity [η] of PSSwastecups and PSSstandard

Sample	[η] (mL.g^{-1})
PSSwastecups	28.8
PSSstandard	75.9

From the results presented in table 2 one can verify that the viscosimetric molar weight of the PSSstandard is higher than the molar weight of the PSSwastecups. This difference between the molar weights doesn't affect the exchange capacity of the materials as may be verified through the results shown in table 1.

A complete description regarding the transport properties for this system may be acquired from the water sorption through the membranes. The sorption technique is a tool for evaluating the membranes, since it may be phenomenologically described as a distribution of penetrating material into two or more phases, including processes of adsorption, absorption, incorporation of the penetrating material into micro voids, cluster formation and other mixture processes [11].

Figure 2 and 3 show the curve of membrane water uptake and reduced kinetic sorption ($\Delta m_t/m_e$) versus the square root of time, where m_t is the water weight in time t, and m_{eq} is the weight in the equilibrium.

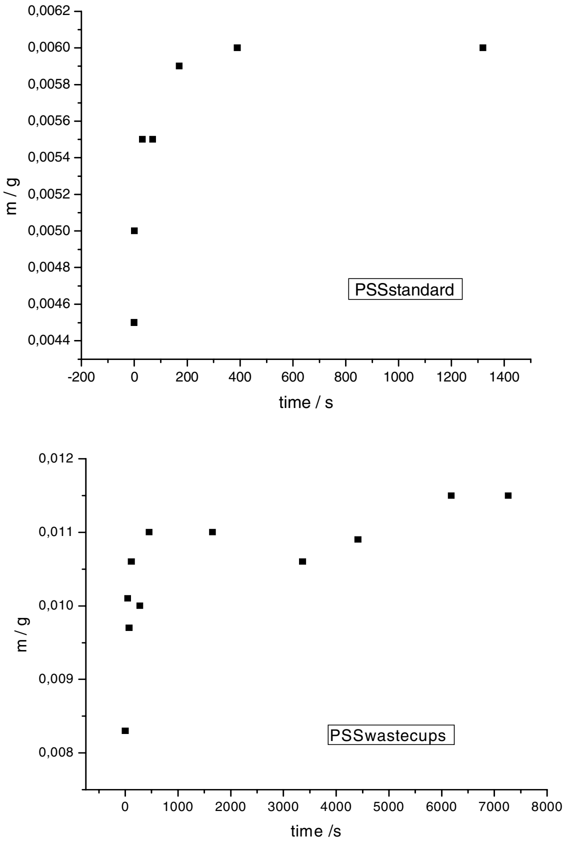
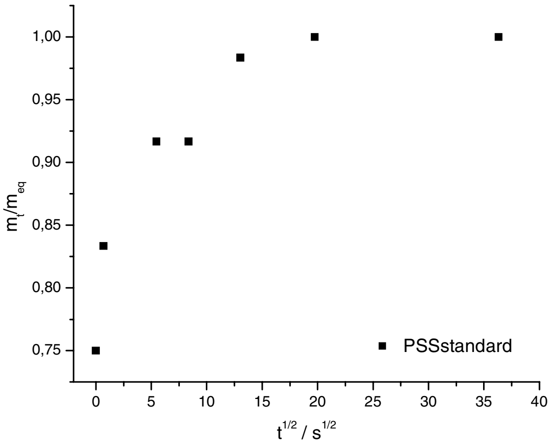


Figure 2. Kinetic of membranes water uptake



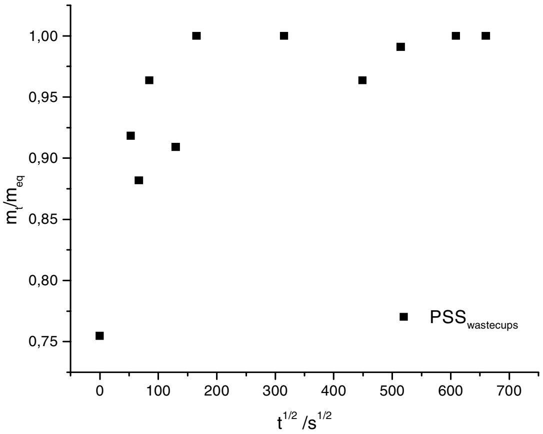


Figure 3. The reduced sorption curves as a function of $t^{1/2}$ / $s^{1/2}$

Considering that the curves of kinetic sorption present a region were the water sorption is linear in function of the square root of time, it will be assumed a Fickian behavior. Therefore, the determination of the average diffusion coefficient for the studied membrane will be possible through equation 1:

$$D = [(\Delta m_t/m_{eq})/\Delta t^{½}]^2 . l^2 . \pi/16 \qquad (1)$$

In equation (1), D is the average diffusion coefficient, t is the time and l is the membrane thickness.

From the sorption technique it is also possible to determine the content of water that was absorbed during the sorption process. The results obtained from the sorption data analyses are presented in table 3.

Table 3. Transport parameters for PSS membranes

Samples	D / $cm^2.s^{-1}$	% H_2O
PSSstandard	$3.18.10^{-10}$	11.5
PSSwastecups	$7.25.10^{-12}$	34.0

The main difference between the values of the diffusion and water sorption may be attributed to the difference in the molar weight of the two studied polymers. The decrease in the molar weight may influence the membrane formation, there is a decrease in the chain coiling, causing the creation of low-density regions. These regions may be responsible for the increase in the water sorption, what would explain why the PSSwastecups membrane presents higher water absorption, since this membrane is produced from a lower molar weight material.

The decrease in the diffusion coefficient for the PSSwastecups membrane is related to its high water content. According to Aranda and coworkers[10], the increase in the water content in a membrane may cause a decrease in the diffusion coefficient when clusters are formed. The interactions between water molecules in the cluster would decrease their diffusion rate in the medium. Although there is a decrease in the water diffusion rate, the cluster formation may favor the ionic transport.

4. Conclusion

It was shown the possibility of using wasted polystyrene cups as raw material in the production of ion exchange membranes. The produced membranes presented good workability and exchange capacity of 1.3 ± 0.1 meq/g. The transport properties demonstrated that the sulfonated material significantly increases water absorption, what is relevant in the industry, since most of the separation processes deal with the presence of ions whose means of transport is the water. The PSSstandard showed a viscosimetric molar weight higher than PSSwastecups due the difference between intrinsic viscosity (PSSstandard $[\eta]$ is approximately 3 times PSSwastecup $[\eta]$). This fact has influence over the membrane formation, and consequently, over the transport properties. PSSwastecups absorbs more water than PSSstandard, what is due to the presence of less macromolecule coiling, producing low-density regions. As a result, the decrease in the water diffusion coefficient for PSSwastecups was observed.

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